nating from an excited state correlated with the $(^1\Delta)$NH and $(^2E)Cr^{III}$ electronic configurations and mediated by metal-to-ligand back-bonding.

Registry No. $Cr(NH_3)_5N_3^{2+}$, 22317-10-8; $Co(NH_3)_5F^{2+}$, 15392-06-0.

Supplementary Material Available: Quantum yield data for 254-nm irradiations of $Cr(NH_3)_5N_3^{2+}$ in the presence of $Co(NH_3)_5F^{2+}$ (Table SI) and Figures S1–S3, showing variations of ϕ_{nitrene} with irradiation time, $[H^+]$, and I_a (5 pages). Ordering information is given on any current masthead page.

References and Notes

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Trans Effects in Octahedral Complexes: Substitution of Chloromethyl- and Dichloromethylpentaaquochromium(III) Ions by Thiocyanate Ion[1]

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Equilibrium and kinetic data were evaluated for formation of the 1:1 complexes of NCS^- with $(H_2O)_5CrCH_2Cl^{2+}$ and $(H_2O)_5CrCHCl_2^{2+}$. Equilibrium is established within <100 s, which is unusually rapid for Cr(III) substitution. This corresponds to replacement of only a single H_2O molecule for both NCS^- and CH_3OH as entering groups, verified for NCS^- by species tests and equilibrium constant determinations and for CH_3OH by chemical analysis. The formation constants for NCS^- are 10.4 and 12.8 M^{-1} for $CrCH_2Cl^{2+}$ and $CrCHCl_2^{2+}$, respectively. The kinetic data for anation follow the expression $k_{an} = A[NCS^-]/(1 + C[NCS^-])$ and are consistent with both a limiting S_N1 and an ion-pairing mechanism.

Introduction

Recent publications[2-5] have cited the large trans labilizing effect of an alkyl group in cobalt complexes, particularly in vitamin B_{12} and related model complexes containing a planar tetradentate macrocycle.

In the present work we report equilibrium and kinetic studies on anation reactions of two complexes which are members of the family $(H_2O)_5CrR^{2+}$. The particular R groups studied, CH_2Cl and $CHCl_2$, are complexes in which decomposition of the Cr–C bond via protonolysis occurs very slowly[6] in contrast to more rapid protonolysis of simple alkyls.[7]

Demonstration of an appreciable kinetic trans effect in pentaaquochromium complexes has been accomplished only rarely, although other workers have noted some substantial effects particularly for coordinated iodide and sulfite ions[8a-d] and also for the trifluoromethyl complex $(H_2O)_5CrCF_3^{2+}$.[8e] In the present paper we report (1) proof that only a single water molecule, and therefore most likely that in the trans position, undergoes rapid substitution, based on competition between H_2O and CH_3OH, (2) equilibrium constants for the two anation reactions, and (3) kinetic data for the reactions in eq 1 and 2.

$$(H_2O)_5Cr{-}CH_2Cl^{2+} + SCN^- = trans\text{-}(H_2O)_4Cr(NCS)(CH_2Cl)^+ + H_2O \qquad (1)$$

$$(H_2O)_5Cr{-}CHCl_2^{2+} + SCN^- = trans\text{-}(H_2O)_4Cr(NCS)(CHCl_2)^+ + H_2O \qquad (2)$$

After completion of this work there appeared in the recent literature[9] an independent determination of the equilibrium constant and kinetics of reaction 2. The published results, as discussed later, are in substantial agreement with ours as regards the equilibrium formulation but in considerable disagreement concerning kinetics; our data show rates only $\sim 10^{-3}$ of theirs and with a different dependence upon $[SCN^-]$.

