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Substitution Reactions of Five-Coordinate Complex Ions. 1. Kinetics of Thiocyanate and Cyanide Substitution in a Five-Coordinate Nickel(II) Complex in Methanol

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Extensive mechanistic studies of ligand substitution reactions in solution have been reported for four-coordinate and six-coordinate transition metal complexes.[1,2] Few studies can be found in the chemical literature concerning ligand substitution of five-coordinate transition metal complexes. Our interest in the kinetics of substitution in five-coordinate complexes stems from an attempt to correlate kinetic data with differences in electronic environment imposed on the metals resulting from donor effects of group 5 and 6 elements.

Pearson, Muir, and Venanzi[3] reported results of an investigation of ligand substitution in a series of five-coordinate platinum(II) and palladium(II) complexes containing the tetradentate ligand tris(*o*-diphenylarsinophenyl)arsine, in methanol. Morgan and Tobe[4] reported kinetics of a study with platinum(II) and palladium(II) complexes containing the tetradentate ligand tris(*o*-dimethylarsinophenyl)arsine, in methanol. We report here the results of an investigation of ligand substitution in a nickel(II) complex in methanol solution that is isostructural[5] with the platinum(II) and palladium(II) complexes previously reported.

Experimental Section

Chemicals. Sodium thiocyanate and the starting material for tris(*o*-diphenylarsinophenyl)arsine, *o*-bromoaniline, were obtained from Eastman Organic Chemicals. Ultrapure nickel(II) chloride tetrahydrate and nickel(II) perchlorate hexahydrate were obtained from Alfa Inorganics, Inc. Dichloromethane and methanol used were Spectroquality grade obtained from Matheson Coleman and Bell. All other chemicals used were reagent grade.

Synthesis and Analysis of QAS. Tris(*o*-diphenylarsinophenyl)arsine, QAS, was prepared[6] as previously reported 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.[7] Calcd for $C_{54}H_{42}As_4$: C, 65.45; H, 4.28; As, 30.26. Found: C, 66.00; H, 4.20; As, 29.70.

Synthesis and Analysis of [NiCl(QAS)]ClO$_4$. The complex chlorotris(*o*-diphenylarsinophenyl)arsinenickel(II) perchlorate was prepared as reported by Dyer, Hartley, and Venanzi.[5] To 0.10 g of $NiCl_2{\cdot}4H_2O$ (0.50 mmol) and 0.18 g of $Ni(ClO_4)_2{\cdot}6H_2O$ (0.50 mmol) in a three-neck flask fitted with stirring bar, funnel, and reflux condenser was added 5 ml of ethanol. A pale green solution formed upon stirring to which 0.99 g of QAS (1.0 mmol) was added followed by addition of 20 ml of dichloromethane. After 15 min of refluxing, 20 ml of ethanol was added. The dichloromethane was stripped off, and the flask contents were cooled to 0 °C for several hours, filtered, and washed with cold ethanol yielding 1.09 g (92%) of dark blue crystals. The product decomposed at 321 °C in agreement with a literature value of 321–322 °C. Anal.[7] Calcd for $NiC_{54}H_{42}As_4Cl_2O_4$: Ni, 4.96; C, 54.77; H, 3.57; As, 25.30; Cl, 5.99; O, 5.40. Found: Ni, 4.88; C, 54.50; H, 3.65; As, 23.89; Cl, 6.10; O, not determined.

The ultraviolet–visible spectrum of the complex in dichloromethane solution was obtained. Positions of the absorptions bands (319, 459, and 617 nm) were in agreement with literature values.

Synthesis and Analysis of [Ni(NCS)(QAS)]ClO$_4$. Isothiocyanatotris(*o*-diphenylarsinophenyl)arsinenickel(II) perchlorate was prepared as previously reported.[5] To 0.20 g of $Ni(NO_3)_2{\cdot}6H_2O$ (0.69 mmol) in 5 ml of ethanol was added a solution of 0.11 g of sodium thiocyanate (1.4 mmol) in 5 ml of ethanol. The solution was filtered into a solution of 0.50 g of QAS (0.50 mmol) in 10 ml of dichloromethane and refluxed for 15 min. This solution was then filtered into a solution of 0.50 g of sodium perchlorate monohydrate (3.6 mmol) and the dichloromethane was stripped off by partial vacuum. Resulting black crystals were filtered and dried in a vacuum oven yielding 0.54 g (89%). Agreement with the literature was obtained for the decomposition point and for the positions of absorption bands for dichloromethane solutions of the complex in the ultraviolet and visible spectral range (316, 446, and 585 nm).

