5.3%, 144 ($C_4H_4F_4O^+$) 31.1%, 140 ($C_4H_3F_3O_2{}^+$) 61.6%, 127 ($C_2H_2F_2O_2P^+$) 1.6%, 105 ($C_2H_2O_3P^+$) 100%, 98 ($H_3PO_4{}^+$) 7.1%, and 63 ($PO_2{}^+$) 13.9%. Air hydrolysis of $Cl_2P(O)OCH_2(CF_2)_2CH_2OP(O)Cl_2$ also gave the bis(phosphate).

**Hydrolysis of $Cl_2P(O)OCH_2(CF_2)_4CH_2OP(O)Cl_2$.** The hydrolysis was carried out as above. The white solid remaining after the volatile materials were removed had a melting point of 170 °C. The $^1H$ NMR of $(HO)_2P(O)OCH_2(CF_2)_4CH_2OP(O)(OH)_2$ had a peak at $\delta$ 7.6 (OH) and a triplet of doublets centered at $\delta$ 4.4 ($J_{P-CH_2} = 6.91$ Hz, $J_{H-F} = 13.9$ Hz). The $^{19}F$ NMR spectrum had two complex triplets centered at $\phi$ −117.97 and −121.16. The $^{31}P\{^1H\}$ NMR spectrum had a resonance at $\delta$ −1.9, and the $^{31}P$ NMR spectrum was a triplet. The FAB mass spectrum has peaks at *m/e* 423 ($M^+ + 1$, $C_6H_9F_8O_8P_2{}^+$) 0.4%, 405 ($C_6H_7F_8O_7P_2{}^+$) 0.1%, 325 ($C_6H_6F_8O_4P^+$) 0.2%, 161 ($C_2H_4F_2O_4P^+$) 0.1%, 127 ($C_2H_2F_2O_2P^+$) 0.1%, 102 ($HF_2O_2P^+$) 100%, 81 ($H_2O_3P^+$) 1.1%, 77 ($CH_2O_2P^+$) 0.6%, 64 ($C_2H_2F_2{}^+$) 1.1%, and 51 ($CF_2H^+$). Air hydrolysis of the tetrachloro compound also results in the bis(phosphate).

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# Kinetics and Mechanism for Reduction of Ammine and Haloammine Complexes of Gold(III) by Iodide

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The rate-determining step in the reduction of $Au(NH_3)_4{}^{3+}$ by iodide in acidic aqueous solution is the ligand substitution

$$Au(NH_3)_4{}^{3+} + I^- \rightarrow Au(NH_3)_3I^{2+} + NH_3$$

with $k^{298} = (1.52 \pm 0.03) \times 10^3\ M^{-1}\ s^{-1}$, $\Delta H^{\ddagger} = 54.6 \pm 1.1$ kJ mol$^{-1}$, and $\Delta S^{\ddagger} = -1 \pm 4$ J mol$^{-1}$ K$^{-1}$ in 1.0 M $NaClO_4$ with pH 2.3, as determined by stopped-flow spectrophotometry. In a subsequent rapid reductive elimination, attack by free iodide on $Au(NH_3)_3I^{2+}$ or *trans*-$Au(NH_3)_2I_2{}^+$ (the latter formed in a rapid trans substitution) leads to the final products $AuI_2{}^-$ and iodine. The same products are formed when *trans*-$Au(NH_3)_2X_2{}^+$ (X = Cl, Br) reacts with iodide. For X = Br reduction of the complex probably takes place by direct reductive elimination via one of the bromide ligands, without any initial substitution. This reaction is too fast for the stopped-flow technique at 25.0 °C: $k^{277.3} = (3.4 \pm 0.5) \times 10^6\ M^{-1}\ s^{-1}$. For X = Cl, reduction takes place with the parameters $k^{298} = (2.91 \pm 0.05) \times 10^5\ M^{-1}\ s^{-1}$, $\Delta H^{\ddagger} = (32.8 \pm 1.5)$ kJ mol$^{-1}$, and $\Delta S^{\ddagger} = -30 \pm 6$ J mol$^{-1}$ K$^{-1}$, which probably correspond to a rate-determining substitution of chloride by iodide followed by rapid reduction via the iodide ligand. However, it cannot be excluded that this reaction represents a borderline case, where direct reduction and substitution have very similar rates.

