the complex.[8] Except for the base-hydrolysis reaction,[10] the S- to N-bonded product ratio was also leaving-group dependent, even within the induced aquation group of reactions, and there was no obvious correlation of this S- to N-bonded ratio, or the total $SCN^-$ competition, with ion pairing of the reactants.[8] These results appear to preclude a classic pentacoordinate intermediate $[(NH_3)_5Co]^{3+}$, but they also seem to eliminate ion pairs as the direct source of competition products.

Mixed-anion studies were initiated to probe this aspect further.[3,4] In particular, the effect of the more strongly ion-pairing anion $SO_4^{2-}$ for a range of different competitors was examined for the classic induced aquation, nitrosation of $[(NH_3)_5CoN_3]^{2+}$, a reaction for many years believed to involve the reduced coordination number intermediate $[(NH_3)_5Co]^{3+}$. The results of this work showed that, while anions certainly affected the rate, $SO_4^{2-}$ had no effect on the competition. The widely accepted preassociation mechanism was therefore in trouble on this important aspect.

The present work was undertaken in the belief that the effects of ion pairing both on rate and products could be quantified much more readily for the simple spontaneous aquation reactions because the rate law should not suffer the complications found[3,4] for induced aquation. This has proven to be so. In the present work we have shown that $SCN^-$ competes with water for the vacated coordination site arising in the substitution process in precisely the same way when $[(NH_3)_5CoX]^{n+}$ is the reactant ion (or the $[(NH_3)_5CoX]^{n+},SCN^-$ ion pair) as when the $[(NH_3)_5CoX]^{n+}, SO_4^{2-}$ ion pair is the reactant.

This remarkable result emphasizes our continued view that preassociation of the competing anion is not required for direct product formation. Rather, there must be a common product-determining species formed from the free cation or any of its ion pairs because anion entry is not rate determining, and this species survives for a time sufficient to sample its inherited ion atmosphere. For the $[(NH_3)_5CoX]^{n+}$ substitution chemistry, we maintain that this intermediate is the very short lived $[(NH_3)_5Co]^{3+}$, despite being a species of demonstrably variable lifetime[8] that appears to depend upon its rate of generation.

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**Supplementary Material Available:** Tables I and II, listing kinetic data (2 pages). Ordering information is given on any current masthead page.

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# Ligand-Scrambling Reactions of Cyano(trialkyl/triarylphosphine)gold(I) Complexes: Examination of Factors Influencing the Equilibrium Constant

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The ligand-scrambling reaction of $R_3PAuCN$ (to form $(R_3P)_2Au^+$ and $Au(CN)_2^-$) has been studied for R = Ph, Me, Et, *i*-Pr, and Cy (Cy = cyclo-$C_6H_{11}$).[1] The reactions are conveniently studied by $^{31}P$ and $^{13}C$ NMR spectroscopy. The phenyl complex undergoes rapid ligand exchange and must be cooled to approximately 240 K to observe sharp resonances for the individual equilibrium components. All of the aliphatic complexes are in the slow exchange limit allowing observation by NMR spectroscopy at room temperature. The cyclohexyl complex equilibrated slowly, requiring several days to reach equilibrium, while the other complexes equilibrated within the time required to measure the spectrum. Equilibrium constants ($K_{eq} = [(R_3P)_2Au^+][Au(CN)_2^-]/[R_3PAuCN]^2$) were measured by integration of $^{31}P$ NMR spectra of methanol solutions of the complexes. For the ethyl complex, $K_{eq}$ is dependent on the initial concentration, $[Et_3PAuCN]_0$, and the ionic strength of the medium. The concentration dependence is attributed to the ionic strength effect of the reaction products. The effects of the phosphine substituents on $K_{eq}$ were compared at 240 K in 0.25M $NH_4NO_3$ methanol solutions. The $K_{eq}$ values (±esd) are as follows: $Ph_3PAuCN$, 0.112 ± 0.005; $Me_3PAuCN$, 0.37 ± 0.05; $Et_3PAuCN$, 0.24 ± 0.02; *i*-$Pr_3PAuCN$, 0.29 ± 0.03; $Cy_3PAuCN$, 0.49 ± 0.02. A convenient new procedure for preparing AuCN, the precursor of $R_3PAuCN$, from $Me_2SAuCl$ was developed. Of the $R_3PAuCN$ complexes studied, *i*-$Pr_3PAuCN$ and $Cy_3PAuCN$ have not been reported in the literature.

## Introduction

Recently, we examined the solid-state structure and solution equilibria of cyano(triethylphosphine)gold(I), $Et_3PAuCN$.[2] In the solid state, the gold is coordinated to a phosphine and cyanide ligand, but in solution, the complex undergoes a novel ligand scrambling reaction:

$$2Et_3PAuCN \rightleftharpoons (Et_3P)_2Au^+ + Au(CN)_2^- \qquad (1)$$

The equilibrium constant for the reaction was shown to be dependent upon the solvent, increasing with the polarity and/or polarizability of the solvent.

Ligand scrambling reactions of gold(I) complexes that are initiated by the presence of excess ligands have been known for some time.[3] The reaction in eq 1, however, does not require the presence of excess ligand. Its importance is just becoming recognized; such reactions may significantly alter the solution chemistry of gold(I) complexes used in the treatment of rhematoid arthritis.[2,4] Ligand scrambling reactions analgous to eq 1 have been reported for a variety of anionic complexes,[4a,5] but to our knowledge, (mpt)AuCN (mpt = 1-methylpyridine-2-thione)[6] and $(NH_2)_2CSAuI$[7] are the only other neutral gold(I) complexes reported to undergo similar ligand exchange. Two extreme cases of the ligand scrambling reaction given in eq 1 are the complexes (tetrahydrothiophene)gold(I) iodide[8] and (pyridine)chlorogold(I),[9] which exist in the solid state as the ionic complexes $[Au(THT)_2^+][AuI_2^-]$ and $[(py)_2Au^+][AuCl_2^-]$, respectively.