Synthesis and Analysis of [Ni(CN)(QAS)]ClO$_4$. A solution of 0.013 g of NaCN (0.27 mmol) in 20 ml of ethanol was added dropwise to a solution of 0.33 g of [NiI(QAS)]ClO$_4$ (0.26 mmol) in 20 ml of warm dichloromethane. The dichloromethane was removed by boiling the mixture. The brown complex obtained was dried in the vacuum oven. The decomposition point was 338–339 °C. Ultraviolet and visible spectra and the decomposition temperature were in agreement with literature values (maximum absorbtion bands: 259, 292, and 465 nm).

Kinetic Measurements and Data Analysis. The wavelengths of greatest difference in molar absorptivity between $[NiCl(QAS)]^+$ and $[Ni(NCS)(QAS)]^+$ in CH_3OH and $[NiCl(QAS)]^+$ and $[Ni(CN)(QAS)]^+$ in CH_3OH were found to be 585 and 465 nm, respectively. Solutions of these complexes in methanol appeared to obey Beer's law at the above wavelengths. Visible spectra taken of reaction mixtures after completion of several reactions indicated that the expected substitution products were obtained and were formed in a nearly 1:1 stoichiometric ratio.

A Beckman DU spectrophotometer fitted with a thermostatically controlled variable-temperature compartment and a rapid-mixing syringe[8] and a Durrum stopped-flow spectrophotometer were used to obtain kinetic data. Reactions were initiated by mixing the appropriate freshly prepared solutions with the temperature being held at 25 ± 0.2 °C. Concentrations of entering ligands were kept in large excess of complex concentrations so that the reaction data were pseudo first order.

Kinetic data gave straight-line plots using the standard integrated first-order rate expression

$$\ln (A_t - A_\infty) = -k_{obsd}t + \ln (A_0 - A_\infty) \qquad (1)$$

where A is absorbance. The average deviation of the kinetic data was approximately 5% for replicate experiments.

Results and Discussion

The tetradendate structure of tris(*o*-diphenylarsinophenyl)arsine, QAS, and the tripod arrangement of QAS in coordination of nickel(II) to form trigonal-bipyramidal complexes are shown in Figure 1. The stoichiometry representing the net substitution process of [NiCl(QAS)]ClO$_4$

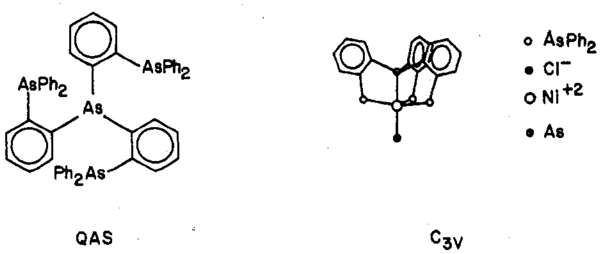

Figure 1. Tetradentate structure of QAS and tripod arrangement of the tetradentate ligand in $[NiCl(QAS)]^+$ illustrating C_{3v} symmetry.

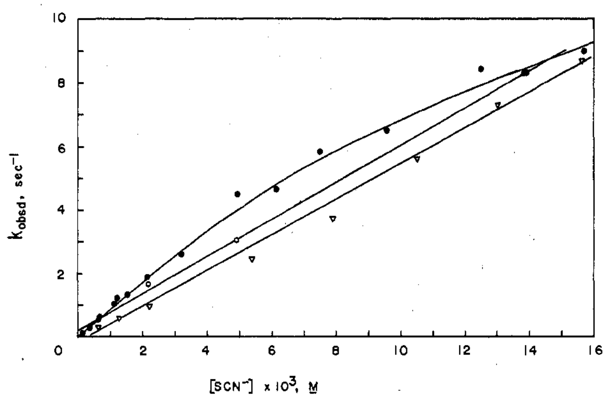

Figure 2. Relationship between experimental pseudo-first-order rate constants and thiocyanate concentration for the $[NiCl(QAS)]^+$-SCN^- reaction at 25 °C in methanol: •, $\mu \simeq [SCN^-]$; ○, $\mu = 0.0157$ M maintained by NaCl; ▽, $\mu = 0.0157$ M maintained by $NaBPh_4$.

by thiocyanate and cyanide in methanol is given by

$$[NiCl(QAS)]^+ + L^- \rightarrow [NiL(QAS)]^+ + Cl^- \quad (2)$$

where L = NCS or CN.

