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Kinetics of Aquation, Mercury(II)-Assisted Aquation, and Base Hydrolysis of Some Chloro(diamine)(diethylenetriamine)chromium(III) Complexes

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Received September 1, 1976

AIC60643X

Spectrophotometrically determined kinetic parameters for the rates of aquation (1.0 M H^+) of *a,bc,dfe*-[CrCl(AA)(dien)]$ZnCl_4 \cdot H_2O$ (AA = en, pn, tmd) are 10^6k_{298} (s^{-1}) = 22.4, 19.2, 21.8; E_a (kJ mol^{-1}) = 89.2, 93.7, 91.0; log [PZ (s^{-1})] = 10.97, 11.70, 11.27; $\Delta S_{298}^{\ddagger}$ (J K^{-1} mol^{-1}) = −43, −29, −37, respectively. Values for the second-order rate constants for the Hg^{2+}-assisted aquation (μ = 1.0 M) are 10^2k_{298} (M^{-1} s^{-1}) = 2.36, 2.26, and 2.16 for AA = en, pn, and tmd, respectively. In basic solution ([OH^-] = 0.05–0.3 M, μ = 1.0 M), values for the second-order rate constants are 10^3k_{298} (M^{-1} s^{-1}) = 7.33, 8.46, and 7.67, respectively, and kinetic parameters for AA = en are (units as above) E_a = 106 kJ mol and $\Delta S_{298}^{\ddagger}$ = +60 J K^{-1} mol^{-1}. Associative interchange mechanisms are most likely for these reactions.

Introduction

The rate of chloride replacement by water (aquation) or hydroxide ion (base hydrolysis) has been measured for several chloro(diamine)(triamine)cobalt(III) systems,[1-4] e.g., isomers of[5] $CoCl(en)(dien)^{2+}$,[1,2] $CoCl(tmd)(dien)^{2+}$,[3] $CoCl(en)(dpt)^{2+}$,[2] $CoCl(tmd)(dpt)^{2+}$,[3] and $CoCl(Metmd)(dien)^{2+}$.[4] For aquation and Hg^{2+}-assisted aquation, the reaction rate is not particularly sensitive to changes of geometry within a particular isomeric series, but the enhanced rate caused by the expansion of the ring size is well illustrated using this type of Co(III) complex.[2,3] Base hydrolysis rates are, however, dependent on the geometry and Co(III) complexes with a *mer*-$RNH(CH_2)_xNH(CH_2)_xNHR$ polyamine system (x = 2 or 3) cis to the leaving group react some 2–3 orders or magnitude faster than isomeric complexes containing the *fac* configuration for the polyamine.[2-4]

The synthesis of $CrCl(AA)(dien)^{2+}$ complexes (AA = en, pn, tmd), all with the *a,bc,dfe* configuration[6,7] (Figure 1), has allowed us to measure aquation, Hg^{2+}-asssted aquation, and base hydrolysis reaction rates for some Cr(III) complexes of this type. Thus we are able to compare the effect of C-substitution and increase in ring size in these Cr(III) complexes relative to their Co(III) analogues.

A preliminary report on the rate of aquation (0.1 M H^+) of the $CrCl(AA)(dien)^{2+}$ complexes at 323 K has been published.[6]

Experimental Section

The *a,bc,dfe*-[MCl(AA)(dien)]$ZnCl_4 \cdot H_2O$ salts were prepared as described previously.[3,6,8,9] *a,bc,dfe*-[CrCl(en)(dien)]$Cl \cdot ClO_4$ crystallized slowly from a solution of the $ZnCl_4^{2-}$ salt containing excess $NaClO_4$. This behavior parallels that of the isomeric Co(III) analogue.[8] Crystal data are as follows for [CrCl(en)(dien)]$Cl \cdot ClO_4$, $CrC_6H_{21}N_5Cl_3O_4$: fw 385.6; monoclinic, $C2$, Cm, or $C2/m$; a = 14.45, b = 8.04, c = 13.89 Å; β = 108°; ρ_{measd}(bromobenzene/1,2-dibromoethane) = 1.78 g cm^{-3}, $\rho_{calcd}(Z = 4)$ = 1.68 g cm^{-3}.