Because of the novelty of this ligand-scrambling reaction and its possible biological implications, the effects of several extrinsic and intrinsic influences on the extent of the reaction were systematically examined. The extrinsic influences examined here are the initial concentration of the complexes, $[R_3PAuCN]_0$, and

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(1) List of abbreviations: Ph = phenyl, Me = methyl, Et = ethyl, *i*-Pr = isopropyl, Cy = cyclohexyl, $R_3P$ = trialkyl/triarylphosphine, $R_3PO$ = trialkyl/triarylphosphine oxide.

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the ionic strength of the medium. The steric hindrance and the electronic properties of the phosphine are the intrinsic factors examined. For this study, we synthesized and characterized a series of $R_3PAuCN$ complexes and measured the equilibrium constants ($K_{eq}$) for their ligand scrambling reactions.

The phosphines selected in this study have a wide range of steric and electronic properties. Tolman has used two parameters, the cone angle, $\theta$, and an electronic parameter, $\nu_{CO}$, to order the steric and electron-donating properties of phosphines.[10a] $\nu_{CO}$ is the frequency of the $A_1$ carbonyl mode of $Ni(CO)_3L$ dissolved in $CH_2Cl_2$. In comparing two phosphines, a lower $\nu_{CO}$ value reflects a larger net electron-donating ability, (including $\sigma$-donating and $\pi$-accepting interactions).[10] $\theta$ and $\nu_{CO}$ values for the different phosphines are provided in the Discussion section (Table III). A second parameter that may be used to order the electron-donating ability of a phosphine is the ${}^1J_{Se-P}$ value[11] measured for the corresponding $R_3PSe$ compound (also given later in Table III). Generally, a decrease in the ${}^1J_{SeP}$ value reflects a increase in the Lewis basicity of the phosphine.

## Experimental Section

**Reagents.** Deuterated methanol-$d_1$, $Ph_3P$, $Et_3P$, and $Cy_3P$ were obtained from Aldrich. $Me_3P$ and $i\text{-}Pr_3P$ were purchased from Strem Chemicals. The 99% $K^{13}CN$ was purchased from Stohler Isotope Chemicals. $Me_2SAuCl$ was prepared according to a published procedure.[12]

**AuCN.** In a darkened room, $Me_2SAuCl$ (0.3709 g, 1.26 mmol) was slurried in 15 mL of acetone. Under a nitrogen purge, an aqueous solution of KCN (0.1746 g, 2.68 mmol in 8 mL) was slowly added with stirring. (In some cases sufficient $K^{13}CN$ was used to yield $Au^{13}CN$ that was 25–30% ${}^{13}CN^-$ enriched.) After the solution was stirred and purged with $N_2$ for 10 min, the colorless solution was filtered to remove solid impurities. Concentrated $H_2SO_4$ (4.6 mL) was slowly added to the $KAu(CN)_2$ solution. The lemon yellow precipitate was isolated by centrifugation and washed twice with double-distilled $H_2O$, twice with absolute EtOH, and twice with anhydrous ether. The AuCN was allowed to dry overnight in the desiccator over $P_2O_5$. Yellow AuCN was obtained (0.1571 g, 0.704 mmol, 73.8%): $\nu_{CN} = 2238$ cm$^{-1}$; Literature value = 2236 cm$^{-1}$.[13] Anal. Calcd for AuCN: C, 5.39; H, 0.0; N, 6.28. Found: C, 5.41; H, 0.25; N, 6.33.

**$R_3PAuCN$.** All of the $R_3PAuCN$ complexes were prepared by the addition of $R_3P$ to an excess of AuCN(s) (or $Au^{13}CN$, 25–30% enriched) in methanol. (Acetone was used as the solvent in preparing the $i\text{-}Pr_3PAuCN$). $Cy_3P$ and $Ph_3P$ were added as solids while $Et_3P$, $i\text{-}Pr_3P$, and $Me_3P$ were added as liquids under a nitrogen flow with stirring. In all preparations, the reaction was almost immediate, but stirring was continued for $\sim 1/2$ h. The excess AuCN was removed by centrifugation. Chilling and/or slow evaporation of the solvent from the decantate yielded white crystals of $R_3PAuCN$, which were washed with cold, anhydrous ether. All of the complexes gave satisfactory elemental analysis. Analytical data are available as supplementary material.

**Vibration Spectra.** Infrared (IR) spectra of the complexes were recorded on a Nicolet MX-10 spectrophotometer from 4800 to 400 cm$^{-1}$ as Nujol mulls on NaCl plates. $\nu_{CN}$ values are available as supplementary material.