Solutions of $[NiCl(QAS)]ClO_4$ in methanol were observed to undergo slow decomposition with precipitation of QAS becoming noticeable in 4 h[9] at 25 °C. For this reason, reactant solutions were freshly prepared prior to each set of kinetic experiments and stored in an ice bath. It was also observed that the excess amounts of cyanide and thiocyanate ligands in the presence of product complexes accelerated the rates of decomposition of the product complexes. However, even the greatest rates of decomposition of cyano and thiocyanato complexes were orders of magnitude slower than the substitution reactions studied in eq 2.

In a study of an analogous complex, $[PtBr(QAS)]^+$, Pearson, Muir, and Venanzi[3] reported that a tenfold increase in ionic strength, using NaBr, did not alter values of the observed rate constants. For this reason, initial studies on $[NiCl(QAS)]^+$ were conducted neglecting the effect of ionic strength. Experimentally observed pseudo-first-order rate constants for eq 2, given in Table I, are a linear function of thiocyanate and cyanide concentrations up to ca. 0.003 M as shown in Figure 2. Deviation from linearity occurred for entering ligand concentrations above this region. The observed behavior for $[NiCl(QAS)]^+$ reactions appears to be similar to that reported for the $[PtBr(QAS)]^+$–I^- reaction.

Kinetic experiments in which ionic strength was held constant at 0.0157 M with added $NaBPh_4$ and NaCl were conducted on the $[NiCl(QAS)]^+$ reaction with thiocyanate. Plots of k_{obsd} vs. thiocyanate concentration were linear, unlike the results reported for $[PtBr(QAS)]^+$. The slopes of the two plots of constant ionic conditions are approximately the same with $k_2^{NaBPh_4} = 570 \pm 10\ M^{-1}\ s^{-1}$ and $k_2^{NaCl} = 580 \pm 12\ M^{-1}\ s^{-1}$ with the intercepts being nearly zero. A higher concentration of salt to give a greater ionic strength would minimize the effect of increasing contribution of NaSCN to the ionic background. However, caution was taken so as to prevent precipitation of the reactant complex as the tetraphenylborate salt.

An unambiguous explanation of these limited data is not possible. The curved-line relationship for variable ionic strength in Figure 2 could be due to ionic background alone. Alternatively, this behavior could be attributed to the formation of outer-sphere aggregates similar to those discussed by Tobe[10] for substitution reactions of octahedral complexes in nonaqueous solution. A combination of both ionic strength and aggregate formation could account for this behavior.

Because leaving groups in the platinum(II) and nickel(II) five-coordinate complexes are different, a direct comparison between the two systems cannot be made. One noticeable feature can be made in comparison. *Substitution in these five-coordinate nickel(II) complexes is not orders of magnitude faster than in the corresponding platinum(II) complex as would be predicted for aqueous solutions of six-coordinate complexes on the basis of water-exchange rates.*[2] The error of such a prediction lies in assumption of similar mechanisms being operative between hexaaquometal ions in water, on one hand, and five-coordinate sterically fixed nickel(II) complex metal ions in methanol, on the other.

Platinum(II) and palladium(II) complexes with QAS[3] and Qas[4] are reported to be stable in methanol for long periods of time. Nickel(II) complexes containing QAS do not possess the same stability and slowly undergo decomposition to give solvated nickel(II) and precipitated ligand, QAS. It is also interesting to note that cyanide substitution for chloride in $[NiCl(QAS)]^+$ does not appear to be orders of magnitude faster than thiocyanato substitution for chloride, as reported for $[PtBr(QAS)]^+$.