## Introduction

Reduction of square-planar gold(III) complexes takes place as reductive eliminations via an attack by the reducing agent on a coordinated ligand and concomitant two-electron transfer to the metal.[3-6] However, many good reductants featuring nonmetal centers are also efficient nucleophiles, and when gold(III) complexes are allowed to react with e.g. iodide, thiocyanate, or thioethers, it is often a close run as to whether the approach of a reducing ligand to the square-planar gold(III) complex results in a ligand substitution via a pentacoordinated transition state (followed eventually by reductive elimination in a subsequent step) or in a direct reductive elimination.[7] It is known that substitution is faster than reduction for the reactions between tetrachloroaurate(III) and thiocyanate[4] and thiosulfate.[8]

The presence in the gold(III) substrate complex of ligands capable of acting as efficient bridges for electron transfer favor direct reduction. For instance, in the reaction between tetrabromoaurate(III) and thiocyanate, direct reduction by thiocyanate proceeds at a rate comparable to the rate for bromide/thiocyanate substitution.[4] Examples of gold(III) substrate/reductant combinations for which the direct reduction clearly dominates include the reactions between tetrachloroaurate(III) and triphenylarsine[9] and hydroxylammonium.[10]

The reductions of tetrachloroaurate(III) and tetrabromoaurate(III) by iodide represent borderline cases for which it has been difficult to establish whether the rate-determining step is a ligand substitution or a direct reduction.[5,11] Comparison with the rate of bromide/chloride exchange in tetrahaloaurate(III)[12] has led to the conclusion that direct reduction of tetrabromoaurate(III) with iodide is faster than substitution of bromide by iodide, whereas for tetrachloroaurate(III) the question still remains unsettled.[5] The present study of the reaction between iodide and the series of well-characterized[13-18] ammine gold(III) complexes $Au(NH_3)_4{}^{3+}$, *trans*-$Au(NH_3)_2Cl_2{}^+$, and *trans*-$Au(NH_3)_2Br_2{}^+$ was

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**Table I.** Observed First-Order Rate Constants for Reaction between $Au(NH_3)_4^{3+}$ and Excess Iodide in Acidic Perchlorate Solution[a]

| $t$/°C | $10^5C_{Au}$/M | $10^3C_I$/M | $k_{exptl}$/s$^{-1}$ |
|---|---|---|---|
| 25.2 | 1.52 | 25.0 | 39 |
| 25.1 | 1.42 | 24.7 | 36 |
| | | 22.2 | 32 |
| | | 19.7 | 27.3 |
| | | 14.8 | 21.7 |
| 25.2 | 1.52 | 10.0 | 14.1 |
| | | 7.49 | 11.0 |
| | 1.36 | 5.05 | 7.8 |
| | | 4.04 | 6.4 |
| | | 2.53 | 4.2 |
| | | 1.52 | 2.61 |
| | | 0.51 | 1.02 |
| 25.1 | 1.67 | 2.46 | 3.8[b] |
| | | | 4.0[c] |
| | 0.84 | | 4.0 |
| 5.7 | 1.46 | 2.63 | 0.82 |
| 15.0 | 1.60 | 2.70 | 1.90 |
| 33.6 | | | 7.8 |
| 45.0 | 1.63 | 2.41 | 16.1 |
| 25.1 | 1.46 | 4.89 | 63[d] |
| | | | 34[e] |
| | | | 22.5[f] |

[a] All experiments had $[H^+] = 5$ mM and the ionic strength $\mu = 1.00$ M except as otherwise noted. Values of $k_{exptl}$ represent the mean of several experiments with an average error between 1 and 5%. [b] $[H^+] = 0.5$ mM. [c] $[H^+] = 51$ mM. [d] $\mu = 1.01 \times 10^{-2}$ M. [e] $\mu = 5.01 \times 10^{-2}$ M. [f] $\mu = 10.01 \times 10^{-2}$ M.

undertaken in an attempt further to elucidate the interplay between substitution and reduction when gold(III) complexes react with a reducing ligand such as iodide.

