1088 *Inorg. Chem.* **1992**, *31*, 1088-1090

Contribution from Ames Laboratory and the Department of Chemistry,
Iowa State University, Ames, Iowa 50011

A Novel Photochemical, pH-Controlled Synthesis of Organochromium Complexes

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

Received July 19, 1991

The irradiation of aqueous solutions of Cr^{2+} and RX (R = primary, secondary, and tertiary alkyl; X = Br, Cl) at 254 nm and pH 3 yields the organochromium cations $(H_2O)_5CrR^{2+}$. 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 Cr^{2+} then yields the desired organochromium complexes. In the presence of alcohols as cosolvents, the nature of the group R in $(H_2O)_5CrR^{2+}$ depends on the pH. At pH 3, R is derived from RX, and at pH 0, from the alcohol. The photochemical method was used to prepare, among others, the novel *tert*-butylchromium(III) ion $(H_2O)_5CrC(CH_3)_3{}^{2+}$. In the presence of scavengers for Cr^{2+} and/or $^{\bullet}C(CH_3)_3$ this complex decomposes rapidly by homolysis of the Cr–C bond, $k_h = 0.60\ s^{-1}$ at 25.0 °C.

Introduction

The pentaaquaorganochromium(III) complexes, $(H_2O)_5CrR^{2+}$ (hereafter CrR^{2+}), have proved to be a useful and important class of organometallic complexes.[1] They undergo a wide variety of reactions, such as electrophilic substitution, unimolecular, bimolecular, and oxidative[2] homolysis, accelerated trans-substitution,[3] and photochemical cleavage of the chromium–carbon bond.[4] Both thermal and photochemical homolyses can be used conveniently for homogeneous generation of both C-centered radicals and Cr^{2+}.

The principal preparative route to CrR^{2+} is based on the capture of carbon-centered radicals by Cr^{2+}, $Cr^{2+} + R^{\bullet} \rightarrow CrR^{2+}$. 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

$$Cr^{2+} + H_2O_2 \xrightarrow{H^+} Cr^{3+} + OH^{\bullet} \quad (1)$$

$$OH^{\bullet} + RH \rightarrow R^{\bullet} + H_2O \quad (2)$$

$$OH^{\bullet} + (CH_3)_2SO \rightarrow CH_3^{\bullet} + CH_3SO_2H \quad (3)$$

method also works for $R = CH_3$[5] (eq 3), but not for other unsubstituted alkyl radicals. Prior to this work, these radicals were generated in reactions of Cr^{2+} with alkyl hydroperoxides (eqs 4 and 5).[6]

$$Cr^{2+} + RC(CH_3)_2OOH \xrightarrow{H^+} Cr^{3+} + RC(CH_3)_2O^{\bullet} \quad (4)$$

$$RC(CH_3)_2O^{\bullet} \rightarrow R^{\bullet} + (CH_3)_2CO \quad (5)$$

Alkyl halides RX (X = Cl, 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).[7] However, with the exception of R = benzyl,[8] Cr^{2+} does not

$$RX + e^- \rightarrow R^{\bullet} + X^- \quad (6)$$

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

We have now developed a method, based on the photochemistry of Cr^{2+}, that utilizes alkyl halides as a source of alkyl radicals in the presence of 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 Cr^{2+} were prepared by Zn/Hg reduction of Cr^{3+} in dilute $HClO_4$. The hydroperoxide $C(CH_3)_3C(CH_3)_2OOH$ was prepared by a literature procedure[9] and standardized iodometrically.

Table I. Yields of Photochemically Prepared Organochromium Complexes[a]

RX	% CrR^{2+} in H_2O[b]	% CrR^{2+} in H_2O/CH_3CN (1:1)[c]
C_2H_5Br	60	
C_2H_5Cl	26	
1-C_3H_7Br	16	
2-C_3H_7Br	40	80
$(CH_3)_3CBr$		40
$(CH_3)_3CCH_2Br$		20
$NC(CH_2)_4Br$	80	

[a] $[Cr^{2+}]_0$ = 1.5–3 mM, $[H^+]$ = 1 mM. [b] Solutions were saturated with RX. [c] [RX] = 0.05–0.1 M.