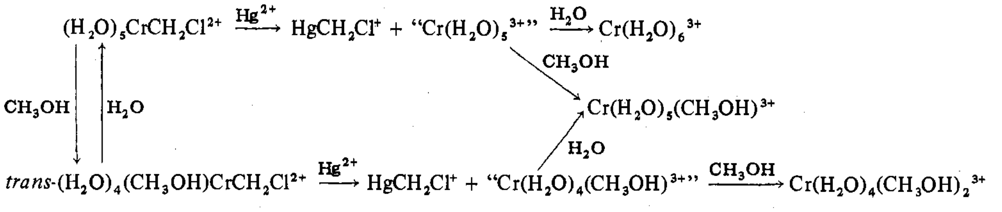
Results

Induced Solvolysis. Reaction of $CrCH_2Cl^{2+}$ with Hg^{2+} results in alkyl transfer (eq 3),[6] a reaction which has a rate

$$CrCH_2Cl^{2+} + Hg^{2+} \rightarrow Cr^{3+} + HgCH_2Cl^+ \qquad (3)$$

constant of 0.59 $dm^3\ mol^{-1}\ s^{-1}$ (25.0 °C, in water, $\mu = 1.0$ M).[9]

Scheme I



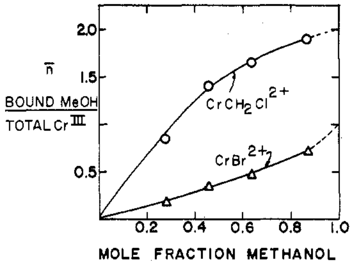


Figure 1. Variation of $\bar{n}$, the number of methanol molecules bound to Cr(III), upon reaction of $CrCH_2Cl^{2+}$ and $CrBr^{2+}$ with Hg(II) in mixed solvents containing various mole fractions of methanol.

The same reaction carried out in mixed methanol–water solvent[11] affords a means of determining quantitatively the extent to which this particular organochromium complex, initially containing in its first coordination sphere only water molecules in addition to the chloromethyl group, undergoes solvent exchange prior to induced solvolysis.

Presentation of the results is simplified if we assume that only a single water molecule in the chloromethylchromium(III) cations is labile to substitution by methanol in the time allowed, say <100 s. The resulting situation is shown in Scheme I.[12]

Ferraris and King[11] developed this method to show that solvolysis of $(H_2O)_5CrX^{2+}$ by Hg^{2+} in mixed solvent leads to a mixture of solvento–Cr(III) products which was the same regardless of group X (Cl or Br or I). They thereby established a common intermediate for the reactions, presumably the five-coordinate $Cr(H_2O)_5^{3+}$.

But if the starting complex contains one or more molecules of coordinated water which undergo substitution *prior* to reaction with Hg^{2+}, as we suggest for the unique trans H_2O in $(H_2O)_5CrCH_2Cl^{2+}$, then the intermediate produced by reaction with Hg^{2+} may contain mixed solvent. We used the separation and analysis procedures of King et al.[11] to determine, over a variety of solvent ratios, a value for $\bar{n}$, the average number of methanol molecules bound in the primary coordination sphere of Cr(III)

$$\bar{n} = \frac{\text{total } [CH_3OH] \text{ in Cr(III) products}}{[\text{Cr(III)}]_{\text{total}}} \tag{4}$$

The variation of $\bar{n}$ with mole fraction of methanol is depicted in Figure 1, which also shows similar data for $(H_2O)_5CrBr^{2+}$ from the literature.[11b] The values for $CrCH_2Cl^{2+}$ extrapolate to a limit of $\bar{n} \simeq 2$ at unit mole fraction of methanol.

Equilibrium Constants for Thiocyanate Anation. Spectrophotometric methods were used to determine equilibrium constants for reactions 1 and 2 at 25.0 °C and $\mu = 1.00$ M. In both reactions marked spectral shifts and intensifications occur upon addition of NCS^-, as shown in Figure 2 which shows reactant spectra as well as spectra of the 1:1 thiocyanate complexes. The equilibrium constant for each reaction was evaluated from the measured absorbance (D) of each solution in a cell of path length b, which can be expressed in terms of the molar absorptivities of uncomplexed CrR^{2+} (ϵ_0) and of its 1:1 complex with thiocyanate (ϵ_1)

$$\frac{D}{b[\text{CrR}]_T} = \frac{\epsilon_1 K[\text{SCN}^-] + \epsilon_0}{1 + K[\text{SCN}^-]} \tag{5}$$