## Experimental Section

**Chemicals and Solutions.** $[Au(NH_3)_4](NO_3)_3$, *trans*-$[Au(NH_3)_2Cl_2]Cl\cdot{}^1/_3H_2O$, and *trans*-$[Au(NH_3)_2Br_2]Br\cdot NH_4Br\cdot 2H_2O$ were synthesized as described previously.[13,14,16] Gold solutions were prepared immediately before measurement from 1.00 M stock solutions of $NaClO_4$ (Baker's p.A., recrystallized once), $HClO_4$ (BDH AnalaR), HCl (Merck p.A.) and NaBr (Merck p.A.). Iodide solutions were prepared from NaI (Merck Suprapur) and 1.00 M $NaClO_4$. All solutions were flushed with nitrogen to remove dissolved oxygen, and the water was doubly distilled from quartz. All solutions had the ionic strength 1.00 M, except where otherwise stated.

**Apparatus.** Spectra were recorded by use of a Cary-Varian 219 spectrophotometer, and the kinetics were followed with a Durrum-Gibson modified stopped-flow instrument. Temperatures were accurate to within ±0.1 °C.

**Kinetics.** The reactions were started by mixing equal volumes of acidic gold(III) solutions and neutral sodium iodide solutions directly in the stopped-flow instrument. Tables I and II review the experiments. The reaction between $Au(NH_3)_4^{3+}$ and iodide was monitored by use of the transmittance decrease at 390 nm, where $I_3^-$ and $I_2$ have large molar absorptivities[19,20] and $Au(NH_3)_4^{3+}$, $AuI_2^-$, and $I^-$ are practically transparent.[18] Similarly, the reaction between *trans*-$Au(NH_3)_2Cl_2^+$ and iodide was observed as a transmittance decrease at 285 nm, where the molar absorptivity of *trans*-$Au(NH_3)_2Cl_2^+$ is ca. 1100 cm$^{-1}$ M$^{-1}$,[16] much smaller than those of $I_2$ and $I_3^-$.[19,20] Reaction between *trans*-$Au(NH_3)_2Br_2^+$ and iodide was followed by a transmittance increase at the absorbance maximum for *trans*-$Au(NH_3)_2Br_2^+$ at 255 nm with $\epsilon = 32\,000$ cm$^{-1}$ M$^{-1}$.[16] Solutions of the chloro and bromo complexes contained small concentrations of chloride (10.0 mM HCl before mixing) and bromide (1.2 mM NaBr before mixing), respectively, in order to suppress formation of aqua or hydroxo complexes.

Pseudo-first-order rate constants were calculated from experiments with excess iodide (30-fold or more where possible). Since the reactions of *trans*-$Au(NH_3)_2X_2^+$ with iodide are very rapid, most of the experiments with those complexes were performed at low temperature.

## Results

**Stoichiometry.** Figure 1 shows a plot of the absorbance at 350 nm of equilibrated solutions of the three complexes studied, with varying total concentrations of gold and with an excess of iodide.

