

# A Novel Photochemical, pH-Controlled Synthesis of Organochromium Complexes

Andreja Bakac,\* James A. Janni, and James H. Espenson\*

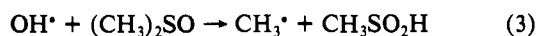
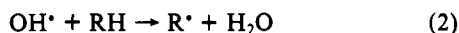
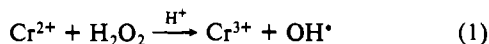
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The irradiation of aqueous solutions of  $\text{Cr}^{2+}$  and  $\text{RX}$  ( $\text{R}$  = primary, secondary, and tertiary alkyl;  $\text{X}$  =  $\text{Br}$ ,  $\text{Cl}$ ) at 254 nm and pH 3 yields the organochromium cations  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$ . The method is based on the photochemical generation of hydrated electrons and subsequent reduction of the alkyl halides to carbon-centered radicals. The colligation with  $\text{Cr}^{2+}$  then yields the desired organochromium complexes. In the presence of alcohols as cosolvents, the nature of the group  $\text{R}$  in  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$  depends on the pH. At pH 3,  $\text{R}$  is derived from  $\text{RX}$ , and at pH 0, from the alcohol. The photochemical method was used to prepare, among others, the novel *tert*-butylchromium(III) ion  $(\text{H}_2\text{O})_5\text{CrC}(\text{CH}_3)_3^{2+}$ . In the presence of scavengers for  $\text{Cr}^{2+}$  and/or  $\text{C}(\text{CH}_3)_3$  this complex decomposes rapidly by homolysis of the  $\text{Cr}-\text{C}$  bond,  $k_h = 0.60 \text{ s}^{-1}$  at 25.0 °C.

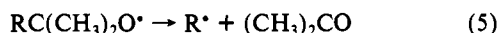
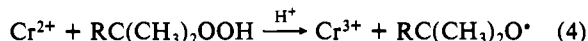
## Introduction

The pentaquaorganochromium(III) complexes,  $(\text{H}_2\text{O})_5\text{CrR}^{2+}$  (hereafter  $\text{CrR}^{2+}$ ), have proved to be a useful and important class of organometallic complexes.<sup>1</sup> They undergo a wide variety of reactions, such as electrophilic substitution, unimolecular, bimolecular, and oxidative<sup>2</sup> homolysis, accelerated trans-substitution,<sup>3</sup> and photochemical cleavage of the chromium-carbon bond.<sup>4</sup> Both thermal and photochemical homolyses can be used conveniently for homogeneous generation of both C-centered radicals and  $\text{Cr}^{2+}$ .

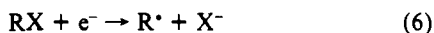
The principal preparative route to  $\text{CrR}^{2+}$  is based on the capture of carbon-centered radicals by  $\text{Cr}^{2+}$ ,  $\text{Cr}^{2+} + \text{R}^\bullet \rightarrow \text{CrR}^{2+}$ . Functionalized radicals derived from alcohols, ethers, carboxylic acids, nitriles, etc. can be quite conveniently generated by a modified Fenton reaction (eqs 1 and 2). A variation of this



method also works for  $\text{R} = \text{CH}_3$ <sup>5</sup> (eq 3), but not for other unsubstituted alkyl radicals. Prior to this work, these radicals were generated in reactions of  $\text{Cr}^{2+}$  with alkyl hydroperoxides (eqs 4 and 5).<sup>6</sup>



Alkyl halides  $\text{RX}$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) are among the most convenient sources of alkyl groups in organic and organometallic synthesis. Unlike the hydroperoxides, they are readily available and quite stable. One-electron reduction cleanly yields alkyl radicals (eq 6).<sup>7</sup> However, with the exception of  $\text{R} = \text{benzyl}$ ,<sup>8</sup>  $\text{Cr}^{2+}$  does not



reduce alkyl halides, which has so far prevented their use in synthesis of  $\text{CrR}^{2+}$ .

We have now developed a method, based on the photochemistry of  $\text{Cr}^{2+}$ , that utilizes alkyl halides as a source of alkyl radicals in the presence of  $\text{Cr}^{2+}$ . This method was used to prepare several known complexes, as well as some novel ones.