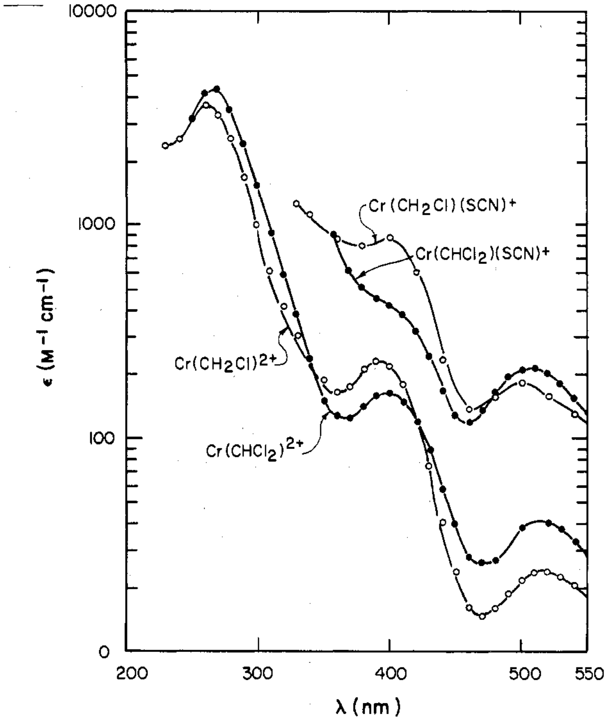


Figure 2. UV–visible spectra of the complexes studied.

where $[\text{CrR}]_T$ represents the total concentration of organochromium, $[\text{CrR}^{2+}] + [\text{CrR(NCS)}^+]$, and K the equilibrium constant for reaction 1 or 2. Rearrangement affords eq 6,

$$\Delta\epsilon = \frac{D - \epsilon_0 b[\text{CrR}^{2+}]}{b[\text{CrR}^{2+}]_T} = \epsilon_1 - \epsilon_0 - \left(\frac{\Delta\epsilon}{[\text{SCN}^-]}\right)\frac{1}{K} \tag{6}$$

which suggests a linear plot of $\Delta\epsilon$ vs. $\Delta\epsilon/[\text{SCN}^-]$ with intercept $\epsilon_1 - \epsilon_0$ and slope $-K^{-1}$.

For the complex $CrCH_2Cl^{2+}$, equilibrium absorbance data were determined in two ways: from spectra of a series of solutions containing various $[\text{SCN}^-]$ which had been aged for a sufficient time such that reaction 1 was at equilibrium and (at λ 351 nm) from the initial and final absorbance readings in each kinetic run. Data at the four wavelengths[13] plotted according to eq 6 are shown in Figure 3, in which least-squares lines are drawn. The values of $K_1/\text{dm}^3\ \text{mol}^{-1}$ are 10.9 ± 0.5 (λ 351 nm), 10.4 ± 0.8 (470), 9.8 ± 0.7 (500), and 10.2 ± 0.7 (550). The overall "best" value we cite is $K_1 = 10.4 \pm 0.6\ \text{M}^{-1}$.

For the complex $CrCHCl_2^{2+}$, the equilibrium constant was evaluated only by the second method, with $K_2 = 12.7 \pm 0.8\ \text{M}^{-1}$.

Further support was found for the formulation made here that the solutions of $CrCH_2Cl^{2+}$ in the presence of NCS^- contain two and only two absorbing species, the parent complex and its 1:1 adduct. Coleman, Varga, and Mastin[14] have described a graphical method of determining the rank of the absorbance matrix $\|D_{ij}\|$ (the absorbance value of a given solution j at wavelength i is designated D_{ij}). The original article should be consulted for details, and we present here the test for the presence of two absorbing species shown in Figure 4.

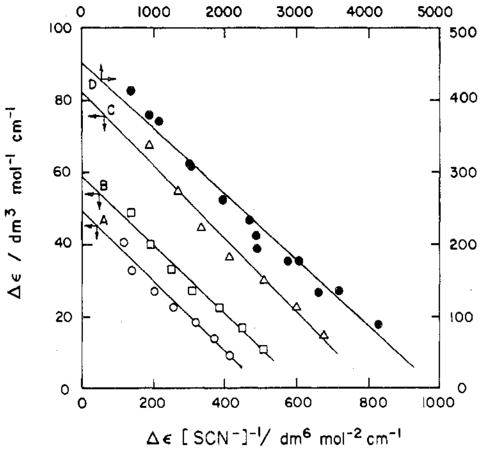


Figure 3. Plots according to eq 6 to determine K_1 at various wavelengths: A, 550 nm; B, 470 nm; C, 500 nm; D, 351 nm.