**${}^{31}P\{{}^1H\}$ and ${}^{13}C\{{}^1H\}$ Nuclear Magnetic Resonance Spectroscopy.** All ${}^{31}P\{{}^1H\}$ and ${}^{13}C\{{}^1H\}$ spectra were obtained on a Bruker WP 250 multinuclear spectrometer at 101.3 and 62.9 MHz, respectively. $[R_3PAuCN]_0$ varied from 0.010 to 0.10 M, depending upon the experiment. Spectra were obtained at 297, 240, or 200 K, and the solvent used was deuterated methanol $CH_3OD$. For some of the ${}^{13}C$ NMR spectra, 25–30% ${}^{13}CN^-$-enriched complexes, $R_3PAu^{13}CN$, were used to shorten the acquistion time required to see the $R_3PAuCN$ and $Au(CN)^-$[14] and to facilitate observation of ${}^2J_{PC}$. $T_1$ values for the phosphorous nuclei in $(R_3P)_2Au^+$ and $R_3PAuCN$ were measured by the inversion recovery method.[15] Integrated ${}^{31}P$ spectra were acquired by using appropriate delay times ($\geq 4\ T_1$) and pulse angles ($\alpha = 45°$).

**Table I.** NMR Data[a] for $R_3P$, $R_3P$, $R_3PO$, and $R_3PAuCN$

| | | $R_3PAuCN$ | | | $(R_3P)_2Au^+$ | $R_3P$ | $R_3PO$ |
|---|---|---|---|---|---|---|---|
| R | *T*, K | δ(P) | ${}^2J_{PC}$, Hz | δ(CN) | δ(P) | δ(P) | δ(P) |
| Ph | 200 | 36.2 | 126.0 | 156.2 | 41.6 | −7.8 | 30.4 |
| Me | 297 | −3.3 | 129.4 | 158.3 | 5.1 | −64.1 | 45.5 |
| Et | 297 | 35.1 | 122.2 | 160.4 | 43.2 | −20.6 | 57.2 |
| *i*-Pr | 297 | 65.0 | 116.4 | 160.9 | 74.0 | 18.1 | 62.2 |
| Cy | 297 | 53.5 | 116.4 | 160.9 | 62.4 | 8.2 | 53.5 |

[a] In $CH_3OD$ at 297 K (except for R = Ph); chemical shifts are in ppm from internal TMP or TMS; concentrations ranged from 0.05 to 0.10 M.

**Evaluation of $K_{eq}$.** One of the primary goals of this study was to examine the effects of ionic strength, concentration, steric hindrance, and ligand basicity on the equilibrium constant for reaction 2. A convenient

$$2R_3PAuCN \rightleftharpoons (R_3P)_2Au^+ + Au(CN)_2^- \qquad (2)$$

method for measuring $K_{eq}$ is by quantitative integration of the ${}^{31}P$ NMR spectra. In the ${}^{31}P$ NMR spectra, only the $R_3PAuCN$ and $(R_3P)_2Au^+$ are observed. Concentrations for $R_3PAuCN$, $(R_3P)_2Au^+$, and $Au(CN)_2^-$ can be calculated from the relative intensities, *I*, of the phosphine resonances and the initial $R_3PAuCN$ concentration:

$$[R_3PAuCN]_{eq} = \frac{(I(R_3PAuCN)_{eq})[R_3PAuCN]_0}{I(R_3PAuCN)_{eq} + {}^1\!/_2 I((R_3P)_2Au^+)_{eq}} \qquad (3)$$

$$[(R_3P)_2Au^+]_{eq} = \frac{({}^1\!/_2 I((R_3P)_2Au^+)_{eq})[R_3PAuCN]_0}{I(R_3PAuCN)_{eq} + {}^1\!/_2 I((R_3P)_2Au^+)_{eq}} \qquad (4)$$

$$[Au(CN)_2^-]_{eq} = [(R_3P)_2Au^+]_{eq} \qquad (5)$$

## Results

**Synthesis of $R_3PAuCN$.** In order to verify that the ligand-scrambling reaction previously reported[2] for $Et_3PAuCN$ and $Ph_3PAuCN$ also occurs for other $R_3PAuCN$ complexes, two new complexes (R = *i*-Pr, Cy) were prepared in addition to the known complexes (R = Me, Et, Ph). The precursor complex for preparing the $R_3PAuCN$ complexes was AuCN; a new procedure for preparing this material from $Me_2SAuCl$ was developed and used here:

$$Me_2SAuCl \xrightarrow{\text{excess KCN}} \xrightarrow{H^+} AuCN + Me_2S + KCl \qquad (6)$$

Reaction of the solid AuCN with $R_3P$ in appropriate solvents yielded $R_3PAuCN$ for R = Ph, Me, Et, *i*-Pr, and Cy:

$$R_3P + AuCN(s) \rightarrow R_3PAuCN \qquad (7)$$

Several attempts to prepare $(C_6F_5)_3PAuCN$ were unsuccessful. Addition of $(C_6F_5)_3P$ to AuCN results in no reaction (eq 8).

$$(C_6F_5)_3PAuCl + CN^- \xrightarrow{-Cl^-} \text{"}(C_6F_5)_3PAuCN\text{"} \overset{\longrightarrow}{\cancel{\longleftarrow}} AuCN + (C_6F_5)_3P \qquad (8)$$

Conversely, reaction of KCN with $(C_6F_5)_3PAuCl$ (prepared by displacement of $Me_2S$ from $Me_2SAuCl$ by $(C_6F_5)_3P$) gives AuCN, $(C_6F_5)_3P$, and KCl instead of the expected $(C_6F_5)_3PAuCN$ (eq 8). These results indicate that the poor Lewis basicity of the $(C_6F_5)_3P$ renders the expected $(C_6F_5)_3PAuCN$ thermodynamically unstable with respect to AuCN under the conditions used here.