Aquation Kinetics. Pseudo-first-order rate constants were obtained from spectrophotometric scans of solutions of the $ZnCl_4^{2-}$ salts dissolved in 1.0 M $HClO_4$, using the previously described techniques.[2,6]

Hg^{2+}-Assisted Aquation Kinetics. These reactions were followed spectrophotometrically at constant wavelength (375 nm) as outlined previously[2] except that the use of a 5.00-cm temperature-controlled reaction cell required a reduction in the reactant concentrations (Table III).

Base Hydrolysis Reactions. Solutions (25 mL, ca. 4.4 mM) of the Cr(III) complexes as $ZnCl_4^{2-}$ or $Cl \cdot ClO_4^{2-}$ (AA = en) salts were prepared in 1.0 M $NaClO_4$. Stock solutions of NaOH (0.05–0.3 M) were prepared with the appropriate $NaClO_4$ solution to give a final ionic strength of 1.0 M. Aliquots of these solutions (5.0 mL, at the appropriate temperature) were mixed and transferred to the 5.00-cm temperature-controlled reaction cell. Spectral scans or fixed-wavelength (375 nm) scans were then started. Half-lives of about 5 min were observed with the highest [OH^-] used (at 298 K) and the reproducibility of the observed pseudo-first-order rate constant was about 3%. Interference from $Zn(OH)_2$ precipitation was observed with an OH^-:Zn^{2+} ratio of less than 25.

Instrumentation. All spectrophotometric measurements were made with a JASCO ORD/UV-5 recording spectrophotometer.

Results

Some 160 kinetic runs have allowed us to determine the aquation, Hg^{2+}-assisted aquation, and base hydrolysis rates of chloride release from three *a,bc,dfe*-[CrCl(AA)(dien)]$ZnCl_4 \cdot H_2O$ complexes at μ = 1.0 M.

Pseudo-first-order aquation rate constants, defined by the equation

$$-d[\text{complex}]/dt = k_H[\text{complex}] \qquad (1)$$

are presented in Table I. The change in ionic strength from 0.1[6] to 1.0 M at 323 K results in a 30% decrease in reaction rate. From the temperature dependence of k_H, activation parameters E_a, log PZ, and $\Delta S_{298}^{\ddagger}$ (Table II) have been calculated[10] using the standard equations.[11]

Addition of Hg^{2+} to acidic solutions of the Cr(III) complexes results in an increase in the formation of the aqua complexes, at a rate proportional to the [Hg^{2+}].[12] Table III lists the observed pseudo-first-order rate constants ([Hg^{2+}] ≥ 10·[Cr(III)]) at 298 K (μ = 1.0 M) and the second-order rate constants calculated from these. Data for $CoCl(NH_3)_5^{2+}$, *a,bc,dfe*-$CoCl(pn)(dien)^{2+}$,[8] and *a,bc,dfe*-$CoCl(tmd)(dien)^{2+}$ [3] are also reported as well as the previously determined[2] rate constant for *a,bc,dfe*-$CoCl(en)(dien)^{2+}$.

Conditions for base hydrolysis were also chosen ([OH^-] ≥ 25[Cr(III)]) to give pseudo-first-order rate constants (k_{obsd}, Table IV), and provided this ratio of reactants was maintained, interference from precipitated $Zn(OH)_2$ did not occur.

Plots of k_{obsd} vs. [OH^-] were linear with a small positive intercept. These intercepts (Table IV, footnotes *g*, *i*, *j*), however, were somewhat larger than could be accounted for on the basis of background aquation (Table II) (especially for AA = pn, tmd). Deliberate addition of Zn^{2+} (1.0, 2.0, 3.0, 5.0 mM) to solutions of [CrCl(en)(dien)]$Cl \cdot ClO_4$ (2.0 mM) in 0.195 M NaOH showed that the rate was independent of [Zn^{2+}] and that $Zn(OH)_4^{2-}$ was not a background catalyst. Thus the cause of the larger than expected intercept remains obscure. Nevertheless, the slope accurately reflects the value of the second-order rate constant for base hydrolysis (Table IV).