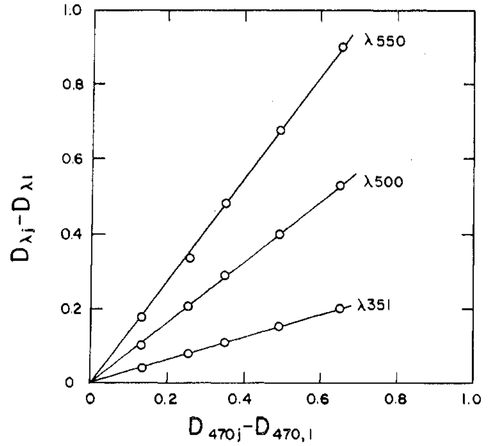


Figure 4. Graphical test[14] for the existence of only two absorbing species in solutions of $CrCH_2Cl^{2+}$ and varying $[NCS^-]$. Absorbance data were taken in 10-cm cells for five solutions with $0.022 < [NCS^-] < 0.21$ M and 2.26×10^{-3} M $CrCH_2Cl^{2+}$ at four wavelengths, one of which, 470 nm, was taken as the standard to define the abscissa. (The ordinate at λ 351 nm is scaled by 1/10 for purposes of graphical display.)

The test at each wavelength, compared to one of the wavelengths arbitrarily chosen as standard, gives an excellent straight line, thus supporting the assignment made.

Over a longer period of time, slow secondary reactions set in, and the Cr–C bond is evidently cleaved. This very slow reaction does appear to occur more rapidly than in the parent complexes, however, but its nature was not investigated.

Kinetics of Thiocyanate Anation. The kinetic data were obtained with a large and varying excess of NCS^-. Within each run the kinetic data were exactly consistent with a scheme of opposing pseudo-first-order reactions, thus characterizing each run by a value of k_{obsd}, the apparent rate constant for the approach to equilibrium

$$\ln [(D_t - D_\infty)/(D_0 - D_\infty)] = -k_{obsd} t \qquad (7)$$

A number of alternatives for further processing of the kinetic data can be considered,[1a] but for purposes of simplicity only the single most satisfactory method will be presented. This method uses the independently evaluated equilibrium constant to transform (eq 8) the composite constant k_{obsd} into a k_{an}, the

$$k_{an} = k_{obsd}/\{1 + (K[NCS^-])^{-1}\} \qquad (8)$$

$$k_{an} = A[NCS^-]/(1 + C[NCS^-]) \qquad (9)$$

pseudo-first-order rate constant for the anation process. Each experiment at different $[NCS^-]$ affords a value of k_{an}. Linear double reciprocal plots of k_{an}^{-1} vs. $[NCS^-]^{-1}$ were obtained, Figure 5, in accord with the rate law of eq 9. They yield the following least-squares values: $CrCH_2Cl^{2+}$ $A = 0.178 \pm 0.004$ M^{-1} s^{-1}, $C = 0.85 \pm 0.18$ M^{-1}; $CrCHCl_2^{2+}$ $A = 0.0624 \pm 0.0017$ M^{-1} s^{-1}, $C = 1.35 \pm 0.18$ M^{-1}. These parameters together with the equilibrium constant for the given reaction were used via eq 8 and 9 to recompute values of k_{obsd}, with an average error in k_{obsd} of 4.9% ($CrCH_2Cl^{2+}$) and 3.4% ($CrCHCl_2^{2+}$).