**${}^{31}P\{{}^1H\}$ NMR Spectra of $R_3P$ and $R_3PO$.** The free phosphines and their oxides were characterized by ${}^{31}P$ NMR spectroscopy to ensure their possible identification in preparations of $R_3PAuCN$. Their chemical shifts, in the solvents used here, are given in Table I and are consistent with those found in the literature.[16]

**${}^{31}P\{{}^1H\}$ NMR Spectra of $R_3PAuCN$ Complexes.** The ${}^{31}P$ NMR spectrum of $Et_3PAuCN$ in $CH_3OD$ was previously reported.[2] At 297 K, resonances occur at 43.2 and 35.1 ppm and were assigned

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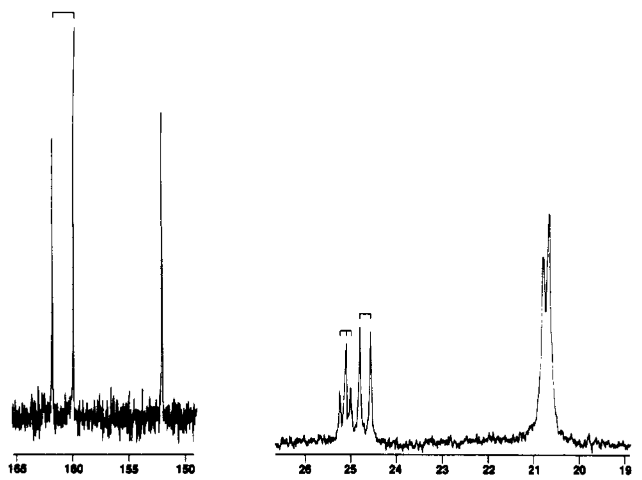

**Figure 1.** $^{13}C\{^1H\}$ NMR spectrum of 0.05 M *i*-$Pr_3PAu^{13}CN$ (25% enriched) in $CH_3OD$ at 297 K. Spectral assignments relative to internal TMS are as follows: *i*-$Pr_3PAu^{13}CN$, $\delta(CH_3) = 20.7$, $\delta(CH) = 24.7$ ($^1J_{PC} = 30.3$ Hz), $\delta(CN) = 160.9$ ($^2J_{PC} = 116.4$ Hz); $[(i\text{-}Pr_3P)_2Au^+]$, $\delta(CH_3) = 20.8$, $\delta(CH) = 25.1$ ($^1J_{PC} + {}^3J_{P'C} = 14.3$ Hz); $[Au(CN)_2^-]$, $\delta(CN) = 152.1$.

to $(Et_3P)_2Au^+$ and $Et_3PAuCN$, respectively. In the limit of slow ligand exchange, the $^{31}P$ NMR spectra of $R_3PAuCN$ (R = Ph, Me, *i*-Pr, Cy) in $CH_3OD$ (Table I) are similar to that of $Et_3PAuCN$. In no case were resonances observed for free $R_3P$ or $R_3PO$. The resonances were assigned on the basis of the coupling constants, $^2J_{PC}$, observed for the $^{13}CN^-$ enriched (25–30%) complexes; the $R_3PAu^{13}CN$ resonance appears as a doublet that flanks the singlet resonance for the unenriched $R_3PAuCN$. For each phosphine, the resonance for $(R_3P)_2Au^+$ appears downfield of the resonance for $R_3PAuCN$. This is consistent with other studies in the literature.[3a,17] Thus, the two resonances demonstrate that these complexes undergo the same type of ligand scrambling in solution as $Et_3PAuCN$ (eq 2).

The spectrum of $Ph_3PAuCN$ is an exception to the pattern described. At 297 K, a single average resonance at 38.1 ppm without any $^2J_{PC}$ is observed. When the temperature is lowered to 200 K, resonances are observed at 41.6 and 36.0 ppm corresponding to $(Ph_3P)_2Au^+$ and $Ph_3PAuCN$, respectively. Carbon–phosphorous coupling ($^2J_{PC} = 126$ Hz) is also resolved at this lower temperature for the $^{13}CN$ enriched complex.[2] The observation of an average resonance at room temperature is due to rapid ligand exchange between $Ph_3PAuCN$ and $(Ph_3P)_2Au^+$. A lower limit for the phosphine exchange rate at 297 K estimated from chemical shift differences is $k > 3.6 \times 10^3\ s^{-1}$.[18] An upper limit for the exchange at 200 K is $k < 1.8 \times 10^3\ s^{-1}$.[18]

**$^{13}C\{^1H\}$ NMR of $R_3PAuCN$.** The ligand-scrambling reaction observed in the $^{31}P$ NMR spectra of the complexes was further characterized by $^{13}C$ NMR spectroscopy. The $^{13}CN^-$ enriched complexes were used to obtain the spectra in order to shorten the time required to observe the metal-bound cyanide species.[14] With the exception of the $Ph_3PAuCN$ spectrum, which was not well resolved, the $^{13}C$ NMR spectra obtained for these complexes in $CH_3OD$ at 297 K paralleled that of $Et_3PAuCN$.[2] A typical spectrum for one of the complexes, *i*-$Pr_3PAuCN$, is shown in Figure 1. The resonances were assigned in a manner similar to that of $Et_3PAuCN$[2] and are typical of aliphatic carbons.[19] The $^1J_{PC}$ coupling constant is expressed as an absolute value and is comparable to those in other systems.[20] Virtual coupling, which occurs when $J_{PP'}$ for $(R_3P)_2Au^+$ is large,[21] was resolved for all of the complexes except $Ph_3PAuCN$. For all of the complexes, the cyanide resonance for $R_3PAuCN$ (Table I) was downfield of the $Au(CN)_2^-$ resonance, which occurs at 151.8 ± 0.4 ppm. The $^2J_{PC}$ values obtained are identical with those measured in the $^{31}P$ NMR spectra. A summary of $^{13}C$ NMR data for the complexes is available as supplementary material.