Discussion

While the mechanism for the aquation of chloro(amine)cobalt(III) complexes is by no means established with certainty, the general opinion is that an essentially dissociative (D or I_d) pathway is operative.[13-15] Thus, the 20-fold increase in aquation rate[16] of $CoCl(MeNH_2)_5^{2+}$ relative to that of $CoCl(NH_3)_5^{2+}$ (Table II) is consistent with this mechanism. Increasing chelation (e.g., in $CoCl(en)(dien)^{2+}$) causes a decrease in the reaction rate relative to that of $CoCl(NH_3)_5^{2+}$

Table I. Spectrophotometrically Determined Pseudo-First-Order Rate Constants for the Aquation of Some $CrCl(AA)(dien)^{2+}$ Complexes in 1.0 M $HClO_4$

AA^a	T, K	$10^4 k_H$,[b] s^{-1}	$10^4 k_H$(calcd),[c] s^{-1}
en	312.93	1.21 ± 0.04	1.22
		1.28 ± 0.02	
	317.14	1.94 ± 0.04	1.92
		1.81 ± 0.04	
	320.18	2.51 ± 0.04	2.65
	323.33	3.72 ± 0.08	3.68
		3.87 ± 0.08	
		3.85 ± 0.11	
	326.29	4.87 ± 0.20	4.97
		4.94 ± 0.26	
		4.92 ± 0.38	
pn	312.93	1.18 ± 0.03	1.15
		1.14 ± 0.03	
	315.62	1.84 ± 0.03	1.56
	319.80	2.33 ± 0.03	2.48
	323.33	3.79 ± 0.06	3.67
		3.84 ± 0.14	
	326.26	4.91 ± 0.24	4.99
		4.95 ± 0.15	
tmd	312.93	1.21 ± 0.03	1.23
		1.28 ± 0.03	
	317.14	1.97 ± 0.06	1.96
	320.19	2.53 ± 0.06	2.72
	323.38	3.72 ± 0.10	3.81
		3.72 ± 0.10	
	326.28	5.11 ± 0.27	5.15
		5.37 ± 0.16	
		5.67 ± 0.20	
		5.28 ± 0.34	
		5.48 ± 0.18	
	328.18	6.01 ± 0.13	6.24
		6.21 ± 0.17	
		5.80 ± 0.39	

[a] [Cr(III)] ≈ 2 mM as $ZnCl_4^{2-}$ salts. [b] Mean k_{obsd} determined from point-by-point calculations plus or minus the standard deviation. [c] k_H calculated from the activation parameters listed in Table II.

but the reasons for this are difficult to establish as the increase in activation entropy (favoring an increase in k) is offset by an increase in activation (favoring a decrease in k). Also evident is a small "six-membered ring effect" resulting in a 2.4-fold rate increase in changing the bidentate chelate from en to tmd (Table II). These same trends are manifest in the Hg^{2+}-assisted aquation of the Co(III) complexes, with the additional slight increase in rate (attributed to steric assistance[17]) in changing from en to pn.

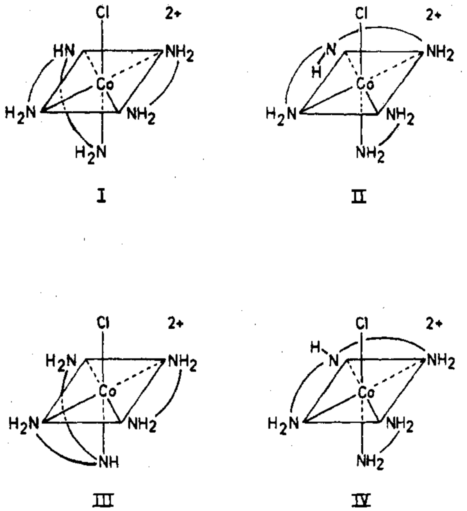

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Figure 1. Geometric isomers possible for $MCl(AA)(dien)^{2+}$. The complexes used in this work have the *a,bc,dfe* configuration (III). When AA = pn, the number of possible isomers is doubled because of the alternate modes of coordination of the unsymmetric diamine. The $MCl(pn)(dien)^{2+}$ complexes used in this work have the *a,bc,dfe* configuration rather than the alternative *a,cb,dfe* configuration.[8]