**Table II.** Observed First-Order Rate Constants for the Reaction of *trans*-$Au(NH_3)_2X_2^+$ (X = Cl, Br) with Iodide in Acidic 1.0 M $NaClO_4$[a]

| X | $t$/°C | $10^6C_{Au}$/M | $10^4C_I$/M | $k_{exptl}$/s$^{-1}$ | $(10^{-4}k_{exptl}/[I^-])$/ s$^{-1}$ M$^{-1}$ | |
|---|---|---|---|---|---|---|
| Cl | 4.0 | 3.67 | 2.31 | 16 ± 2 | 6.9 | 10 ± 2 |
| | | 4.61 | 2.41 | 18 ± 2 | 7.5 | |
| | | 10.50 | 5.13 | 60 ± 5 | 11.7 | |
| | | 3.67 | 5.78 | 61 ± 10 | 11 | |
| | | 3.67 | 5.78 | 65 ± 5[b] | 11.2 | |
| | | 3.67 | 11.6 | 110 ± 30 | 10 | |
| | 6.2 | 7.4 | 2.00 | 22 ± 2 | | 11 ± 1 |
| | 13.2 | 7.4 | 2.00 | 34 ± 3 | | 17 ± 2 |
| | 17.7 | 6.8 | 1.81 | 37 ± 3 | | 20 ± 2 |
| | 24.5 | 9.3 | 2.22 | 65 ± 5 | | 29 ± 3 |
| | 32.4 | 9.3 | 2.22 | 99 ± 8 | | 44 ± 4 |
| | 32.5 | 6.8 | 1.81 | 68 ± 6 | | 37 ± 4 |
| Br | 4.2 | 1.07 | 0.300 | 106 ± 16 | 350 | 330 ± 30 |
| | | 1.07 | 0.336 | 119 ± 20[b] | 350 | |
| | | 1.07 | 0.480 | 150 ± 50 | 310 | |

[a] All experiments had $[H^+] = 5.0$ mM, except as otherwise noted. [b] $[H^+] = 50$ mM.

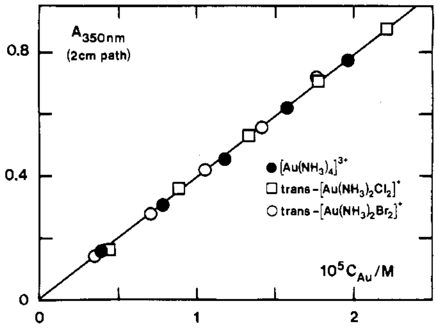

**Figure 1.** Absorbance at 350 nm of equilibrated solutions at 25 °C as a function of total gold concentration for excess iodide (5.0 mM for all solutions; medium 0.95 M $NaClO_4$ + 50 mM $HClO_4$).

The plot shows that the same reaction product is formed in all three reactions. The slope of the line gives the molar absorptivity of the product as $(1.97 \pm 0.02) \times 10^4$ cm$^{-1}$ M$^{-1}$. This corresponds to an equilibrium mixture of $I_2$ (22%) and $I_3^-$ (78%), which has an apparent $\epsilon = 1.96 \times 10^4$ cm$^{-1}$ M$^{-1}$ as calculated from $\epsilon_{I_2}$,[19] $\epsilon_{I_3^-}$,[20] the equilibrium constant for reaction 1,[21] and $[I^-] = 5.0$ mM. The gold(I) complex formed has a negligible absorbance at 350 nm.

$$I_2 + I^- \rightleftarrows I_3^- \qquad (1)$$

Each gold(III) complex consumes between four and five iodides depending on $[I^-]$, according to stoichiometric reactions 2 and 3,

$$Au(NH_3)_4^{3+} + 4I^- + 4H^+ \rightarrow AuI_2^- + I_2 + 4NH_4^+ \qquad (2)$$

$$trans\text{-}Au(NH_3)_2X_2^+ + 4I^- + 2H^+ \rightarrow AuI_2^- + I_2 + 2NH_4^+ + 2X^- \qquad (3)$$

which are followed by equilibrium 1. Formation of gold(I) ammine, chloro, and bromo complexes is negligible for the acidic medium used with an excess of iodide.[7] The redox equilibrium of eq 4 has an equilibrium constant of 2.5 M$^{-1}$ and is consequently almost completely displaced to the left (less than 0.03% Au(III) for $C_{Au} < 10^{-4}$ M).[7]

$$AuI_2^- + I_2 \rightleftarrows AuI_4^- \qquad (4)$$

**Reaction 2.** For the experimental conditions used, the reaction was observed to be first-order both with respect to gold(III) complex and iodide (Table I). Reaction 1 is rapid on the time scale of the present experiments.[22] A plot of the observed pseudo-first-order rate constants of Table I vs. the concentration