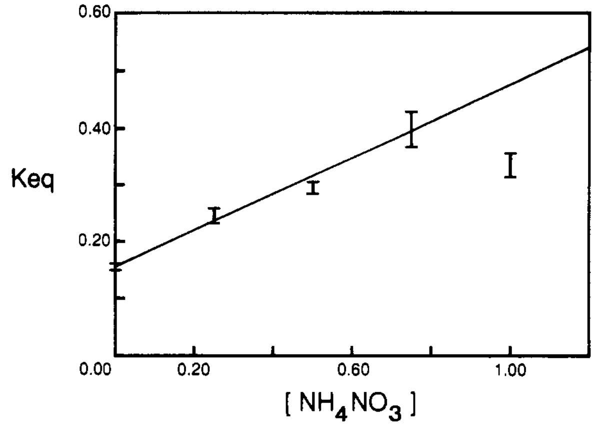

**Figure 2.** $K_{eq}$ vs $[NH_4NO_3]$ for $Et_3PAuCN$ (0.05 M in $CH_3OD$) at 297 K. Concentrations of $NH_4NO_3$ were 0, 0.25, 0.51, 0.75, and 1.0 M, the average number of acquisitions was 60, the sweep width was 10000 Hz, the relaxation delay was 3–4 times the $T_1$ value, and the pulse angle was 45° or less.

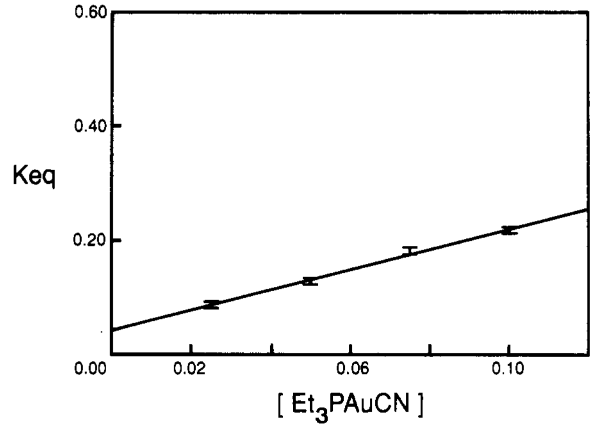

**Figure 3.** $K_{eq}$ vs $[Et_3PAuCN]_0$ in $CH_3OD$ at 297 K. Concentrations of $Et_3PAuCN$ were 0.025, 0.050, 0.075, and 0.10 M, the average number of acquisitions was 60 for each sample, the sweep width was 10000 Hz, the relaxation delay was 3–4 times the $T_1$ value, and the pulse angle was 45° or less.

**Dependence of $K_{eq}$ on Ionic Strength.** The first external influence examined was the ionic strength of the solution. Since ionic complexes are generated from the ligand-scrambling reaction, a change in the ionic strength of the solution should have an effect on $K_{eq}$. Because the $T_1$ values of $Et_3PAuCN$ and $(Et_3P)_2Au^+$ were known,[2] $Et_3PAuCN$ was used for experiments involving changes in ionic strength.

The requirements for the salt used to control the ionic strength of the solution were (1) component ions with low affinities for gold(I), (2) sufficient solubility in methanol, and (3) availability in anhydrous form. $NH_4NO_3$ met all of the criteria. $^{31}P$ NMR spectra were acquired for $Et_3PAuCN$ (0.05 M) in $CH_3OD$ with $NH_4NO_3$ at concentrations ranging from 0 to 1.0 M. The measured $K_{eq}$ values are the averages of at least four determinations. A plot of $K_{eq}$ versus the concentration of the salt (Figure 2) is linear and steadily increasing up to 0.75 M $NH_4NO_3$. This direct relationship between $K_{eq}$ and $[NH_4NO_3]$ is consistent with the Debye–Hückel theory since ionic species are produced as a result of the ligand scrambling (eq 2). Increasing the ionic strength results in an increase of the activity coefficients for $(R_3P)_2Au^+$ and $Au(CN)_2^-$ with a subsequent increase in $K_{eq}$. At 1.0 M $NH_4NO_3$, the $K_{eq}$ decreases slightly, perhaps due to solvation

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**Table II.** $^{31}P\{^1H\}$ NMR Chemical Shifts and $T_1$ Values[a]

| | $R_3PAuCN$ | | $(R_3P)_2Au^+$ | |
|---|---|---|---|---|
| R | $\delta(P)$ | $T_1$, s | $\delta(P)$ | $T_1$, s |
| Ph | 36.4 | 7.4 | 42.1 | 7.4 |
| Me | −3.0 | 7.9 | 6.5 | 8.5 |
| Et | 34.9 | 6.0 | 43.9 | 5.3 |
| *i*-Pr | 64.4 | 5.6 | 73.3 | 5.8 |
| Cy | 53.6 | 2.7 | 62.4 | 2.2 |

[a] In $CH_3OD$ at 240 K with 0.25 M $NH_4NO_3$; chemical shifts are in ppm relative to internal TMP.

effects or ion-pairing. Such a deviation is expected since a concentration of 1.0 M $NH_4NO_3$ is well beyond the limits of the Debye–Hückel theory.