The mechanism of aquation of chloro(amine)chromium(III) complexes is believed[14] to take place via a more associative pathway (I_a), as there is a 15-fold *decrease* in the aquation rate of $CrCl(MeNH_2)_5^{2+}$ relative to that of $CrCl(NH_3)_5^{2+}$ (Table II). The present data for $CrCl(AA)(dien)^{2+}$ complexes also reflect this change in mechanism in the following aspects: (a) Increasing chelation causes a rate *increase* relative to $CrCl(NH_3)_5^{2+}$ and this arises mainly from an increase in the entropy of activation (as $E_a = 91 \pm 2$ kJ mol^{-1} for the pentaaminechlorochromium(III) complexes). (b) The aquation rate is essentially independent of the ring size or ring substituents. (c) The Hg^{2+}-assisted aquation rates also follow the above two points.

For an I_a mechanism, steric effects are expected to show up in the approach of the nucleophile, rather than in the release of the leaving group. Thus, in $CrCl(MeNH_2)_5^{2+}$, the bulky ligands restrict the approach of the water molecule and a rate decrease relative to $CrCl(NH_3)_5^{2+}$ occurs.[14] If approximately constant solvation effects are assumed for these chromium(III) pentaamine complexes, then a rate increase relative to $CrCl(NH_3)_5^{2+}$ is probably due to a more facile attack by the incoming water molecule.

The independence of the aquation or Hg^{2+}-assisted aquation rates of ring size or ring substituents for Cr(III) contrasts markedly with the case of Co(III) analogues. This contrast has been noticed previously in the *trans*-$MCl_2(AA)(BB)^+$ systems.[18-21] The increase in rate with increasing ring size in chloro(amine)cobalt(III) complexes has been attributed to the more ready distortion to a dissociated trigonal-bipyramid

Table II. Activation Parameters for the Aquation of Some $MCl(N)_5^{2+}$ Complexes

M	$(N)_5^a$	$[H^+]$, M	$10^6 k_{298}$, s^{-1}	E_a, kJ mol^{-1}	log [PZ (s^{-1})]	$\Delta S_{298}^{\ddagger}$, J K^{-1} mol^{-1}	Ref
Cr	$(NH_3)_5$		9.5	89.3	10.62	−50	*b*
Cr	$(MeNH_2)_5$		0.63	97		−47	*c*
Cr	(en)(dien)	1.0	22.4	89.2 ± 2.1	10.97	−43 ± 4	*d*
Cr	(pn)(dien)	1.0	19.2	93.7 ± 2.2	11.70	−29 ± 4	*d*
Cr	(tmd)(dien)	1.0	21.8	91.0 ± 2.2	11.27	−37 ± 4	*d*
Co	$(NH_3)_5$		1.76	96.7 ± 1.0	11.19	−39 ± 2	*b*
Co	$(MeNH_2)_5$		36.7	91.8		−30	*e*
Co	(en)(dien)	1.0	0.094	113 ± 4	12.84	−7 ± 8	*f*
Co	(tmd)(dien)	1.0	0.216	110 ± 3	12.69	−10 ± 6	*g*

[a] Chelated complexes have the *a,bc,dfe* configuration (Figure 1). [b] Computer-calculated from various sources. [c] A. Rodgers and P. J. Staples, *J. Chem. Soc.*, 6834 (1965). [d] This work. [e] S. C. Chan and K. Y. Hui, *Aust. J. Chem.*, **20**, 2529 (1967). [f] Reference 2. [g] References 3 and 4.