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**Table III.** Rate Constants and Activation Parameters at 25 °C[a]

| reactants | reacn | $k$/M$^{-1}$ s$^{-1}$ | $\Delta H^{\ddagger}$/kJ mol$^{-1}$ | $\Delta S^{\ddagger}$/J K$^{-1}$ mol$^{-1}$ | ref |
|---|---|---|---|---|---|
| $Au(NH_3)_4^{3+} + H_2O$ | subst | $6 \times 10^{-8}$ | ~109 | ~−13 | 13 |
| $Au(NH_3)_4^{3+} + Cl^-$ | subst | 0.36 | 81 ± 2 | 20 ± 2 | 18 |
| $Au(NH_3)_4^{3+} + Br^-$ | subst | 3.4 | 73 ± 3 | 8 ± 3 | 14 |
| $Au(NH_3)_4^{3+} + I^-$ | subst | $(1.52 \pm 0.03) \times 10^3$ | 54.6 ± 1.1 | −1 ± 4 | this work |
| *trans*-$Au(NH_3)_2Cl_2^+ + I^-$ | subst[c] | $(2.91 \pm 0.05) \times 10^5$ | 32.8 ± 1.5 | −30 ± 6 | this work |
| *trans*-$Au(NH_3)_2Br_2^+ + I^-$ | redn[c] | $>10^7$ [b] | | | this work |
| *trans*-$Au(NH_3)_2Cl_2^+ + Br^-$ | subst | $2.2 \times 10^3$ | 28 ± 1 | −87 ± 4 | 16 |
| *trans*-$Au(NH_3)_2Br_2^+ + Cl^-$ | subst | $3.3 \times 10^2$ | 35 ± 2 | −78 ± 2 | 16 |

[a] 1.00 M $HClO_4/NaClO_4$ aqueous solution. [b] Estimated, $k^{4.2\ °C} = (3.4 \pm 0.5) \times 10^6$ M$^{-1}$ s$^{-1}$ from data in Table II. [c] This assignment is based on rate comparisons; cf. text.

of excess iodide is linear with a slope of 1420 ± 30 M$^{-1}$ s$^{-1}$ and without any significant intercept. The rate was independent of the hydrogen ion concentration (0.5 mM < [H$^+$] < 51 mM).

A plot of the second-order rate constants calculated from Table I as a function of $\mu^{1/2}/(1 + \mu^{1/2})$ for ionic strength $\mu$ < 100 mM according to Brønsted[23] and Bjerrum[24] (cf. also ref 25) is linear with slope −3.00 ± 0.02. An Arrhenius plot of the temperature dependence (5.7–45 °C) of the second-order rate constants is also linear. Activation parameters and rate constants are given in Table III.

**Reaction 3.** Those are rapid for the stopped-flow method, and most of the measurements were performed at low temperatures to decrease the rates. For X = Br, only measurements at 4.2 °C had satisfactory precision. Table II reviews the experiments. Plots of the pseudo-first-order rate constants vs. concentration of excess iodide are linear through the origin and give the rate constants of Table III, and again no hydrogen ion dependence was observed. An Arrhenius plot of the temperature dependence for the reaction of the chloride complex is linear in the temperature interval investigated (4.0–32.5 °C). The rate constants and activation parameters are given in Table III.

## Discussion

**Reaction 2.** Iodide can act both as a reductant and as an efficient nucleophile toward gold(III) complexes. The experimental rate law for the reaction between $Au(NH_3)_4^{3+}$ and iodide (eq 5), valid for 25.0 °C and 0.5 mM < [H$^+$] < 51 mM, is

$$k_{\text{exptl}} = (1.52 \times 10^3)[I^-][Au(NH_3)_4^{3+}] \qquad (5)$$

compatible with at least three different mechanisms, (i)–(iii).