**Dependence of $K_{eq}$ on $[R_3PAuCN]_0$.** The second external factor that was examined was an apparent effect of $[R_3PAuCN]_0$ on $K_{eq}$. $^{31}P$ NMR spectra were acquired in methanol at $Et_3PAuCN$ concentrations ranging from 0.025 to 0.10 M. Each $K_{eq}$ value obtained is an average of at least seven measurements. A plot of $K_{eq}$ versus $[Et_3PAuCN]_0$ (Figure 3) is linear with the value of $K_{eq}$ steadily increasing. This direct relationship between $K_{eq}$ and $[Et_3PAuCN]_0$ is consistent with the effects of ionic strength on $K_{eq}$. An increase in $[R_3PAuCN]_0$ generates more $(R_3P)_2Au^+$ and $Au(CN)_2^-$ resulting in larger $K_{eq}$ values.

**$K_{eq}$ for $R_3PAuCN$.** In order to explore the effects of steric hindrance and phosphine basicity on the scrambling, $K_{eq}$ for the series of complexes, $R_3PAuCN$, was measured under a standard set of conditions. First, a constant $[R_3PAuCN]_0$ was used because $K_{eq}$ is dependent upon concentration. Second, $K_{eq}$ was measured at 240 K. This was high enough to prevent crystallization of $Me_3PAuCN$, yet low enough to allow us to resolve the resonances for $Ph_3PAuCN$ and $(Ph_3P)_2Au^+$, which are in rapid exchange at 297 K. Third, 0.25 M $NH_4NO_3$ was added to each solution to maintain a constant ionic strength, so that the effects of different phosphines on $K_{eq}$ could be directly studied without complications due to the ions generated by the ligand scrambling.

A series of $^{31}P$ NMR measurements were made by using 0.02 M $R_3PAuCN$ in $CH_3OD$ and 0.25 M $NH_4NO_3$ at 240 K. The concentration for the $Ph_3PAuCN$ was 0.01 M because its solubility in $CH_3OD$ at 240 K was limited. This slight decrease in concentration should not affect $K_{eq}$ since the added $NH_4NO_3$ determines the ionic strength. Concentrations of the other complexes were not decreased to 0.01 M because this would have increased the acquisition time. $T_1$ values were evaluated by the inversion–recovery method so that the spectra could be quantitatively integrated; they appear in Table II along with the chemical shifts for $R_3PAuCN$ and $(R_3P)_2Au^+$. The $K_{eq}$ values, which are averages of at least 12 determinations, are listed in Table III along with the cone angles, $\theta$,[10] electronic parameters, $\nu_{CO}$,[10] and $^1J_{SeP}$[22] values of the phosphines. Clearly the nature of the $R_3P$ affects the $K_{eq}$ value; the relationships between $K_{eq}$, $\nu_{CO}$, $J_{SeP}$, and $\theta$ will be discussed more fully below.

**Slow Equilibration of $Cy_3PAuCN$.** Initial attempts to measure $K_{eq}$, as described above, for the tricyclohexylphosphine complex produced disparate values. These values, more properly designated as $Q$, measured the ratio [products]/[reactants] before the system was at equilibrium. We tentatively attributed this anomalous behavior to slow equilibration due to the bulkiness of the $Cy_3P$ groups. When several weeks was allowed for equilibration with the sample at −15 °C a value of 0.49 ± 0.02 was obtained.

Two experiments were designed to examine this hypothesis and to ensure that the $K_{eq}$ value of 0.49 ± 0.02 is, indeed, the equilibrium constant. In the first experiment, equimolar amounts of $[(Cy_3P)_2Au^+][ClO_4^-]$ and $KAu(CN)_2$ were added to a sample of $Cy_3PAuCN$ with $Q = 0.0046 \pm 0.001$. If the ligand scrambling was rapid, the $Q$ obtained after the addition of the $(Cy_3P)_2Au^+$ and $Au(CN)_2^-$ should remain as 0.0046 ± 0.001. Integration of the $^{31}P$ NMR spectrum, obtained immediately after the addition, yielded a $Q$ value of 0.192 ± 0.006. This larger value demonstrates that the $Cy_3PAuCN$ system requires a longer time to reach equilibrium than the other $R_3PAuCN$ complexes. In a second experiment, equimolar quantities of $(Cy_3P)_2Au^+$ and $Au(CN)_2^-$ were dissolved in $CH_3OD$. Initially, $Q$ was 0.58 ± 0.05 but a second measurement several weeks later yielded $Q = 0.528 \pm 0.005$. This value is close to the $K_{eq}$ value of 0.49 ± 0.02 obtained when the equilibrium is approached from the opposite direction.

**Table III.** Comparison of $K_{eq}$[a] with Phosphine Steric[b] and Electronic Parameters[b]

| $R_3PAuCN$ | $K_{eq}$ (esd) | $\theta$, deg | $\nu_{CO}$, cm$^{-1}$ | $^1J_{SeP}$, Hz[c] | ref |
|---|---|---|---|---|---|
| $Ph_3PAuCN$ | 0.112 (5) | 145 | 2069 | 734 | 22a |
| $Me_3PAuCN$ | 0.37 (5) | 118 | 2064 | 684 | 22b |
| $Et_3PAuCN$ | 0.24 (2) | 137[d] | 2062 | 691 | 22a |
| *i*-$Pr_3PAuCN$ | 0.29 (3) | 160 | 2059 | 713 | 22c |
| $Cy_3PAuCN$ | 0.49 (2) | 170 | 2056 | 683 | 22c |

[a] In $CH_3OD$ with 0.25 M $NH_4NO_3$ at 240 K. [b] See ref 10a. [c] $^1J_{SeP}$ values that are reported for the $R_3PSe$ derivatives are known to be negative but are used as absolute values in this paper. [d] See ref 26.