## Experimental Section

Alkyl halides were obtained commercially (Aldrich) and used without purification. Solutions of  $\text{Cr}^{2+}$  were prepared by  $\text{Zn}/\text{Hg}$  reduction of

**Table I.** Yields of Photochemically Prepared Organochromium Complexes<sup>a</sup>

RX	% $\text{CrR}^{2+}$	
	in $\text{H}_2\text{O}$ <sup>b</sup>	in $\text{H}_2\text{O}/\text{CH}_3\text{CN}$ (1:1) <sup>c</sup>
$\text{C}_2\text{H}_5\text{Br}$	60	
$\text{C}_2\text{H}_5\text{Cl}$	26	
1- $\text{C}_3\text{H}_7\text{Br}$	16	
2- $\text{C}_3\text{H}_7\text{Br}$	40	80
$(\text{CH}_3)_3\text{CBr}$		40
$(\text{CH}_3)_3\text{CCH}_2\text{Br}$		20
$\text{NC}(\text{CH}_2)_4\text{Br}$	80	

<sup>a</sup>  $[\text{Cr}^{2+}]_0 = 1.5\text{--}3 \text{ mM}$ ,  $[\text{H}^+] = 1 \text{ mM}$ . <sup>b</sup> Solutions were saturated with  $\text{RX}$ . <sup>c</sup>  $[\text{RX}] = 0.05\text{--}0.1 \text{ M}$ .

**Table II.** Characterization of  $\text{CrCH}(\text{CH}_3)_2^{2+}$  and  $\text{CrC}(\text{CH}_3)_3^{2+}$

	$\text{CrCH}(\text{CH}_3)_2^{2+}$ <sup>a</sup>	$\text{CrC}(\text{CH}_3)_3^{2+}$
$\lambda_{\text{max}}/\text{nm}$	400 (488), 290 (2330)	407 (450), 311 (1700)
$\epsilon/\text{M}^{-1} \text{ cm}^{-1}$		
$k_a/\text{s}^{-1}$ <sup>b</sup>	$9.9 \times 10^{-5}$ ( $1.05 \times 10^{-4}$ )	$7.2 \times 10^{-5}$ <sup>c</sup>
$(k_a + k_h)/\text{s}^{-1}$	$3.14 \times 10^{-4}$ ( $2.83 \times 10^{-4}$ )	0.615 <sup>d,e,f</sup> 0.655 <sup>d,e,g</sup> 0.540 <sup>e,f,h</sup> 0.60 ± 0.06 (av)

<sup>a</sup> Literature kinetic data<sup>10</sup> are given in parentheses. <sup>b</sup>  $[\text{H}^+] = 0.05\text{--}0.5 \text{ M}$ ,  $\mu = 1.0 \text{ M}$  ( $\text{HClO}_4 + \text{NaClO}_4$ ), 25.0 °C. <sup>c</sup>  $[\text{Cr}^{2+}] = 0.09 \text{ M}$ . <sup>d</sup> Photochemical preparation. <sup>e</sup> 25.0 °C,  $\mu = 0.5 \text{ M}$ . <sup>f</sup> 0.009–0.020 M  $(\text{NH}_3)_5\text{CoCl}^{2+}$  was used as scavenger. <sup>g</sup> 0.025 M  $(\text{CH}_3)_3\text{COOH}$  was used as scavenger. <sup>h</sup> Peroxide preparation.

$\text{Cr}^{3+}$  in dilute  $\text{HClO}_4$ . The hydroperoxide  $\text{C}(\text{CH}_3)_3\text{C}(\text{CH}_3)_2\text{OOH}$  was prepared by a literature procedure<sup>9</sup> and standardized iodometrically.

Irradiations were carried out in a Rayonet RPR-100 photochemical reactor equipped with a circular array of 16 RPR-2537A lamps. Cary 219 and Perkin-Elmer Lambda Array 3840 spectrophotometers were used for collection of spectral and some kinetic data. Reactions with half-lives shorter than 5 s were monitored by use of a Durrum D-110 stopped-flow spectrophotometer. Gaseous products were analyzed by use of a Hewlett-Packard 5790 gas chromatograph calibrated with commercially available alkanes, alkenes, and alkyl halides.