Table III. Spectrophotometrically Determined Rate Constants for the Hg^{2+}-Assisted Aquation of Some $MCl(N_5)^{2+}$ Complexes in Acidic Solution at μ = 1.0 M and 298 K[a]

Complex[b]	$[HClO_4]$, M	$[Hg^{2+}]_i$, mM	$10^4 k_{obsd}$,[c] s^{-1}	$10^2 k_{Hg}$,[d] $M^{-1}\,s^{-1}$	Mean $10^2 k_{Hg}$, $M^{-1}\,s^{-1}$	Ref
$CrCl(NH_3)_5^{2+}$					0.87	*e*
$CrCl(en)(dien)^{2+}$	0.82 (2)[f]	30.2	7.36 ± 0.08	2.43 ± 0.03		
	0.88 (2)	20.2	4.62 ± 0.04	2.28 ± 0.02	2.36 ± 0.09	*g*
$CrCl(pn)(dien)^{2+}$	0.82 (2)	30.2	6.37 ± 0.05	2.23 ± 0.02		
	0.88 (2)	20.2	4.56 ± 0.2	2.30 ± 0.09	2.26 ± 0.09	*g*
$CrCl(tmd)(dien)^{2+}$	0.82 (4)	30.2	6.44 ± 0.3	2.13 ± 0.1		
	0.88 (2)	20.2	4.52 ± 0.2	2.24 ± 0.1	2.16 ± 0.11	*g*
$CoCl(NH_3)_5^{2+}$ [h]	0.82 (2)	30.2	37.1 ± 0.7	12.3 ± 0.2		
	0.88 (2)	20.2	24.5 ± 0.2	12.2 ± 0.1	12.2 ± 0.2	*g*
$CoCl(en)(dien)^{2+}$					0.495	*i*
$CoCl(pn)(dien)^{2+}$	0.82 (2)	30.2	1.64 ± 0.02	0.544 ± 0.01		
	0.88 (2)	20.2	1.15 ± 0.02	0.569 ± 0.01	0.558 ± 0.01	*g*
$CoCl(tmd)(dien)^{2+}$	0.82 (3)	30.2	13.5 ± 0.3	4.47 ± 0.1		
	0.88 (3)	20.2	10.2 ± 0.3	5.02 ± 0.1	4.74 ± 0.3	*g*

[a] [M(III)] ≈ 2 mM and λ = 375 nm for this work. [b] As $ZnCl_4^{2-}$ salts except for $MCl(NH_3)_5^{2+}$. Chelate complexes have the *a,bc,dfe* configuration (Figure 1). [c] Mean plus or minus the standard deviation. [d] $k_{Hg} = k_{obsd}/[Hg^{2+}]_i$. [e] Reference 12; μ = 2.0 M. [f] Numbers in parentheses are the number of individual determinations. [g] This work. [h] As the ClO_4^- salt. [i] Reference 2.

Table IV. Rate Constants for the Base Hydrolysis of Some $CrCl(AA)(dien)^{2+}$ Complexes at μ = 1.0 M