The above experiments confirmed that the initial disparate values of $Q$ are due to slow ligand scrambling. This is unusual since many gold(I) complexes are labile and their ligand-scrambling reactions occur rapidly (usually complete within minutes or less).[3a,6,23] Indeed, for all of the other $R_3PAuCN$ complexes, $K_{eq}$ remained constant over time with the possible exception of *i*-$Pr_3PAuCN$, which may have shown a slight increase. The unusual behavior of the $Cy_3PAuCN$ can be attributed to its extremely large steric bulk ($\theta$ = 170°). It is likely that the ligand scrambling occurs by an associative mechanism with a three-coordinate transition state or intermediate.[3a,6,23] Such a mechanism would be inhibited by the large steric bulk of the $Cy_3P$. Further evidence of the large steric bulk of the $Cy_3P$ is the failure of $[(Cy_3P)_3Au^+]$ to form in solution when excess $Cy_3P$ is added to $[(Cy_3P)_2Au^+]$.[17] Similar species have been observed by $^{31}P$ NMR for phosphines with smaller cone angles, e.g., $Me_3P$,[3c] $Et_3P$,[3b] and $Ph_3P$.[24]

## Discussion

**Driving Forces for the Ligand Scrambling.** The ligand-scrambling reaction of the $R_3PAuCN$ complex is given by

$$2R_3PAuCN \rightleftharpoons (R_3P)_2Au^+ + Au(CN)_2^- \qquad (2)$$

If the reaction were driven solely by randomization due to entropy, $[R_3PAuCN]$ would be twice $[(R_3P)_2Au^+]$ and $[Au(CN)_2^-]$, yielding a $K_{eq}$ of 0.25. Similar ligand scrambling reactions have been observed for anionic complexes of the type $Au(X)I^-$, where X = $SCN^-$[5a] and $CN^-$,[5b] and the neutral complex $(NH_2)_2CSAuI$.[7] When their equilibrium constants ($K_{rd}$) are recalculated according to eq 7, the values are 0.50, 0.50, and 0.63, respectively. These values indicate that the reaction is not driven solely by randomization. In this study, the $K_{eq}$ values obtained (Table III) are both greater than and less than 0.25, suggesting that additional factors influence the extent of ligand scrambling. These factors can be divided into extrinsic and intrinsic influences whose magnitude of effect on $K_{eq}$ are similar.

The extrinsic influences include (1) the ionic strength of the solution and (2) the initial concentration of the $R_3PAuCN$. A third external influence that was examined in an earlier study is solvent polarity/polarizability.[2] That study demonstrated that $K_{eq}$ increases as the polarity/polarizability of the solvent increases.[25] Our present data demonstrate that increasing either the ionic strength or the $[R_3PAuCN]_0$ also increases the extent of ligand scrambling. In both studies, the increase in $K_{eq}$ can be

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(22) In order to obtain a set of reasonably consistent $^1J_{Se-P}$ values we used those that were obtained in chloroform and/or methylene chloride. (a) Kuhn, N.; Schumann, H. *J. Organomet. Chem.* **1986**, *304*, 181. (b) McFarlane, W.; Rycroft, D. S. *J. Chem. Soc., Dalton Trans.* **1973**, 2161. (c) Dean, P. A. W. *Can. J. Chem.* **1979**, *57*, 754.

(23) Isab, A. A.; Hormann, A. L.; Coffer, M. T.; Shaw, C. F., III. *J. Am. Chem. Soc.* **1988**, *110*, 3278.

(24) Muetterties, E. L.; Alegranti, C. W. *J. Am. Chem. Soc.* **1972**, *94*, 6386.

(25) The previously published[2] $K_{eq}$ values for $Et_3PAuCN$ were miscalculated. Corrected values are 0.018 (4) in $CDCl_3$, 0.034 (8) in $C_6D_6$, 0.20 (6) in $CH_3OD$, and 0.092 (4) in $(CD_3)_2SO$.

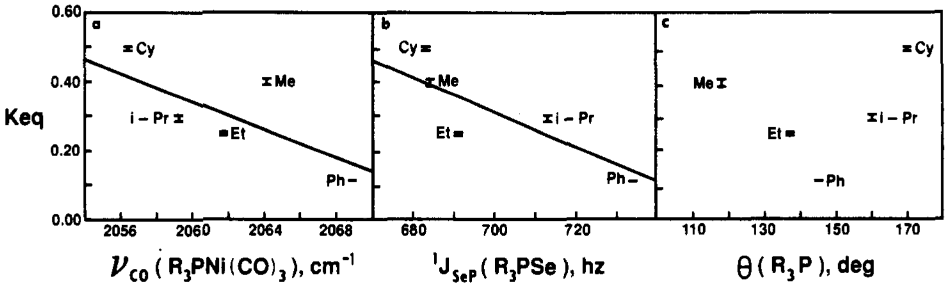

**Figure 4.** (a) $K_{eq}$ vs electronic parameter $\nu_{CO}$ of the phosphines. (b) $K_{eq}$ vs $^1J_{SeP}$ of the phosphines. (c) $K_{eq}$ vs cone angle, $\theta$, of the phosphines. $T$ = 240 K; $[R_3PAuCN]_0$ = 0.02 M except for $[Ph_3PAuCN]$ = 0.01 M. Number of acquisitions was 120, the sweep width was 10000 Hz, the relaxation delay was 3–4 times the $T_1$ value, and the pulse angle was 45° or less.

attributed to an increase in the activity coefficients for the ionic components of the equilibrium.