All the preparative and kinetic experiments were conducted under argon.

**Photochemical Preparation of  $\text{CrR}^{2+}$  Complexes.** A 1-cm quartz spectrophotometric cell was filled with a thoroughly deaerated, ice-cold solution of 3 mM  $\text{Cr}^{2+}$ , 0.1 M  $\text{RX}$ , and 1 mM  $\text{HClO}_4$  in  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  (1:1, v/v), which was then stirred and irradiated in the photochemical reactor for 20 min. The photolysis was interrupted several times and the cell cooled in ice to slow thermal decomposition of the organochromium products. Typical yields are listed in Table I. The method also worked in the absence of  $\text{CH}_3\text{CN}$ , but the yields were lower owing to the limited solubility of alkyl halides in  $\text{H}_2\text{O}$ . Those experiments utilized saturated solutions of  $\text{RX}$ .

**Photochemical Preparation of  $\text{CrC}(\text{CH}_3)_3^{2+}$ .** Owing to the rapid homolysis of this complex, the photolysis times were shorter (4 min) and concentrations of  $\text{Cr}^{2+}$  higher (6–20 mM) than for the other  $\text{CrR}^{2+}$  complexes. Excess  $\text{Cr}^{2+}$  was needed to stabilize the  $\text{CrC}(\text{CH}_3)_3^{2+}$ .

(9) Milas, N. A.; Sugenor, D. M. *J. Am. Chem. Soc.* **1946**, *68*, 643.

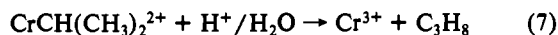
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- Hyde, M. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4463.
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- Anet, F. A. L.; Leblanc, E. *J. Am. Chem. Soc.* **1957**, *79*, 2649.

**Preparation of  $\text{CrC}(\text{CH}_3)_3^{2+}$  by the Peroxide Method.** Typical concentrations used were  $[\text{Cr}^{2+}] = 20 \text{ mM}$ ,  $[\text{C}(\text{CH}_3)_3\text{C}(\text{CH}_3)_2\text{OOH}] = 0.4 \text{ mM}$ , and  $[\text{H}^+] = 3 \text{ mM}$ . The UV-visible spectra were run on freshly prepared solutions. In the calculation of the molar absorptivities in Table II, it was assumed that the conversion of  $\text{C}(\text{CH}_3)_3\text{C}(\text{CH}_3)_2\text{OOH}$  to  $\text{CrC}(\text{CH}_3)_3^{2+}$  was quantitative.

### Results

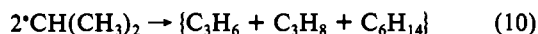
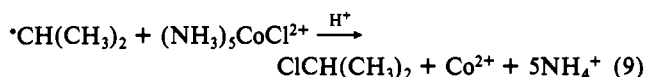
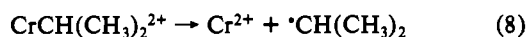
The UV photolysis of aqueous solutions of  $\text{Cr}^{2+}$  and alkyl halides at pH 3 yields the organochromium complexes  $\text{CrR}^{2+}$  (Table I). These complexes were identified by their UV-visible spectra, and several also by their decomposition rates and products, as outlined below.

**$\text{CrCH}(\text{CH}_3)_2^{2+}$ .** Ion-exchange on Sephadex C-25 yielded only two species,  $\text{CrCH}(\text{CH}_3)_2^{2+}$  and  $\text{Cr}^{3+}$ . The decomposition was studied under two sets of conditions. In the presence of excess  $\text{Cr}^{2+}$  the acidolysis (eq 7) yielded  $\text{Cr}^{3+}$  and propane. The kinetics



were in excellent agreement with the literature data<sup>10</sup> (Table II).