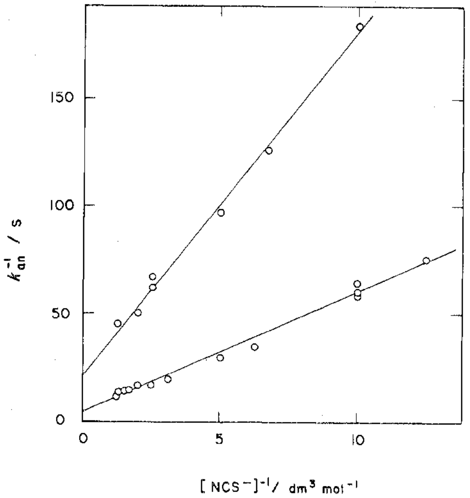


Figure 5. Double reciprocal plots of $1/k_{an}$ vs. $1/[NCS^-]$ for reaction of NCS^- and $CrCH_2Cl^{2+}$ (lower line) and $CrCHCl_2^{2+}$ (upper line). Data at 25.0 °C, μ = 1.00 M.

Table I. Kinetic Data[a] for Substitution of $CrCH_2Cl^{2+}$ and $CrCHCl_2^{2+}$ by NCS^-

	$CrCH_2Cl^{2+}$		$CrCHCl_2^{2+}$	
$[NCS^-]$/ M	10^2k_{obsd}/ s^{-1} [b]	10^2k_{an}/ s^{-1} [c]	10^2k_{obsd}/ s^{-1} [b]	10^2k_{an}/ s^{-1} [c]
0.0800	2.90	1.32		
0.100	3.28	1.67	0.97	0.54
0.100	3.23[d]	1.65		
0.100	3.04[e]	1.55		
0.150			1.20	0.79
0.160	4.46	2.79		
0.200	4.68	3.16	1.43	1.03
0.320	6.36[f]	4.89		
0.400	6.43	5.18	1.91	1.60
0.400			1.76	1.47
0.500	7.19[f]	6.03	2.28	1.97
0.600	7.47	6.44	2.40	2.12
0.640	8.35	7.26		
0.750			2.52	2.28
0.768	8.25	7.33		
0.800	9.25	8.26		

[a] At 25.0 °C, μ = 1.00 M ($LiClO_4$), $[H^+]$ = 0.200 M (except as noted). [b] k_{obsd} is the experimental slope, $-d \ln (D_t - D_\infty)/dt$. [c] k_{an} calculated from k_{obsd} according to eq 8 using $K = 10.4$ M^{-1} ($CrCH_2Cl^{2+}$) and $K = 12.8$ M^{-1} ($CrCHCl_2^{2+}$). [d] $[H^+]$ = 0.500 M. [e] $[H^+]$ = 0.900 M. [f] $[H^+]$ = 0.231 M.

Discussion

We conclude that one of the five water molecules coordinated to the chloromethylchromium cations is unique. The stability studies are consistent with formation of only the 1:1 complexes, and the Coleman–Mastin–Varga test, which makes no assumption about the attainment of equilibrium, substantiates this view.

This alone is not sufficient evidence for a unique substitution, in that successive complexation constants for formation of higher complexes (with a $NCS^-/Cr(III)$ ratio >1) would be expected to drop sharply with each additional NCS^-. Formation[15] of higher complexes between Cr^{3+} and the neutral ligand CH_3OH does not fall off nearly so sharply with successive complexation steps. All members of the series $[(H_2O)_xCr(CH_3OH)_{6-x}]^{3+}$ up to and including $Cr(CH_3OH)_6{}^{3+}$ are isolated after establishment of equilibrium in mixed methanol–water solvent. Based on this, *if* all five solvent coordination positions on the chloromethyl complexes had been equilibrated with solvent in the time allowed, values of $\bar{n}$ approaching 6.0 at high $[CH_3OH]$ should have been found. The experimental limit of $\bar{n}$ at high $[CH_3OH]$ was found to be 2.0 in this system. This result is consistent with the reactions shown in Scheme I, and it constitutes the primary evidence that *one* of the five water molecules is *much* more substitution labile than the other four.[16] The simplest conclusion, therefore, is that the substitution process studied herein represents a trans process.

The spectral data indicate that the products of reactions 1 and 2 have their long-wavelength maxima shifted to shorter wavelengths, suggesting that they contain N-bonded isothiocyanate ions, by comparison with the complexes[17] $Cr(H_2O)_6{}^{3+}$, $(H_2O)_5CrNCS^{2+}$, and $(H_2O)_5CrSCN^{2+}$.