AA	*T*, K	$[OH^-]$,[a] M	$10^4 k_{obsd}$,[b] s^{-1}	$10^4 k_{calcd}$,[c] s^{-1}	$10^3 k_{OH}$, $M^{-1}\,s^{-1}$	$10^3 k_{OH}$(calcd), $M^{-1}\,s^{-1}$
en[d]	293.2	0.195 (2)	7.33 ± 0.3		3.76 ± 0.15[e]	3.67 ± 0.06[f]
	298.2	0.049 (2)	3.78 ± 0.2	4.45 ± 0.25		
		0.098 (5)	8.27 ± 0.4	8.05 ± 0.19		
		0.146 (2)	11.7 ± 0.6	11.56 ± 0.14		
		0.195 (14)	15.2 ± 0.6	15.16 ± 0.12		
		0.244 (3)	19.1 ± 0.9	18.75 ± 0.13		
		0.292 (7)	22.3 ± 0.3	22.34 ± 0.17		
		0.390 (2)	28.4 ± 1.4	29.45 ± 0.29	7.32 ± 0.14[g]	7.49 ± 0.08[f]
	303.2	0.195 (3)	29.3 ± 0.7		15.0 ± 0.35[e]	15.1 ± 0.17[f]
	307.2	0.195 (2)	53.0 ± 2.6		27.2 ± 1.4[e]	28.3 ± 0.48[f]
pn[h]	298.2	0.097 (2)	11.0 ± 0.5	11.0 ± 0.1		
		0.195 (2)	19.2 ± 0.9	19.2 ± 0.06		
		0.292 (2)	27.5 ± 1.4	27.4 ± 0.10	8.46 ± 0.08[i]	
tmd[h]	298.2	0.097 (2)	10.7 ± 0.5	11.1 ± 0.58		
		0.195 (2)	19.1 ± 0.9	18.6 ± 0.37		
		0.292 (2)	25.7 ± 1.3	26.0 ± 0.58	7.67 ± 0.46[j]	

[a] Numbers in parentheses are the number of individual determinations. [b] Observed pseudo-first-order rate constant plus or minus the standard deviation. An error of ±5% is assumed where the number of individual determinations is ≤2. [c] Predicted values from a plot of $10^4 k_{obsd}$ vs. $[OH^-]$. Errors are the computer-calculated standard deviation of the predicted values. [d] As $ZnCl_4^{2-}$ or $Cl{\cdot}ClO_4^{2-}$ salts. In certain runs at 0.195 M OH^-, up to 5.0 mM Zn^{2+} was added to solutions of the $Cl{\cdot}ClO_4^{2-}$ salt (2.0 mM) without changing the value of k_{obsd}. [e] Calculated from the equation $k_{OH} = k_{obsd}[OH^-]^{-1}$. [f] Predicted values from a plot of log k_{OH} vs. T^{-1} plus or minus the standard deviation from the predicted value. Kinetic parameters obtained from this plot are E_a = 105.6 ± 1.4 kJ mol^{-1}, log [*PZ* (s^{-1})] 16.385, and $\Delta S_{298}^{\ddagger}$ = +60.4 ± 3 J $K^{-1}\,mol^{-1}$. [g] From the slope of the k_{obsd} vs. $[OH^-]$ line. The intercept is $(8.6 \pm 3.2) \times 10^{-5}\,s^{-1}$. [h] As $ZnCl_4^{2-}$ salts. [i] From the slope of the k_{obsd} vs. $[OH^-]$ line. The intercept is $(27.4 \pm 1.5) \times 10^{-5}\,s^{-1}$. [j] From the slope of the k_{obsd} vs. $[OH^-]$ line. The intercept is $(36.4 \pm 9.8) \times 10^{-5}\,s^{-1}$.

transition state allowed by the larger ring.[3,6] The fact that chloro(amine)chromium(III) complexes aquate with rates independent of ring size and without steric change in the product[20,21] supports the hypothesis of an associative mechanism that involves little distortion of the nonreplaced groups. Also, the observation that the Hg^{2+}-assisted aquation of the chelated Cr(III) complexes parallels the thermal aquation suggests that rupture of the first formed Cr–Cl–Hg bridge is solvent assisted rather than completely dissociative as postulated for the Co(III) analogues.[22]

The reaction between OH^- and chloro(amine)cobalt(III) complexes has been extensively investigated[14,15,23,24] and a dissociative mechanism via a conjugate base (S_N1cB) is generally accepted. The analogous reaction for chloro(amine)chromium(III) complexes has not received such detailed study, partly because many suitable Cr(III) complexes are decomposed to $Cr(OH)_3$ at the high pH (≥11) required to observe the substitution.[25] The chelated Cr(III) complexes described here, however, hydrolyzed smoothly in sodium hydroxide solution with excellent isosbestic points and no evidence for isomerization or amine loss. Good second-order rate constants were obtained (Table IV) but their values are about 3 orders of magnitude smaller than those obtained for the analogous Co(III) complexes (Table V). Thus, if the conjugate base mechanism were operating for chloro(amine)chromium(III) complexes, the NH protons would have to be ca. 1000 times less acidic than in the analogous Co(III) complexes or else the conjugate base is 1000 times less labile. Neither of these alternatives is particularly attractive.