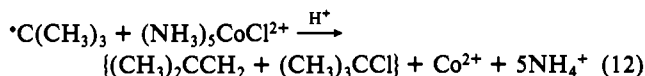
In the presence of excess  $(\text{NH}_3)_5\text{CoCl}^{2+}$ , a scavenger for both the  $\text{Cr}^{2+}$  and  $\cdot\text{CH}(\text{CH}_3)_2$ , the complex underwent parallel homolysis (eqs 8–10) and acidolysis. Under these conditions, (C-



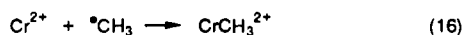
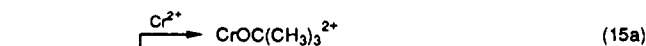
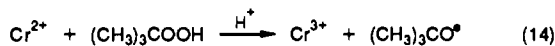
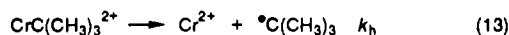
$\text{H}_3)_2\text{CHCl}$  and  $\text{C}_3\text{H}_8$  were major products, along with some propene and 2,3-dimethylbutane, as expected from eqs 7–10. The kinetics were again in good agreement with the literature data (Table II).

**$\text{CrC}(\text{CH}_3)_3^{2+}$ .** In the presence of a large excess of  $\text{Cr}^{2+}$  (0.09 M), the complex decomposed by acidolysis over a period of several hours ( $k = 7.2 \times 10^{-5} \text{ s}^{-1}$  in 0.02 M  $\text{HClO}_4$  at 25.0 °C) and yielded isobutane as the only detectable gaseous product. Scavengers for  $\text{Cr}^{2+}$  and/or  $\cdot\text{C}(\text{CH}_3)_3$  decreased the decomposition time to several seconds and yielded products of radical self-reaction and oxidation. The kinetics were independent of the nature and concentration of the scavenger (Table II), as expected for a homolytic process. An average value of  $0.60 \pm 0.06 \text{ s}^{-1}$  was obtained for  $k_h$  at 25 °C with *t*-BuOOH and  $(\text{NH}_3)_5\text{CoCl}^{2+}$  as scavengers.

When  $(\text{NH}_3)_5\text{CoCl}^{2+}$  was used as a scavenger, both isobutane and isobutene were produced. The proportion of isobutene increased with the concentration of the scavenger, presumably as a result of competition between radical self-reaction and oxidation by  $(\text{NH}_3)_5\text{CoCl}^{2+}$  (eqs 11 and 12).<sup>11</sup>



The other scavenger for  $\text{Cr}^{2+}$ , *t*-BuOOH, yielded  $\text{CrCH}_3^{2+}$ , which was identified by its UV-visible spectrum<sup>1</sup> and acidolysis products ( $\text{CH}_4$  and  $\text{Cr}^{3+}$ ). The chemistry involved is based on the homolysis of the Cr–C bond (eq 13), followed by the known reaction of  $\text{Cr}^{2+}$  with *t*-BuOOH to yield  $\text{CrCH}_3^{2+}$  (eqs 14–16).



(10) Ryan, D. A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 704.

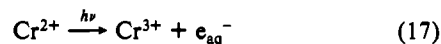
(11) These determinations used a VZ-10 column, which is not useful for detection of the other product, *t*-BuCl.

The majority of  $\text{CrCH}_3^{2+}$  observed was, however, formed prior to homolysis from *t*-BuOOH and the excess of  $\text{Cr}^{2+}$  that is always present in solutions of  $\text{CrC}(\text{CH}_3)_3^{2+}$ .

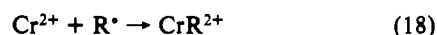
**The pH Effect.** The yields of the  $\text{CrR}^{2+}$  complexes prepared photochemically in  $\text{H}_2\text{O}$  or  $\text{H}_2\text{O}/\text{CH}_3\text{CN}$  decreased dramatically from the values in Table II as the pH of the solution decreased. In fact, no  $\text{CrR}^{2+}$  was detected in 1 M  $\text{HClO}_4$ . However, when alcohols were used as cosolvents, a different picture emerged. For example, a solution of  $\text{CrCH}(\text{CH}_3)_2^{2+}$  was prepared cleanly from  $(\text{CH}_3)_2\text{CHBr}$  at pH 3 in the presence of 25% MeOH. The same experiment conducted at pH 0 yielded  $\text{CrCH}_2\text{OH}^{2+}$  as the only organochromium product. Other alcohols behaved similarly and yielded alcohol-derived organochromium complexes at low pH.