Table II. Characterization of $CrCH(CH_3)_2{}^{2+}$ and $CrC(CH_3)_3{}^{2+}$

	$CrCH(CH_3)_2{}^{2+}$[a]	$CrC(CH_3)_3{}^{2+}$
λ_{max}/nm (ϵ/$M^{-1}\ cm^{-1}$)	400 (488), 290 (2330)	407 (450), 311 (1700)
k_a/s^{-1}[b]	9.9×10^{-5} (1.05×10^{-4})	7.2×10^{-5}[c]
$(k_a + k_h)/s^{-1}$	3.14×10^{-4} (2.83×10^{-4})	0.615[d,e,f] 0.655[d,e,g] 0.540[e,f,h] 0.60 ± 0.06 (av)

[a] Literature kinetic data[10] are given in parentheses. [b] $[H^+]$ = 0.05–0.5 M, μ = 1.0 M ($HClO_4 + NaClO_4$), 25.0 °C. [c] $[Cr^{2+}]$ = 0.09 M. [d] Photochemical preparation. [e] 25.0 °C, μ = 0.5 M. [f] 0.009–0.020 M $(NH_3)_5CoCl^{2+}$ was used as scavenger. [g] 0.025 M $(CH_3)_3COOH$ was used as scavenger. [h] Peroxide preparation.

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 CrR^{2+} Complexes. A 1-cm quartz spectrophotometric cell was filled with a thoroughly deaerated, ice-cold solution of 3 mM Cr^{2+}, 0.1 M RX, and 1 mM $HClO_4$ in H_2O/CH_3CN (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 CH_3CN, but the yields were lower owing to the limited solubility of alkyl halides in H_2O. Those experiments utilized saturated solutions of RX.

Photochemical Preparation of $CrC(CH_3)_3{}^{2+}$. Owing to the rapid homolysis of this complex, the photolysis times were shorter (4 min) and concentrations of Cr^{2+} higher (6–20 mM) than for the other CrR^{2+} complexes. Excess Cr^{2+} was needed to stabilize the $CrC(CH_3)_3{}^{2+}$.

---

(1) Espenson, J. H. *Adv. Inorg. Bioinorg. Mech.* **1982**, *1*, 1 and references therein.

(2) (a) Melton, J. D.; Espenson, J. H.; Bakac, A. *Inorg. Chem.* **1986**, *25*, 4104. (b) Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1988**, *110*, 3453.

(3) Bakac, A.; Espenson, J. H.; Miller, L. P. *Inorg. Chem.* **1982**, *21*, 1557.

(4) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1983**, *22*, 779.

(5) Gold, V.; Wood, D. L. *J. Chem. Soc., Dalton Trans.* **1981**, 2462.

(6) Hyde, M. R.; Espenson, J. H. *J. Am. Chem. Soc.* **1976**, *98*, 4463.

(7) Buxton, G. V.; Greenstock, C. L.; Helman, W. P.; Ross, A. B. *J. Phys. Chem. Ref. Data* **1988**, *17*, 532.

(8) Anet, F. A. L.; Leblanc, E. *J. Am. Chem. Soc.* **1957**, *79*, 2649.

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

0020-1669/92/1331-1088$03.00/0

Preparation of $CrC(CH_3)_3^{2+}$ by the Peroxide Method. Typical concentrations used were $[Cr^{2+}] = 20$ mM, $[C(CH_3)_3C(CH_3)_2OOH] = 0.4$ mM, and $[H^+] = 3$ 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 $C(CH_3)_3C(CH_3)_2OOH$ to $CrC(CH_3)_3^{2+}$ was quantitative.

Results

The UV photolysis of aqueous solutions of Cr^{2+} and alkyl halides at pH 3 yields the organochromium complexes 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.