(i) Consider first a rapid initial substitution of one (or more) of the ammine ligands by iodide according to eq 6, followed by

$$Au(NH_3)_4^{3+} + I^- + H^+ \rightarrow Au(NH_3)_3I^{2+} + NH_4^+ \qquad (6)$$

rate-determining reductive elimination of $I_2$ via attack by an incoming iodide on coordinated iodide, according to eq 7. Re-

$$Au(NH_3)_3I^{2+} + I^- \rightarrow Au(NH_3)_2^+ + I_2 + NH_3 \qquad (7)$$

action 6 is practically completely displaced to the right according to available stability data.[26] The possibility of reaction 6 as a rapid preequilibrium preceding a rate-determining step according to eq 7 can also be excluded since the observed rate constants are independent of pH. A rapid and quantitative reaction according to eq 6 followed by a rate-determining step according to eq 7, however, is expected to give an ionic strength dependence of the +2/−1 type. Since this is not the case, mechanism i can be discarded. This use of the ionic strength dependence is based on the fact that an *initial fast equilibrium* preceding the rate-determining step can be excluded.[25]

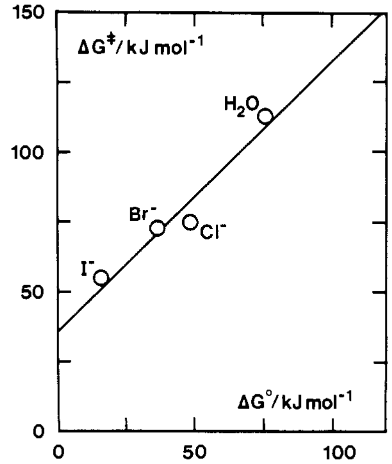

**Figure 2.** Plot of free energy of activation vs. overall free energy change for substitution of one ammonia of $Au(NH_3)_4^{3+}$ by various entering ligands at 25 °C for acidic aqueous solution. Data are from ref. 7 and 31 and the present work.

(ii) The second alternative comprises a rate-determining ligand substitution in the tetraammine complex according to eq 8 followed

$$Au(NH_3)_4^{3+} + I^- \rightarrow Au(NH_3)_3I^{2+} + NH_3 \qquad (8)$$

either by rapid trans substitution,[28] (eq 9), rapid reductive elimination (eq 10), and subsequent rapid substitution in the gold(I) product (eq 11) or by rapid reductive elimination (eq 7), followed

$$Au(NH_3)_3I^{2+} + I^- \rightarrow trans\text{-}Au(NH_3)_2I_2^+ + NH_3 \qquad (9)$$

$$trans\text{-}Au(NH_3)_2I_2^+ + I^- \rightarrow I^- + Au(NH_3)_2^+ + I_2 \qquad (10)$$

$$Au(NH_3)_2^+ + 2I^- \rightarrow AuI_2^- + 2NH_3 \qquad (11)$$

by rapid ligand substitution in the gold(I) product (eq 11). This alternative is in accordance with the rate law, the salt effect, and the lack of a pH dependence. It is further supported by the following two observations.

The free energy of activation for a series of substitution reactions on each of the common substrates $Au(NH_3)_4^{3+}$, $AuBr_4^-$, and $AuCl_4^-$ has been shown to depend linearly on the overall free energy change for the substitution process.[7] The free energy of activation for substitution of $NH_3$ by iodide in $Au(NH_3)_4^{3+}$ (Table III) in combination with the free energy change for the reaction of eq 8 estimated from available stability data[7,31] establish the slope as 0.96 ± 0.16 for $Au(NH_3)_4^{3+}$ as may be seen from Figure 2. The unity slope of the linear free energy relationship indicates a transition state of increased coordination number, as expected for ligand substitutions of d$^8$ square-planar complexes. This

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(26) The equilibrium constant for the reaction of eq 6 is ca. $10^{6.5}$ M$^{-1}$,[27] which gives $[Au(NH_3)_3I^{2+}]/[Au(NH_3)_4^{3+}] > 2 \times 10^5$ for the experimental conditions used.