Table V. Kinetic Parameters for the Base Hydrolysis of Some $MCl(N)_5^{2+}$ Complexes at 298 K

M	$(N)_5$[a]	μ, M	k_{OH}, $M^{-1}\,s^{-1}$	E_a, kJ mol^{-1}	$\Delta S_{298}^{\ddagger}$, J K^{-1} mol^{-1}	Ref
Cr	$(NH_3)_5$	0.1	1.8×10^{-3}	109	+99	*b*
	(en)(dien)	1.0	7.33×10^{-3}	106	+60	*c*
	(pn)(dien)	1.0	8.46×10^{-3}			*c*
	(tmd)(dien)	1.0	7.67×10^{-3}			*c*
Co	$(NH_3)_5$	0.0	0.86	121	+155	*d*
	(en)(dien)	0.1	7.3			*e*
	(tmd)(dien)	1.0	10.6	123	+179	*e*

[a] Chelate complexes have the *a,bc,dfe* configuration (Figure 1). [b] M. A. Levine, T. P. Jones, W. E. Harris, and W. J. Wallace, *J. Am. Chem. Soc.*, 83, 2453 (1961). [c] This work. [d] Reference 15. [e] Reference 3.

Conclusions

The rate data presented in this paper for these $CrCl(AA)(dien)^{2+}$ complexes are difficult to interpret in terms of the dissociative mechanisms that have proved suitable for the Co(III) analogues. Consequently, we believe, along with Swaddle,[14] that the I_a mechanism is more suitable for an understanding of the hydrolysis rate patterns obtained for chloro(amine)chromium(III) complexes.

Acknowledgment. We thank Mr. G. Holloway for the crystal data and the New Zealand Universities Grants Committee for providing funds to purchase instruments used in this work.

Registry No. $CrCl(en)(dien)^{2+}$, 59184-05-3; $CrCl(pn)(dien)^{2+}$, 58806-22-7; $CrCl(tmd)(dien)^{2+}$, 58806-20-5; $CrCl(NH_3)_5^{2+}$, 14482-76-9; $CoCl(NH_3)_5^{2+}$, 14970-14-0; $CoCl(pn)(dien)^{2+}$, 62106-89-2; $CoCl(tmd)(dien)^{2+}$, 46239-66-1; Hg^{2+}, 14302-87-5.

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(5) Abbreviations used: en, $NH_2(CH_2)_2NH_2$; pn, $NH_2CH(CH_3)CH_2NH_2$; tmd, $NH_2(CH_2)_3NH_2$; Metmd, $CH_3NH(CH_2)_3NH_2$; dien, $NH_2(CH_2)_2NH(CH_2)_2NH_2$; dpt, $NH_2(CH_2)_3NH(CH_2)_3NH_2$.

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(7) The nomenclature used is that recommended by the Commission on the Nomenclature of Inorganic Chemistry, *Pure Appl. Chem.*, **28**, 1 (1971). The prefixed lower case letters refer to the position of the donor atoms in the octahedron (*a* and *f* in the axial positions) in the order which these are written in the cation formula. The convention adopted here is that the polyamine ligands are coordinated stepwise from one end in the order of the alphabetical letters.