Intrinsic factors include bond energies and the electronic and steric effects of the phosphine ligands. In $R_3PAuCN$, the phosphorus is trans to a carbon (P–Au–C), whereas in $(R_3P)_2Au^+$ it is trans to a phosphorous (P–Au–P). Likewise, the cyanide is trans to phosphorus in $R_3PAuCN$ and trans to another cyanide in $Au(CN)_2^-$. Unfortunately, neither experimental nor calculated bond energies are available for such complexes. There are, however, a number of empirical correlations that allow us to examine the effect of phosphine basicity and steric bulk on the magnitude of $K_{eq}$.

Two correlations that are frequently used to determine relative basicities of phosphines are the electronic parameter, $\nu_{CO}$ for $R_3PNi(CO)_3$ (values tabulated by Tolman[10a]) and $^1J_{SeP}$ values[11] obtained from the $^{31}P$ or $^{77}Se$ NMR spectra of the selenium derivatives, $R_3PSe$. A decrease in the $\nu_{CO}$ or the $^1J_{SeP}$ value indicates a net increase in the electron-donating ability of a phosphine. For both the $\nu_{CO}$[10a] and the $^1J_{SeP}$[22] parameters, generally linear correlations are obtained (parts a and b of Figure 4, respectively) when they are plotted against $K_{eq}$. This suggests that the electron-donating ability of the phosphine is a major influence on the magnitude of $K_{eq}$, with $K_{eq}$ increasing as the Lewis basicity of the phosphine increases. The most significant deviation from the least-squares fit in Figure 4a is the $K_{eq}$ for $Me_3PAuCN$. The anomalously large value of 0.37 ± 0.05 is most likely due to increased solvation of the $(Me_3P)_2Au^+$ because of its smaller bulk.

The final intrinsic factor that we examined was the steric bulk. The various methods that have been used to quantify the steric bulk of a ligand have recently been summarized in a review.[26] With the exception of $Et_3P$, we have chosen to use the cone angles reported by Tolman[10a] (Table III) because they were available for all of the phosphines in this study. For $Et_3P$, we used the slightly larger value of 137°,[27] which was reported for the same configuration of the ligand found in $Et_3PAuCN$.[2] A plot of $K_{eq}$ versus $\theta$ (Figure 4c) is nonlinear, indicating that there is no direct correlation between the steric bulk of the phosphine and the magnitude of $K_{eq}$. This is expected since all of the species observed by NMR are two-coordinate. If steric bulk was a major influence on the magnitude of $K_{eq}$, the $Cy_3PAuCN$ would have an anomalously small $K_{eq}$; instead, it has the largest, which is consistent with the dependence of $K_{eq}$ on the electron-donating ability of the phosphine.

Finally, some discussion should be devoted to the affinity of the phosphine ligands employed in this study for gold(I). $R_3PAuCN$ was successfully and easily prepared from AuCN and $R_3P$ when R = Ph, Me, Et, *i*-Pr, and Cy. However, attempts to prepare $(C_6F_5)_3PAuCN$ were unsuccessful. An examination of the electronic parameters of the phosphine offers a possible explanation. $\nu_{CO}$ for $(C_6F_5)_3P$ is 2091 cm$^{-1}$; this value is greater than $\nu_{CO}$ for $Ph_3P$ (2069 cm$^{-1}$),[10a] which is the poorest Lewis base among the phosphines successfully employed. Thus the inability to prepare $(C_6F_5)_3PAuCN$ is most likely due to the poor electron-donating ability of the phosphine. Interestingly, the (tris(cyanoethyl)phosphine)gold(I) cyanide complex, $(CNCH_2CH_2)_3PAuCN$, has been prepared from the corresponding chloride complex.[28] $\nu_{CO}$ for the phosphine, $(CNCH_2CH_2)_3P$, is 2078 cm$^{-1}$,[10a] making it a poorer Lewis base than $Ph_3P$ but greater than $(C_6F_5)_3P$. The increased electron-donating ability of the $(CNCH_2CH_2)_3P$ increases its affinity for the gold(I), leading to formation of $(CNCH_2CH_2)_3PAuCN$. Hence, one may use the $\nu_{CO}$ values tabulated by Tolman[10a] to predict the ability of a phosphine to react with AuCN to form $R_3PAuCN$. For $\nu_{CO} < 2078$ cm$^{-1}$, the reaction is favorable; for $\nu_{CO} > 2091$ cm$^{-1}$, it is not. Between these values the formation of the complex $R_3PAuCN$ is not yet predictable.

In summary, we have found that the ligand-scrambling reaction for $R_3PAuCN$ is dependent upon such extrinsic factors as the initial concentration of the $R_3PAuCN$, solvent polarity/polarizability,[2] and the ionic strength of the solution. Any increase in the ionic strength of the solution causes a subsequent increase in the extent of ligand scrambling. We have also demonstrated that $K_{eq}$ is dependent upon the Lewis basicity of the phosphine ligand. Although the correlations with $\nu_{CO}$ and $^1J_{SeP}$ are not completely linear, $K_{eq}$ generally increases with increasing basicity of the phosphine.

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**Supplementary Material Available:** Tables of analytical data for $R_3PAuCN$ (R = Ph, Me, Et, *i*-Pr, Cy) complexes and $^{13}C\{^1H\}$ NMR chemical shifts for 25–30% enriched $R_3PAu^{13}CN$ complexes in $CH_3OD$ (2 pages). Ordering information is given on any current masthead page.

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