(27) Skibsted, L. H.; Bjerrum, J. *J. Indian Chem. Soc.* **1977**, *54*, 102.

(28) The relative trans effect $I^-/NH_3$ is ca. 200:1 for platinum(II) complexes with water or halides as entering ligands[29,30] and is expected to be at least of the same magnitude for gold(III) complexes.[7] Therefore, substitution of the ammonia trans to iodide in $Au(NH_3)_3I^{2+}$ should be ca. 50 times faster than substitution in $Au(NH_3)_4^{3+}$, with statistical factors also considered.

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strongly supports the assumption of the ligand substitution of eq 8 as the rate-determining step in the present case.

The kinetic parameters for ligand substitution in $Au(NH_3)_4^{3+}$ (cf. Table III) shows that the faster the reaction, the smaller the enthalpy of activation. Thus, the kinetic discrimination between incoming ligands for the substrate $Au(NH_3)_4^{3+}$ is mainly an enthalpy effect. The entropy changes are expected to be negative for associative activation. This is the case for water as entering ligand in $Au(NH_3)_4^{3+}$ (cf. Table III). For the halides, the negative contribution to $\Delta S^\ddagger$ from the formation of the transition state is counteracted by changes in solvation due to partial charge neutralization. As expected, this latter effect is less important for iodide than for chloride. Those observations further support the identification of the substitution reaction of eq 8 as rate-determining for the redox process.

(iii) The third possibility is a direct reduction of the tetraammine complex as a result of an attack by iodide directly on coordinated ammonia and concomitant elimination of $INH_3^+$. This is in agreement both with the rate law of eq 5 and with the ionic strength dependence but does not seem very likely in view of the free energy relationship of Figure 2 and the other observations in support of mechanism ii discussed above.

**Reaction 3.** For the reaction of *trans*-$Au(NH_3)_2Cl_2^+$ and *trans*-$Au(NH_3)_2Br_2^+$ with iodide, the present experiments give no direct indication as to whether the rate-determining step is a direct reduction by iodide (eq 12) followed by the reaction of eq

$$trans\text{-}Au(NH_3)_2X_2^+ + I^- \rightarrow X^- + Au(NH_3)_2^+ + XI \qquad (12)$$

11 or a substitution of chloride or bromide, respectively, by iodide (eq 13), followed by rapid trans substitution[28] and/or reduction.

$$trans\text{-}Au(NH_3)_2X_2^+ + I^- \rightarrow trans\text{-}Au(NH_3)_2XI^+ + X^- \qquad (13)$$

A comparison of the rate constants determined for the reaction between *trans*-$Au(NH_3)_2X_2^+$ and iodide with those for ligand substitution reactions of some related gold(III) complexes (cf. Table III) might help to classify those reactions. A comparison of rate constants for a large number of ligand substitution reactions of various gold(III) complexes has shown that the discrimination between various incoming ligands increases with increasing positive charge on the gold(III) complex,[7] e.g. $Au(NH_3)_4^{3+}$ discriminates better between various incoming ligands than does $AuBr_4^-$. A similar trend should be expected when substitution of ammonia in $Au(NH_3)_4^{3+}$ is compared with substitution of bromide in *trans*-$Au(NH_3)_2Br_2^+$. An inspection of the rate constants given in Table III shows that substitution of ammonia in $Au(NH_3)_4^{3+}$ with iodide is $4 \times 10^3$ times faster than with chloride. For *trans*-$Au(NH_3)_2Br_2^+$, on the other hand, the rate constant for reaction with $I^-$ is at least $3 \times 10^4$ times larger than the rate constant for the substitution of bromide with chloride. Thus, reaction with iodide is more than 10 times *faster* than expected for substitution of bromide with iodide. This seems to indicate that the *trans*-$Au(NH_3)_2Br_2^+$/iodide reaction is a direct reduction, in which a noncoordinated iodide reduces the complex via one of the bromide ligands of the complex without any initial substitution.