Table I. Summary of Rate Constants[a] for Substitution of Thiocyanate and Cyanide in $[NiCl(QAS)]^+$

$10^4[[NiCl(QAS)]^+]$, M	10^4[ligand], M	k_{obsd}, s^{-1}	$10^4[[NiCl(QAS)]^+]$, M	10^4[ligand], M	k_{obsd}, s^{-1}
		NaSCN, $\mu \simeq [SCN^-]$			
0.589[b]	1.45	0.127	4.9	49.2	4.5
0.589[b]	3.50	0.288	0.044	61.4	4.7
0.372	5.67	0.55	4.9	74.9	5.8
0.589	6.80	0.62	0.117	95.5	6.5
0.372	12.4	1.22	0.092	125	8.4
0.543	15.5	1.32	4.9	139	8.3
0.372	21.6	1.87	0.093	157	9.0
0.052	32.1	2.59			
		NaCN, $\mu \simeq [CN^-]$			
0.47	5.0	0.338	0.47	50.0	6.0
0.47	8.0	0.68	0.47	60.0	6.9
0.47	10.0	0.94	0.47	70.0	7.7
0.47	15.0	1.61	0.47	80.0	9.0
0.47	20.0	2.20	0.47	90.0	10.0
0.47	25.0	2.81	0.47	100	10.9
0.47	30.0	3.36	0.47	120	11.4
0.47	35.0	4.3	0.47	160	14.3
0.47	40.0	4.7	0.47	200	19.4
		NaSCN, $\mu = 0.0157$ M (Maintained by $NaBPh_4$)			
0.40	6.34	0.27	0.40	79	3.7
0.36	12.7	0.53	0.45	105	5.6
0.40	22.1	0.91	0.45	130	7.3
0.36	54	2.43	0.40	156	8.7
		NaSCN, $\mu = 0.0157$ M (Maintained by NaCl)			
0.589	6.80	0.55	0.589	49.2	3.01
0.370	21.8	1.63	0.589	139	8.3

[a] Reactions were conducted in CH_3OH at 25 °C. [b] k_{obsd} was determined by first fitting experimental data to the second-order rate law and then calculating a first-order rate constant. The values listed are for at least 2 half-lives of each reaction and represent the average of replicate experiments.

Morgan and Tobe[4] have proposed that substitution of bromide in $[PtBr(QAS)]^+$ proceeds via a four-coordinate intermediate formed by the equilibrium dissociation of an equatorial arsenic group. The lack of a large difference in rate between substitution of chloride in [NiCl(QAS)] by cyanide and thiocyanate appears to be consistent with the Tobe mechanism. However, these results, combined with the apparent sluggishness of the nickel(II) complex, could also be consistent with either a dissociative interchange mechanism or attack of a square-pyramidal intermediate formed in a rate-determining intramolecular rearrangement.

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Registry No. $[NiCl(QAS)]^+$, 48244-56-0; $[Ni(CN)(QAS)]ClO_4$, 14238-93-8; NCS^-, 302-04-5; CN^-, 57-12-5.

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Carbene Complexes of Gold(III) and Reactions of the Coordinated Ligand

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Since the preliminary reports by Schoellkopf[2] and Badley,[3] many papers have been published on the addition of nucleophiles, such as alcohols and amines, to coordinated isocyanides affording carbene ligands with two heteroatoms directly bonded to the carbenoid carbon atom; the available results in this area have been reviewed recently.[4] Although examples of complexes of metals in high or relatively high oxidation states are not unknown (e.g., Rh(III)[5] and Pt(IV)[6]), difficulties in the preparation prevented an extensive development in this direction and most of the known carbenoid derivatives have metal ions in a low oxidation state (Hg(II), Pt(II), Pd(II), Mn(I), Fe(II), Ru(II), Rh(I), Au(I)).[4]

Here we report the syntheses of some ionic bis(carbene) complexes of gold(III), obtained by oxidation with halogens of the corresponding gold(I) derivatives. In the latter, the displacement of the coordinated carbene has been shown to be very easy,[7] so it seemed interesting to investigate also this aspect of the reactivity of these new derivatives with the aim of establishing the influence of the different oxidation state of the metal.

Following our preliminary communication,[8] the existence of other carbenoid complexes of gold(III) has been reported.[9]

Experimental Section

Preparation of the Complexes. The preparations of the starting gold(I) carbene complexes $[\{(p\text{-}CH_3C_6H_4NH)_2C\}_2Au]ClO_4$(or BF_4), $[\{(p\text{-}CH_3C_6H_4NH)(C_2H_5O)C\}_2Au]ClO_4$, and $[\{(C_6H_{11}NH)(CH_3\text{-}NH)C\}_2Au]ClO_4$ were carried out as reported elsewhere.[8,14] The gold(III) complexes I and IV–VIII were obtained according to the following general procedure.