The formation constants for the 1:1 complexes of NCS^- with $(H_2O)_5CrCH_2Cl^{2+}$ and $(H_2O)CrCHCl_2{}^{2+}$ are, respectively, $K_1 = 10.4$ and $K_2 = 12.8\ M^{-1}$ at 25 °C, $\mu = 1.0$ M. The latter value agrees with that determined independently by Azran et al., $11 \pm 2\ M^{-1}$, at an unspecified temperature and (constant ?) ionic strength. The analogous complexation[18] of NCS^- and $Cr(H_2O)_6{}^{3+}$ has $K_3 = 74\ M^{-1}$, under the same conditions. The latter must be corrected for the availability of six equivalent water molecules, giving $K_3(\text{cor}) = K_3/6 = 12\ M^{-1}$. Hence the statistically corrected experimental formation constants for the 1:1 complexes of NCS^- with $Cr(H_2O)_6{}^{3+}$, $(H_2O)_5CrCH_2Cl^{2+}$, and $(H_2O)_5CrCHCl_2{}^{2+}$ are all very nearly the same. The reduced ionic charge in the latter two complexes appears to have a negligible effect upon the binding of the anion NCS^-.

The rate acceleration found for the chloromethylchromium(III) cations is enormous, of the order of 10^5. To offer just a single comparison, the pseudo-first-order rate constant for anation at 25 °C, 0.1 M NCS^-, 0.2 M H^+, corresponds to the following half-times: $CrCH_2Cl^{2+}$, 42 s; $CrCHCl_2{}^{2+}$, 128 s; and Cr^{3+}, 9.3×10^6 s.[19] By way of comparison, the half-times for trans-water substitution in the complexes $(H_2O)_5CrX^{2+}$ range from 2.6×10^3 s ($X = I^-$) to 4.3×10^4 s ($X = -NCS^-$). It thus seems that the groups CH_2Cl and $CHCl_2$ are considerably more effective in labilization of trans ligands than even the best of the halide and pseudohalide ions, I^-.

The complex rate law for reactions 1 and 2 is given by eq 10. The rate parameters A and B are related to the overall

$$\frac{d[(H_2O)_4CrR(NCS)^+]}{dt} = \frac{A[(H_2O)_5CrR^{2+}][NCS^-] - B[(H_2O)_4CrR(NCS^+)]}{1 + C[NCS^-]} \tag{10}$$

equilibrium constant, $K = A/B$.

Two mechanisms consistent with this rate law will be considered further. These are I, a limiting S_N1 mechanism (eq 11 and 12), and II, an ion-pairing mechanism (eq 13 and 14). In these formulations the following relations apply: I, $A = k_1k_2/k_{-1}$, $B = k_{-2}$, $C = k_2/k_{-1}$; II, $A = (k_3 + k_{-3})K_{1P}$, $B = k_{-3}$, $C = K_{1P}$.

$$(H_2O)_5CrR^{2+} \underset{-1}{\overset{1}{\rightleftarrows}} (H_2O)_4CrR^{2+} + H_2O \tag{11}$$

$$(H_2O)_4CrR^{2+} + NCS^- \underset{-2}{\overset{2}{\rightleftarrows}} (H_2O)_4CrR(NCS)^+ \tag{12}$$

$$(H_2O)_5CrR^{2+} + NCS^- \overset{K_{1P}}{\rightleftharpoons} [(H_2O)_5CrR^{2+}]\cdot NCS^- \tag{13}$$

$$[(H_2O)_5CrR^{2+}]\cdot NCS^- \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} (H_2O)_5CrR(NCS)^+ + H_2O \tag{14}$$

Although one might advance various arguments in favor of one mechanism over the other, we feel that these are not overwhelmingly convincing. The ion-pairing constants are near $1\ M^{-1}$, however, a value which strikes us a high for interaction of a reaction of this charge type. This alone seems an insufficient basis on which to discount an ion-pairing mechanism.

The one test which would be helpful, to determine whether the ratio A/C remains constant when different anions are used in place of NCS^- (as expected for I but not for II), was not successfully performed. It was not possible to find other nonbasic anions which would substitute to an efficient extent to provide reliable data, and the basic anions such as F^-, which did bind strongly, were complicated by protonation steps which could tend to obscure a simple and unique formulation and thus were not studied extensively.