### Discussion

The photochemical method developed in this work produces good to excellent yields of the organochromium cations  $\text{CrR}^{2+}$  from alkyl bromides and chlorides (Table I).<sup>13</sup> The photochemical step involves the formation of hydrated electrons from  $\text{Cr}^{2+}$  (eq 17).<sup>14</sup> The subsequent chemistry, reduction of alkyl halides by



$e_{\text{aq}}^-$  to yield radicals (eq 6)<sup>7</sup> and the colligation of  $\text{Cr}^{2+}$  with radicals (eq 18) are also well-known and documented.<sup>15</sup>



The reduction of  $\text{H}^+$  to  $\text{H}^\bullet$  by  $e_{\text{aq}}^-$  (eq 19)<sup>7</sup> also enters the picture. Hydrogen atoms so produced react with  $\text{Cr}^{2+}$  to yield the hydridochromium(III) ion,  $\text{CrH}^{2+}$ , which decomposes rapidly to  $\text{Cr}^{3+}$  and  $\text{H}_2$ .<sup>16</sup>



The pH dependence of the yields of  $\text{CrR}^{2+}$  is a result of the competition between  $\text{RX}$  and  $\text{H}^+$  (eqs 6 and 19) for  $e_{\text{aq}}^-$ . As the concentration of  $\text{H}^+$  increases relative to that of  $\text{RX}$ , reaction 6 becomes less competitive, and the yield of  $\text{CrR}^{2+}$  decreases. The optimum pH of 3 is a compromise that allows most of  $e_{\text{aq}}^-$  to react with  $\text{RX}$  and still prevents  $\text{CrR}^{2+}$  from decomposing by base hydrolysis that sets in at  $\text{pH} > 3$ .

The rate constants for the reduction of  $\text{RBr}$  by  $e_{\text{aq}}^-$  ( $k \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ )<sup>7</sup> are approximately 1–2 orders of magnitude larger than those for the reduction of  $\text{RCl}$ , which makes the bromides more convenient as radical precursors. This advantage is, however, less than one might expect, because even the chlorides react with  $e_{\text{aq}}^-$  rapidly. Also, the chlorides are more soluble<sup>13</sup> in  $\text{H}_2\text{O}$  than the bromides, which further increases the usefulness of the chlorides for preparative purposes in purely aqueous solutions. In fact, the yields of  $\text{CrC}_2\text{H}_5^{2+}$  obtained from  $\text{C}_2\text{H}_5\text{Br}$  and  $\text{C}_2\text{H}_5\text{Cl}$  differ by about a factor of 3 (Table I).

The use of  $\text{CH}_3\text{CN}$  as cosolvent proved to be quite advantageous, because  $\text{CH}_3\text{CN}$  increases the solubility of alkyl halides but reacts too slowly with  $e_{\text{aq}}^-$  and carbon-centered radicals<sup>17</sup> under the experimental conditions to have an observable effect on the yields of  $\text{CrR}^{2+}$ . Methanol can also be used at levels up

(12) Erben-Russ, M.; Michel, C.; Bors, W.; Saran, M. *J. Phys. Chem.* **1987**, *91*, 2362.

(13) Alkyl iodides have not been explored as possible photochemical precursors of  $\text{CrR}^{2+}$ . Compared to the bromides and chlorides, iodides are less stable and less soluble in  $\text{H}_2\text{O}$  (Horvath, A. L. *Halogenated Hydrocarbons: Solubility-Miscibility with Water*; Marcel Dekker: New York, 1982). Even more importantly, the direct photolysis of  $\text{RI}$  at 254 nm would introduce additional chemistry which includes the formation of  $\text{I}^\bullet$  and thus  $\text{CrI}^{2+}$  as a side product (*The Chemistry of Functional Groups, Supplement D*; Patai, S., Rappaport, Z., Eds.; Wiley: London, 1983; Chapter 29).

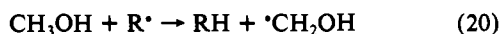
(14) Weiss, J. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 131.

(15) (a) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1989**, *28*, 3901. (b) Cohen, H.; Meyerstein, D. *Inorg. Chem.* **1974**, *13*, 2434.

(16) (a) Cohen, H.; Meyerstein, D. *J. Chem. Soc., Dalton Trans.* **1974**, 2559. (b) Ryan, D. A.; Espenson, J. H. *Inorg. Chem.* **1981**, *20*, 4401.