$CrCH(CH_3)_2^{2+}$. Ion-exchange on Sephadex C-25 yielded only two species, $CrCH(CH_3)_2^{2+}$ and Cr^{3+}. The decomposition was studied under two sets of conditions. In the presence of excess Cr^{2+} the acidolysis (eq 7) yielded Cr^{3+} and propane. The kinetics

$$CrCH(CH_3)_2^{2+} + H^+/H_2O \rightarrow Cr^{3+} + C_3H_8 \qquad (7)$$

were in excellent agreement with the literature data[10] (Table II).

In the presence of excess $(NH_3)_5CoCl^{2+}$, a scavenger for both the Cr^{2+} and $^{\bullet}CH(CH_3)_2$, the complex underwent parallel homolysis (eqs 8–10) and acidolysis. Under these conditions, $(CH_3)_2CHCl$ and C_3H_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).

$$CrCH(CH_3)_2^{2+} \rightarrow Cr^{2+} + {}^{\bullet}CH(CH_3)_2 \qquad (8)$$

$${}^{\bullet}CH(CH_3)_2 + (NH_3)_5CoCl^{2+} \xrightarrow{H^+} ClCH(CH_3)_2 + Co^{2+} + 5NH_4^+ \qquad (9)$$

$$2\,{}^{\bullet}CH(CH_3)_2 \rightarrow \{C_3H_6 + C_3H_8 + C_6H_{14}\} \qquad (10)$$

$CrC(CH_3)_3^{2+}$. In the presence of a large excess of Cr^{2+} (0.09 M), the complex decomposed by acidolysis over a period of several hours ($k = 7.2 \times 10^{-5}\ s^{-1}$ in 0.02 M $HClO_4$ at 25.0 °C) and yielded isobutane as the only detectable gaseous product. Scavengers for Cr^{2+} and/or $^{\bullet}C(CH_3)_3$ 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 $0.60 \pm 0.06\ s^{-1}$ was obtained for k_h at 25 °C with *t*-BuOOH and $(NH_3)_5CoCl^{2+}$ as scavengers.

When $(NH_3)_5CoCl^{2+}$ 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 $(NH_3)_5CoCl^{2+}$ (eqs 11 and 12).[11]

$$2\,{}^{\bullet}C(CH_3)_3 \rightarrow (CH_3)_2CCH_2 + (CH_3)_3CH \qquad (11)$$

$${}^{\bullet}C(CH_3)_3 + (NH_3)_5CoCl^{2+} \xrightarrow{H^+} \{(CH_3)_2CCH_2 + (CH_3)_3CCl\} + Co^{2+} + 5NH_4^+ \qquad (12)$$

The other scavenger for Cr^{2+}, *t*-BuOOH, yielded $CrCH_3^{2+}$, which was identified by its UV–visible spectrum[1] and acidolysis products (CH_4 and Cr^{3+}). The chemistry involved is based on the homolysis of the Cr–C bond (eq 13), followed by the known reaction of Cr^{2+} with *t*-BuOOH to yield $CrCH_3^{2+}$ (eqs 14–16).

$$CrC(CH_3)_3^{2+} \longrightarrow Cr^{2+} + {}^{\bullet}C(CH_3)_3 \quad k_h \qquad (13)$$

$$Cr^{2+} + (CH_3)_3COOH \xrightarrow{H^+} Cr^{3+} + (CH_3)_3CO^{\bullet} \qquad (14)$$

$$(CH_3)_3CO^{\bullet} \xrightarrow{Cr^{2+}} CrOC(CH_3)_3^{2+} \qquad (15a)$$

$$(CH_3)_3CO^{\bullet} \longrightarrow (CH_3)_2CO + {}^{\bullet}CH_3 \quad k = 1.4 \times 10^6\ s^{-1}\ {}^{12} \qquad (15b)$$

$$Cr^{2+} + {}^{\bullet}CH_3 \longrightarrow CrCH_3^{2+} \qquad (16)$$

The majority of $CrCH_3^{2+}$ observed was, however, formed prior to homolysis from *t*-BuOOH and the excess of Cr^{2+} that is always present in solutions of $CrC(CH_3)_3^{2+}$.