The gold(I) complex (ca. 0.5 g) was dissolved in $CHCl_3$ (ca. 30 ml), and iodine in $CHCl_3$ solution (ca. 10^{-2} M) was added in a 1:1 molar ratio. The resulting red solution was evaporated to dryness and the oily residue was stirred under petroleum ether to give the orange crude product. The crude products (ca. >80% yield) were crystallized from CH_2Cl_2 (5 ml) and diethyl ether (15 ml) to give the analytical sample; only complex VI was analyzed as a crude solid.

Reactions with water afford the following three compounds.

(a) *N,N'*-Di-*p*-tolylurea. Compound I (0.6 g, 0.56 mmol) was dissolved in acetone (40 ml), water was added (40 ml), and the solution was kept under vigorous stirring at room temperature. In a short time (ca. 1 h) the red complex II was formed; after stirring of the suspension A overnight, the red complex disappeared, the solution B became white and strongly acidic, and a white precipitate was formed. The precipitate (0.11 g, 0.46 mmol, 41% on nitrogen) was filtered, crystallized from hot ethanol, and identified as *N,N'*-di-*p*-tolylurea through its melting point, ir spectrum, and elemental analyses. The solution B was concentrated under vacuum at room temperature to half-volume, extracted with CH_2Cl_2 (*caution*! saturated solutions of $HClO_4$ in CH_2Cl_2 are reported to be highly explosive[10]), and evaporated to dryness; an oily residue was obtained, which solidified under petroleum ether, yielding $[\{(ArNH)_2C\}_2Au]I$, IX, which decomposed on attempted crystallization. In a separate experiment the suspension A was filtered and compound II was isolated and characterized; on pumping (0.01 Torr) to constant weight, II gave III, which was not obtained on pumping I.

From complex I or IV, *N,N'*-di-*p*-tolylurea was obtained also if the reaction was carried out in strictly deoxygenated solvents and by using acetonitrile or methanol in place of acetone. In methanol, however, refluxing was necessary to accomplish the reaction.

(b) *N*-Methyl-*N'*-*p*-tolylurea. Compound VI (0.55 g, 0.65 mmol) was dissolved in acetone (20 ml) and water (20 ml) was added. After stirring of the mixture 9 days at room temperature, the solution was acidic and nearly colorless while a gold mirror formed. The solution was filtered and concentrated to afford a pale yellow crude product (0.18 g, 0.11 mmol, 85% on the starting complex) which was crystallized from ethanol–water and identified as *N*-methyl-*N'*-*p*-tolylurea through its melting point, elemental analyses, and ir and NMR spectra.

(c) *N*-*p*-Tolylurethane. Complex VII (0.57 g, 0.65 mmol) was dissolved in acetone (80 ml), and water (80 ml) was added. Immediately, a red precipitate was formed; after 2 days of stirring, the red precipitate disappeared, the solution was nearly colorless and acidic, and a yellow oil separated plus traces of gold. The oil was extracted with CH_2Cl_2, dried over Na_2SO_4, and then evaporated to dryness. The oily residue was solidified under petroleum ether (several portions) to afford $\{(ArNH)(C_2H_5O)C\}AuI$, X. The petroleum ether solution was evaporated to dryness to give an oily residue; ir and NMR spectra gave evidence of the presence of a mixture. The oily residue was extracted with CCl_4, evaporated to dryness, extracted with cyclohexane, and evaporated again to yield a sticky oily material, identified as *N*-*p*-tolylurethane by ir and NMR spectra.

Reactions with Water in the Presence of LiCl (or NaCl). Compound I (0.68 g, 0.62 mmol) was dissolved in acetone (20 ml); water (20 ml) and a large excess of LiCl (or NaCl) were added and the solution was stirred overnight. A white precipitate was filtered and crystallized from $CHCl_3$–Et_2O to afford the white, crystalline, analytical sample of $[\{(ArNH)_2C\}_2Au]Cl$, XI.

Reactions of Compounds I and IV with Triphenylphosphine. (a) In Acetone. Compound I (or IV) (0.75 g) was dissolved in acetone and Ph_3P was added (molar ratio 1:4). In a few minutes, the solution became colorless, and a white, crystalline product was formed (0.53 g, 0.62 mmol, 88%) which was filtered and crystallized from $CHCl_3$–petroleum ether affording $(Ph_3P)_2AuI$, XII. The filtered solution was evaporated to a small volume, filtered, and then evaporated to dryness. The residue was taken up with $CHCl_3$ and