(17) Ross, A. B.; Neta, P. *Rate Constants for Reactions of Aliphatic Carbon-Centered Radicals in Aqueous Solution*; National Bureau of Standards: Washington, DC, 1982.

to 25% at pH 3. At higher concentrations, CH<sub>3</sub>OH competes with Cr<sup>2+</sup> for R<sup>•</sup> (eq 20),<sup>17</sup> which results in the formation of some CrCH<sub>2</sub>OH<sup>2+</sup>.



While pure aqueous or mixed CH<sub>3</sub>CN/H<sub>2</sub>O solutions yield no organochromium ions at pH 0, solutions containing alcohols (CH<sub>3</sub>OH, C<sub>2</sub>H<sub>5</sub>OH, and 2-C<sub>3</sub>H<sub>7</sub>OH) yield the (hydroxyalkyl)-chromium complexes derived from the solvent alcohol. This is consistent with the proposed reaction mechanism. At pH 0, all the hydrated electrons are scavenged by H<sup>+</sup> to yield H<sup>•</sup> (eq 19). In purely aqueous solutions, H<sup>•</sup> reacts with Cr<sup>2+</sup> and yields CrH<sup>2+</sup>, but in mixed H<sub>2</sub>O/alcohol solutions, H<sup>•</sup> is scavenged by alcohols and yields  $\alpha$ -hydroxyalkyl radicals (eq 21). Colligation with Cr<sup>2+</sup> produces CrCR<sup>1</sup>R<sup>2</sup>OH<sup>2+</sup>.



The *tert*-butylchromium ion, CrC(CH<sub>3</sub>)<sub>3</sub><sup>2+</sup>, was prepared and characterized for the first time in the course of this work. Its identity was established by a number of tests. The same complex is produced by two different methods, photochemically from (CH<sub>3</sub>)<sub>3</sub>CBr and thermally from the hydroperoxide. In the presence

of excess Cr<sup>2+</sup>, the only gaseous decomposition product is isobutane, formed by acidolysis. The other decomposition mode is homolysis. This was clearly established by the inhibiting effect of Cr<sup>2+</sup> and by the invariability of the rate constant  $k_h$  (0.60 s<sup>-1</sup>) with the concentration and nature of the scavenger ((NH<sub>3</sub>)<sub>5</sub>CoCl<sup>2+</sup> and *t*-BuOOH). The rate constant  $k_h$  is the largest measured for an organochromium complex, in full accord with the known steric effect of the alkyl group on homolysis.<sup>18,19</sup>

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**Registry No.** Cr<sup>2+</sup>, 7440-47-3; C<sub>2</sub>H<sub>5</sub>Br, 74-96-4; C<sub>2</sub>H<sub>5</sub>Cl, 75-00-3; 1-C<sub>3</sub>H<sub>7</sub>Br, 106-94-5; 2-C<sub>3</sub>H<sub>7</sub>Br, 75-26-3; (CH<sub>3</sub>)<sub>3</sub>CBr, 507-19-7; (C<sub>2</sub>H<sub>5</sub>)<sub>3</sub>CCH<sub>2</sub>Br, 630-17-1; NC(CH<sub>2</sub>)<sub>4</sub>Br, 5332-06-9; (H<sub>2</sub>O)<sub>5</sub>CrC<sub>2</sub>H<sub>5</sub><sup>2+</sup>, 52653-39-1; (H<sub>2</sub>O)<sub>5</sub>CrC<sub>3</sub>H<sub>7</sub><sup>2+</sup>, 52653-40-4; (H<sub>2</sub>O)<sub>5</sub>CrCH(CH<sub>3</sub>)<sub>2</sub><sup>2+</sup>, 60764-48-9; (H<sub>2</sub>O)<sub>5</sub>CrC(CH<sub>3</sub>)<sub>2</sub><sup>2+</sup>, 138666-90-7; (H<sub>2</sub>O)<sub>5</sub>CrCH<sub>2</sub>C(CH<sub>3</sub>)<sub>3</sub><sup>2+</sup>, 52653-41-5; (H<sub>2</sub>O)<sub>5</sub>Cr(CH<sub>2</sub>)<sub>4</sub>CN<sup>2+</sup>, 138693-66-0; (H<sub>2</sub>O)<sub>5</sub>Cr(CH<sub>3</sub>)<sub>3</sub>C(CH<sub>3</sub>)<sub>2</sub>OOH, 62696-04-2.