The pH Effect. The yields of the CrR^{2+} complexes prepared photochemically in H_2O or H_2O/CH_3CN decreased dramatically from the values in Table II as the pH of the solution decreased. In fact, no CrR^{2+} was detected in 1 M $HClO_4$. However, when alcohols were used as cosolvents, a different picture emerged. For example, a solution of $CrCH(CH_3)_2^{2+}$ was prepared cleanly from $(CH_3)_2CHBr$ at pH 3 in the presence of 25% MeOH. The same experiment conducted at pH 0 yielded $CrCH_2OH^{2+}$ 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 CrR^{2+} from alkyl bromides and chlorides (Table I).[13] The photochemical step involves the formation of hydrated electrons from Cr^{2+} (eq 17).[14] The subsequent chemistry, reduction of alkyl halides by e_{aq}^- to yield radicals (eq 6)[7] and the colligation of Cr^{2+} with radicals (eq 18) are also well-known and documented.[15]

$$Cr^{2+} \xrightarrow{h\nu} Cr^{3+} + e_{aq}^- \qquad (17)$$

$$Cr^{2+} + R^{\bullet} \rightarrow CrR^{2+} \qquad (18)$$

The reduction of H^+ to $H^{\bullet}$ by e_{aq}^- (eq 19)[7] also enters the picture. Hydrogen atoms so produced react with Cr^{2+} to yield the hydridochromium(III) ion, CrH^{2+}, which decomposes rapidly to Cr^{3+} and H_2.[16]

$$e_{aq}^- + H^+ \rightarrow H^{\bullet} \qquad (19)$$

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

The rate constants for the reduction of RBr by e_{aq}^- ($k \sim 10^{10}\ M^{-1}\ s^{-1}$)[7] are approximately 1–2 orders of magnitude larger than those for the reduction of 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_{aq}^- rapidly. Also, the chlorides are more soluble[13] in H_2O than the bromides, which further increases the usefulness of the chlorides for preparative purposes in purely aqueous solutions. In fact, the yields of $CrC_2H_5^{2+}$ obtained from C_2H_5Br and C_2H_5Cl differ by about a factor of 3 (Table I).

The use of CH_3CN as cosolvent proved to be quite advantageous, because CH_3CN increases the solubility of alkyl halides but reacts too slowly with e_{aq}^-[7] and carbon-centered radicals[17] under the experimental conditions to have an observable effect on the yields of CrR^{2+}. Methanol can also be used at levels up

---

(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.

(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 CrR^{2+}. Compared to the bromides and chlorides, iodides are less stable and less soluble in H_2O (Horvath, A. L. *Halogenated Hydrocarbons: Solubility-Miscibility with Water*; Marcel Dekker: New York, 1982). Even more importantly, the direct photolysis of RI at 254 nm would introduce additional chemistry which includes the formation of $I^{\bullet}$ and thus 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. 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_3OH competes with Cr^{2+} for $R^{\bullet}$ (eq 20),[17] which results in the formation of some $CrCH_2OH^{2+}$.

$$CH_3OH + R^{\bullet} \rightarrow RH + {}^{\bullet}CH_2OH \tag{20}$$

While pure aqueous or mixed CH_3CN/H_2O solutions yield no organochromium ions at pH 0, solutions containing alcohols (CH_3OH, C_2H_5OH, and 2-C_3H_7OH) 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^+ to yield $H^{\bullet}$ (eq 19). In purely aqueous solutions, $H^{\bullet}$ reacts with Cr^{2+} and yields CrH^{2+}, but in mixed H_2O/alcohol solutions, $H^{\bullet}$ is scavenged by alcohols and yields α-hydroxyalkyl radicals (eq 21). Colligation with Cr^{2+} produces $CrCR^1R^2OH^{2+}$.

$$H^{\bullet} + R^1R^2CH_2OH \rightarrow R^1R^2\dot{C}OH + H_2 \tag{21}$$

The *tert*-butylchromium ion, $CrC(CH_3)_3{}^{2+}$, 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 $(CH_3)_3CBr$ and thermally from the hydroperoxide. In the presence of excess Cr^{2+}, 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^{2+} and by the invariability of the rate constant k_h (0.60 s^{-1}) with the concentration and nature of the scavenger ($(NH_3)_5CoCl^{2+}$ 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.[18,19]

Acknowledgment. This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Chemical Sciences Division, under Contract W-7405-Eng-82.