We earlier remarked that our kinetic data for reaction 2 are not in agreement with the results of a recently published kinetic study,[9] despite the close agreement of the equilibrium constant values. Our data take the form shown in eq 10 with these values for $CrCHCl_2{}^{2+}$: $A = 6.2 \times 10^{-2}\ M^{-1}\ s^{-1}$, $B = 4.9 \times 10^{-3}\ s^{-1}$, $C = 1.4\ M^{-1}$ (25.0 °C, $\mu = 1.00$ M). In contrast, the other workers[9] report $A = 46.4\ M^{-1}\ s^{-1}$, $B = 4.4\ s^{-1}$, and $C \sim 0$ (T and μ unspecified). We offer no explanation for these discrepancies but do add that in a search for rapid absorbance changes, such as those which might accompany ion-pair formation, we made spectral scans immediately after mixing solutions of CrR^{2+} and SCN^-. In no case were rapid absorbance changes noted; the absorbance values were the same as those for the parent $(H_2O)_5CrR^{2+}$ complex and changed steadily and slowly to the final equilibrium values. Only on long standing were further changes noted, and although not investigated in detail, they corresponded to an apparent cleavage of the Cr–C bond. We suggest that the more rapid process noted by other workers, considering their equilibrium constant is the same as ours, may be caused by an unidentified catalytic species present in their solutions. A possible candidate for such a catalyst is Cr^{2+}, considering its catalytic effect on other Cr(III) substitutions and its use in the reaction used to prepare the starting complex. This idea is discounted, however, by the negligible rate of chromium exchange[20] between Cr^{2+} and $CrCHCl_2{}^{2+}$ (in the absence of SCN^-, however) as well as by its failure to catalyze aquation of $CrCF_3{}^{2+}$.[8e]

Spreer[8e] does not provide quantitative rate data for the substitution of F^- into the coordination sphere of $(H_2O)_5CrCF_3{}^{2+}$, but notes that the "color change...occurred in less than 5 min." This suggests to us two features: (a) that the mean reaction times in all of the systems are correctly of the order of minutes and not milliseconds and (b) that there is but a modest difference in reactivity between members of the family $(H_2O)_5CrR^{2+}$, in the order $CHCl_2 < CH_2Cl < CF_3$, consistent with effects attributed[9] to the soft base character or polarizability of the group R.

The reaction intermediate, whether the five-coordinate complex or the ion pair, must apparently not be subject to intramolecular rearrangement, as an interchange of cis and trans H_2O's, for example, would ultimately equilibrate all five positions, and we have shown that this is not so.

Experimental Techniques

Materials. The organochromium complexes were prepared and isolated as described by Dodd and Johnson,[6] but with certain variations to obtain especially pure product after ion-exchange chromatography. Espenson and Leslie[20] report precise details of the procedure. The UV–visible spectra of these complexes show these maxima, given as λ/nm (ϵ/dm^3 mol^{-1} cm^{-1}): $CrCH_2Cl^{2+}$ 517 (23.4), 393 (225), 265 (3600); $CrCHCl_2{}^{2+}$ 514 (38.7), 396 (157), 266 (4290).

Lithium perchlorate was prepared from the carbonate and purified by recrystallization. Solutions of lithium thiocyanate were prepared from potassium thiocyanate and an excess (ca. 10%) of lithium perchlorate. The precipitated potassium perchlorate was filtered at 0 °C, and the filtrate was analyzed separately for [Li^+] and total thiocyanate, the latter by Volhard titration.

Induced Solvolysis. Solutions of chloromethylchromium(III) ion (typically 300 cm^3 of 10^{-3}–10^{-4} M $CrCH_2Cl^{2+}$ in 0.1 M H^+) were mixed at room temperature with solutions of mercuric nitrate. Both solutions had been made up to the same mole fraction of methanol, and the Hg(II) was added within 100 s of adding methanol to $CrCH_2Cl^{2+}$. The dealkylation reaction was allowed to proceed to completion; its progress was monitored spectrophotometrically as the rate was noticeably slower at higher methanol concentration. The slowest reaction required ca. 15 min to go to completion.