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Chemistry of Metal Carbonyl Anions. 9.[1] Syntheses and Properties of Alkylpentacarbonylmetalate Anions of Chromium and Tungsten

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Received October 1, 1976

AIC60725L

Reactions of $Na_2M(CO)_5$ (M = Cr in THF and W in 1,2-dimethoxyethane (DME)) with various alkyl halides provide $RM(CO)_5^-$ (R = CH_3, C_2H_5, $NCCH_2$, $C_6H_5CH_2$) which have been isolated as bis(triphenylphosphine)iminium (PPN^+) salts. Spectral, chemical, and other properties of these new substances are discussed. Also, a new method for the synthesis of $Na_2W(CO)_5$ by the sodium amalgam reduction of $W(CO)_6$ in DME is reported and discussed with respect to other known preparations of this substance.

Recently we reported on the first general and high-yield synthesis of the pentacarbonylmetalate dianions of chromium, molybdenum, and tungsten[2] and utilized these highly reactive species in the preparation of group 4 metal and metalloidal derivatives of the general formula $R_3EM(CO)_5^-$.[3] In this paper, an extension of this general procedure (eq 1) for the

$$M(CO)_5^{2-} + RCl \rightarrow RM(CO)_5^- + Cl^- \quad (1)$$

preparation of alkylpentacarbonylmetalate anions of chromium and tungsten is reported. While this work was in progress, a preliminary note appeared on two alternate syntheses (eq

$$W(CO)_5Br^- + RLi \rightarrow RW(CO)_5^- + Br^- \quad (2)$$

$$RCOW(CO)_5^- \xrightarrow{h\nu} RW(CO)_5^- + CO \quad (3)$$

2 and 3) for $RW(CO)_5^-$ species,[4] the second of which parallels Isaacs and Graham's synthesis of silyl-, germyl- and stannylpentacarbonylmetalates of Cr, Mo, and W.[5] Previous attempts to prepare alkylpentacarbonylmetalate monoanions of Cr, Mo, and W by the reaction of dialkylmercury with $M_2(CO)_{10}^{2-}$ [6] or alkyllithium reagents with $M(CO)_6$[7] were unsuccessful; however, the latter reaction provided the corresponding acylpentacarbonylmetalates, the precursors to Fischer carbene complexes.[8]

Related $XM(CO)_5^-$ species containing a noncarbonyl carbon–metal bond reported previous to this work include the X = heptafluoro-1-methylpropenyl complex of eq 4, cyanides (eq 5–7), various acetylides (eq 4, 8), methylenephosphoranes (eq 9), substituted vinyls (eq 10), and diphenylmethoxymethyl (eq 11) (M = Cr, Mo, W).

$$2AgX + M_2(CO)_{10}^{2-} \rightarrow 2XM(CO)_5^- + 2Ag \quad (X = C_4F_7,^{9}\ PhC{\equiv}C^{7}) \quad (4)$$

$$Hg(CN)_2 + M_2(CO)_{10}^{2-} \rightarrow 2NCM(CO)_5^- + Hg \quad (5)^{9}$$

$$M(CO)_6 + N(SiMe_3)_2^- \rightarrow NCM(CO)_5^- + (Me_3Si)_2O \quad (6)^{10}$$

$$Cr(CO)_5^{2-} + CN^- + 2H_2O \rightarrow NCCr(CO)_5^- + 2OH^- + H_2 \quad (7)^{11}$$

$$M(CO)_6 + RC{\equiv}C{:}^- \rightarrow RC{\equiv}CM(CO)_5^- + CO \quad (8)^{12}$$

$$(OC)_5CrC(OMe)Ph + HPPh_2 \rightarrow (OC)_5^-CrC(OMe)Ph(^+PPh_2H) \quad (9)^{13}$$

$$(OC)_5CrC(OMe)Me + n\text{-}BuLi \rightarrow [(OC)_5CrC(OMe)CH_2]^-Li^+ + C_4H_{10} \quad (10)^{14}$$

$$(OC)_5WC(OMe)Ph + PhLi \rightarrow [(OC)_5WC(OMe)Ph_2^-Li^+] \ \text{(not isolated)} \quad (11)^{15a}$$

In the course of this work we also developed a convenient new method for the synthesis of $Na_2W(CO)_5$ in 1,2-dimethoxyethane (DME). This salt has previously only been