Registry No. Cr^{2+}, 7440-47-3; C_2H_5Br, 74-96-4; C_2H_5Cl, 75-00-3; 1-C_3H_7Br, 106-94-5; 2-C_3H_7Br, 75-26-3; $(CH_3)_3CBr$, 507-19-7; $(CH_3)_3CCH_2Br$, 630-17-1; $NC(CH_2)_4Br$, 5332-06-9; $(H_2O)_5CrC_2H_5{}^{2+}$, 52653-39-1; $(H_2O)_5CrC_3H_7{}^{2+}$, 52653-40-4; $(H_2O)_5CrCH(CH_3)_2{}^{2+}$, 60764-48-9; $(H_2O)_5CrC(CH_3)_2{}^{2+}$, 138666-90-7; $(H_2O)_5CrCH_2C(CH_3)_3{}^{2+}$, 52653-41-5; $(H_2O)_5Cr(CH_2)_4CN^{2+}$, 138693-66-0; $(H_2O)_5C(CH_3)_3C(CH_3)_2OOH$, 62696-04-2.

---

(18) Kirker, G. W.; Bakac, A.; Espenson, J. H. *J. Am. Chem. Soc.* **1982**, *104*, 1249.

(19) Ruchardt, C. *Top. Curr. Chem.* **1980**, *88*, 1.

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 Aquated 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,[1] and Rudi van Eldik*

Received August 21, 1991

The complex formation reactions of a series of complexes of the type $Pd(R_4en)(H_2O)_2{}^{2+}$ (R_4en = 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 $k_{obs} = k_a + k_b[XMP]$. 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 ΔS^{*} 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 $Pd(en)(H_2O)_2{}^{2+}$ and $Pd(Et_4en)(H_2O)_2{}^{2+}$ (en = ethylenediamine) with the purine nucleosides adenoside and inosine[2] as a model reference system for the more inert *cis*-$Pt(NH_3)_2(H_2O)_2{}^{2+}$ 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.[3,4] Similar results were previously reported for a series of sterically hindered diethylenetriamine–Pd(II) complexes.[5,6] 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.[7]

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.[7] 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.[7] 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.[8] Since DNA also contains a phosphate

---

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

(2) Hohmann, H.; Hellquist, B.; van Eldik, R. *Inorg. Chem.* **1992**, *31*, 345.

(3) Hohmann, H.; van Eldik, R. *Inorg. Chim. Acta* **1990**, *174*, 87 and references cited therein.

(4) Hohmann, H.; Hellquist, B.; van Eldik, R. *Inorg. Chim. Acta* **1991**, *188*, 25.

(5) Kotowski, M., van Eldik, R. *Inorg. Chem.* **1984**, *23*, 3310.

(6) Berger, J.; Kotowski, M.; van Eldik, R.; Frey, U.; Helm, L.; Merbach, A. E. *Inorg. Chem.* **1989**, *28*, 3759.

(7) For recent reviews on this topic, see: Sherman, S. E.; Lippard, S. J. *Chem. Rev.* **1987**, *87*, 1153. Sundquist, W. I.; Lippard, S. J. *Coord. Chem. Rev.* **1990**, *100*, 293. Reedijk, J. *Pure Appl. Chem.* **1987**, *59*, 181. Umapathy, P. *Coord. Chem. Rev.* **1989**, *95*, 129.

0020-1669/92/1331-1090$03.00/0