*trans*-$Au(NH_3)_2Cl_2^+$ is also expected to discriminate between entering ligands to a smaller extent than $Au(NH_3)_4^{3+}$, when substitution of a chloride in *trans*-$Au(NH_3)_2Cl_2^+$ is compared with substitution of ammonia in $Au(NH_3)_4^{3+}$. The values in Table III show that the ratio between the rate constants for $NH_3/Br^-$ and $NH_3/I^-$ substitution in $Au(NH_3)_4^{3+}$ is 440, whereas for *trans*-$Au(NH_3)_2Cl_2^+$ the ratio between the rate constants for $Cl^-/Br^-$ substitution and for reaction with iodide is 130. This lower ratio is fully compatible with a $Cl^-/I^-$ ligand substitution as rate-determining, when *trans*-$Au(NH_3)_2Cl_2^+$ reacts with iodide. There is also the possibility that this reaction represents a borderline case in which the observed overall change is a mixture of parallel substitution and direct reduction and that the observed rate constants and activation parameters are composite quantities. This might explain the opposite trend of $\Delta H^\ddagger$ and $\Delta S^\ddagger$ for reaction of *trans*-$Au(NH_3)_2Cl_2^+$ with bromide and iodide compared to the corresponding reactions of $Au(NH_3)_4^{3+}$, but on the other hand, this alternative seems less probable since the temperature dependence agrees with Arrhenius' equation for a single reaction over a fairly large interval of temperature.

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**Registry No.** $Au(NH_3)_4^{3+}$, 43739-93-1; *trans*-$Au(NH_3)_2I_2^+$, 104090-03-1; *trans*-$Au(NH_3)_2Br_2^+$, 70148-53-7; $I^-$, 20461-54-5.

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# Manganese(0) Radicals and the Reduction of Cationic Carbonyl Complexes: Selectivity in the Ligand Dissociation from 19-Electron Species

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Products and stoichiometry for the cathodic reduction of the series of carbonylmanganese(I) cations $Mn(CO)_5L^+$, where L = CO, MeCN, pyridine, and various phosphines, derive from 1-electron transfer to generate the 19-electron radicals $Mn(CO)_5L^\bullet$ as reactive intermediates. The CO derivative $Mn(CO)_6^+$ affords mainly the anionic $Mn(CO)_5^-$ by the facile ligand dissociation of $Mn(CO)_6^\bullet$ to the 17-electron radical $Mn(CO)_5^\bullet$ followed by reduction. The acetonitrile and pyridine derivatives $Mn(CO)_5NCMe^+$ and $Mn(CO)_5py^+$ produce high yields of the dimer $Mn_2(CO)_{10}$ by an unusual and highly selective heterolytic coupling of $Mn(CO)_5^-$ and the reactant cation. Structural factors involved in the conversion of 19-electron radicals to their 17-electron counterparts are examined in the reduction of the graded series of phosphine derivatives $Mn(CO)_5P^+$, where P = triaryl- and trialkylphosphines. The formation of the hydridomanganese complexes $HMn(CO)_4P$ is ascribed to hydrogen atom transfer to the 19-electron radicals $Mn(CO)_5P^\bullet$ followed by extrusion of CO. The lability of carbonylmanganese radicals is underscored by rapid ligand substitution to afford the bis(phosphine) byproduct $HMn(CO)_3P_2$.

## Introduction

Increased experimental evidence is accruing for the participation of paramagnetic species with an odd number of valence electrons as key, reactive intermediates in a variety of reactions of metal carbonyls.[2,3] For purposes of further discussion, we designate such transient intermediates as carbonylmetal radicals.[4] As such, from a diamagnetic 18-electron metal carbonyl there are two types of radicals possible, viz., the electron-supersaturated 19-electron species and the electron-deficient 17-electron species. These correspond to anion radicals and cation radicals if they are gen-

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