After dealkylation was complete, hydrochloric acid was added (to complex $HgCH_2Cl^+$ and excess Hg^{2+}), and the Cr(III) ions absorbed on a column of Dowex 50W-X8 cation exchange resin. The column was washed with 100 cm^3 of 0.1 M HCl followed by 100 cm^3 of 0.1 M $HClO_4$. The Cr(III) complexes were eluted with 4 M H_2SO_4. After 25 cm^3 of eluent had been collected, the column was allowed to stand for 3 h. Then the rest of the Cr(III) species were eluted. Recovery of Cr(III) was 96–100% complete in 100 cm^3 of eluent. The eluent solution was analyzed for methanol content (50-cm^3 portion) and for total chromium (5-cm^3 portion) by conversion to chromate (ϵ 4830 M^{-1} cm^{-1} at 372 nm). Analysis for methanol was accomplished by the procedure of Jayne and King.[21]

Equilibrium and Kinetic Data. The spectrophotometric data were obtained using a Cary Model 14 recording spectrophotometer with a specially thermostated (±0.1°) cell compartment. The kinetic data were evaluated by standard methods.

Registry No. $(H_2O)_5CrCH_2Cl^{2+}$, 17477-09-7; $(H_2O)_5CrCHCl_2^{2+}$, 17477-10-0; NCS^-, 302-04-5; *trans*-$(H_2O)_4Cr(NCS)(CH_2Cl)^+$, 63950-82-3; *trans*-$(H_2O)_4Cr(NCS)(CHCl_2)^+$, 63976-46-5.

References and Notes

(1) (a) Based in part on the Ph.D. thesis of W.R.B., Iowa State University, 1972. (b) Work performed for U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.

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Palladium(II) Complexes of Benzylphosphorus Ligands[1]

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Palladium(II) complexes and some platinum(II) complexes of the phosphorus ligands Bzl_nPPh_{3-n} (Bzl = $C_6H_5CH_2$, n = 1–3), $(BzlE)_nPPh_{3-n}$ (E = O, S), and $(Bzl_2N)_nPPh_{3-n}$ (n = 1–3) have been prepared and characterized. Characterizaton was achieved by physical data, conductance titrations, and infrared, electronic, and ^1H, $^{13}C\{^1H\}$, $^1H\{^{31}P\}$, and $^{31}P\{^1H\}$ nuclear magnetic resonance spectroscopy. The NMR spectra of the benzylphosphine oxides, sulfides, methiodides, benzyl chlorides, and phosphonium salts have been obtained. Most of the chloride complexes are trans in solution and probably trans in the solid state as well. The complex $[BzlPPh_2]_2PdCl_2$ undergoes reversible thermal isomerization while the complexes $[Bzl_nPPh_{3-n}]_2Pd(N_3)_2$ (n = 1, 2) undergo both reversible thermal and photochemical isomerization in solution. The complex $[Bzl_3P]_2Pd(N_3)_2$ is trans in solution and in the solid state as shown by a complete x-ray structure determination. Addition of excess ligand (L′) to solutions of any of the ML_2X_2 complexes causes ligand exchange and produces mixed-ligand complexes ($MLL'X_2$) but does not catalyze geometric isomerization. Conductance titrations demonstrate the absence of ionic species in all these solutions. Several coupling constant and chemical shift relationships are found and discussed. Computer simulations of the $[ABX]_2$, A, B = ^1H, X = ^{31}P, spin system which results for the intrinsically asymmetric methylenes in several of these compounds have been undertaken and compared with spectra obtained at various field strengths. General conclusions regarding line shapes in the NMR of compounds of this type are drawn.

Introduction

Palladium(II) and platinum(II) form many stable square-planar complexes of the type $(R_3P)_2MX_2$, where X represents a monodentate uninegative anion and R_3P a tertiary phosphine.[3] Complexes of this type have received considerable attention because they serve as model systems for square-planar substitution and isomerization reactions and because these reactions proceed at rates which are conveniently measured by conventional techniques.[4,5] There is currently considerable interest in complexes of sterically hindered phosphines,[6,7] stemming from the fact that many complexes containing sterically hindered phosphines undergo reactions, which, as a class, may be termed "internal-, cyclo-, or ortho-metalation reactions".[8] One of the primary reasons for