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Contribution from the Institute for Inorganic Chemistry, University of Witten/Herdecke, Stockumer Strasse 10, 5810 Witten, Federal Republic of Germany

## Kinetic Study of the Interaction of Aqueated Palladium(II) Complexes with Purine 5'-Nucleoside Monophosphates and Ribose 5'-Monophosphate in Aqueous Solution. Effects of Steric Hindrance and Phosphate-Induced Reactivity

Heribert Hohmann, Björn Hellquist,<sup>1</sup> and Rudi van Eldik\*

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The complex formation reactions of a series of complexes of the type Pd(R<sub>4</sub>en)(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> (R<sub>4</sub>en = N-substituted ethylenediamine, R = H, Me, Et) with ribose, adenosine, inosine, and guanosine 5'-monophosphate were investigated as a function of monophosphate concentration and temperature in the pH range 4–5. In all cases the complex formation with 5'-XMP (X = R, A, I, G) occurs in two consecutive steps for which the pseudo-first-order rate constants fit the equation  $k_{\text{obs}} = k_a + k_b[\text{XMP}]$ . The experiments with ribose monophosphate revealed complex formation rate constants significantly smaller than those reported before for inosine, but larger than those found for adenosine. This trend is also observed for the nucleoside monophosphates for which the rate constants follow the sequence AMP < RMP < IMP < GMP. In addition, all nucleotides react significantly faster than the corresponding nucleosides, demonstrating a significant transition state stabilization effect by the monophosphate group during the complex formation reactions. The systematic variation of the substituents on the en ligand decreases the formation rate constant by as much as 3 orders of magnitude in going from the unsubstituted (R = H) to the most sterically hindered species (R = Et). The complex formation reactions all proceed according to an associative substitution mechanism and are accompanied by significantly negative  $\Delta S^\ddagger$  values. The results are discussed in reference to data available for the corresponding nucleosides and structural information on the final reaction products reported in the literature.

### Introduction

We recently reported a detailed kinetic and mechanistic study of the complex formation reactions of Pd(en)(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> and Pd(Et<sub>4</sub>en)(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> (en = ethylenediamine) with the purine nucleosides adenosine and inosine<sup>2</sup> as a model reference system for the more inert *cis*-Pt(NH<sub>3</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub><sup>2+</sup> antitumor complex. The introduction of steric hindrance on the en ligand enables a kinetic tuning of the lability of the diaqua complex and allows an extrapolation of the data to the less labile Pt(II) complex. The quoted Pd(II) and Pt(II) complexes exhibit very similar thermodynamic properties in terms of complex formation and acid dissociation constants, although their reactivity differs by 5 orders of magnitude.<sup>3,4</sup> Similar results were previously reported for a series of sterically hindered diethylenetriamine-Pd(II) complexes.<sup>5,6</sup> We have now extended our studies to the 5'-monophosphates

of the purine nucleosides, adenosine (AMP), inosine (IMP), and guanosine (GMP) and of ribose (RMP) itself. These substrates represent simple models for the interaction of DNA with metal ions and complexes, which is widely accepted to be an important step in the reaction mechanism of the *cis* Pt(II) antitumor drugs.<sup>7</sup>

Structural studies on reaction products using NMR and X-ray techniques have contributed significantly to resolve the most frequently found binding sites in DNA and DNA constituents.<sup>7</sup> In this respect it has been shown that oxo purines such as guanine and adenine show a strong preference for the N7 binding site, and that a *cis* Pt(II) complex prefers adjacent guanine units in DNA for complexation.<sup>7</sup> However, there are cases known where N1 of the purine ring is involved in coordination to the platinum complex, especially in those cases where the nucleic base bridges two metal centers.<sup>8</sup> Since DNA also contains a phosphate

(1) On leave from the Department of Chemistry, Högskolan, 1 Sundsvall/Harnosand, 85124 Sundsvall, Sweden.  
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