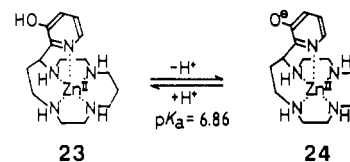The pH-metric titration of **21**, supported by the UV spectroscopic titration, indicates PyOH dissociation with pK_a of 7.13 ± 0.02 (25 °C) to **22** [λ_{max} 242 nm (ϵ 15 000), 299 nm (7900)]. The pK_a value of **21** is lower by 0.7 log unit than that of the diprotonated ligand **1d**, suggesting stronger interaction between the hydroxypyridine and the Cu^{II} ion. The d–d absorption maximum of **22** [536 nm (150)] is not significantly shifted from that of **21** [527 nm (130)], indicating that the apical coordination by the pyridyl N stays before and after PyOH deprotonation. For reference, the pyridyl-bound **3** (M = Cu^{II}) and phenolate-bound **2** (M = Cu^{II})[5,21] showed λ_{max} 518 nm (95) and 557 nm (120), respectively.

In general the 14-membered cyclam ring is well suited for square-planar coordination of Cu^{II}, resulting in strong in-plane interactions, a high-energy d–d transition, large $A_\parallel$ value, and small $g_\parallel$ value.[17,19] Our Cu^{II} complex **21** fits this pattern and therefore we assign the *trans*-cyclam configuration of **21** (and **22**). The failure to detect any other intermediate complex products led us to conclude that **21** is the thermodynamically more stable *trans*-cyclam complex.

Zn^{II}/1d Interaction. The pH-metric titration curve for [**1d**·5H$^+$]$^{5+}$ in the presence of equimolar Zn^{II} ion almost overlapped those for the Ni^{II} and Cu^{II}/**1d** systems, implying the same complexation manner with Zn^{II}, isolable as a diperchlorate salt **23**. The phenol dissociation follows with a pK_a value of 6.86 ± 0.02 to **24**. In the ^1H NMR the lower chemical shift of pyridyl group supports the pyridyl N coordination. We assign the *trans*-cyclam structure to these Zn^{II} complexes. Recently, the *trans*-cyclam configuration was established for **2** (M = Zn^{II}) by an X-ray study.[22,23]

(20) Hathaway, B. J. *Coord. Chem. Rev.* **1982**, *41*, 423.
(21) The Cu^{II} complex (**2**) has a *trans*-cyclam configuration, as determined by X-ray study in ref 5.

23 ⇌ 24, pK_a = 6.86

Conclusion

When the newly synthesized **1d** interacts with Ni^{II}, the *cis*-cyclam–Ni^{II} complex **16** was isolated as a kinetic product, which then converted to a thermodynamically more stable trans complex **18**. The pyridyl N remains a sole fifth donor during this cis to trans isomerization and also during the oxidation of Ni^{II} to Ni^{III}. The pyridyl N pendant plays an important kinetic role in picking up Ni^{II} ion to enhance the rate of Ni^{II}–cyclam interaction. With Cu^{II} and Zn^{II} ions, the 1:1 complexes were also isolated, where the pyridyl N also is the fifth donor.

(22) Kimura, E.; Toriumi, K.; Koike, T. Unpublished result.
(23) An attempt was made to determine Fe^{II} complexation with **1d** in H_2O. However, we failed to obtain reproducible pH titration curves due to decomposition of the complex in solution. The preparation of Fe^{III}–**1d** complex in MeOH solution also failed to yield solid products.

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Kinetics and Mechanism of the Reactions between Alkyl Radicals and Complexes of Cobalt(III) and Ruthenium(III)

Douglas G. Kelley, James H. Espenson,* and Andreja Bakac*

The kinetics of the reactions of $^\bullet C_2H_5$ with cobalt(III) and ruthenium(III) complexes were studied by laser flash photolysis with ABTS$^{\bullet-}$ as a kinetic probe. Some relative rate constants were also determined by a competition method based on product ratios. The substrates included a series of $M(NH_3)_5X^{2+}$ complexes (M = Co, Ru; X = halo, aquo, thiocyanato, azido) and some bis(dimethylglyoximato)halocobalt(III) complexes. The products of these reactions are largely (>90%) the ethyl halide and ethyl thiocyanate, substantiating an inner-sphere mechanism. Minor but regular yields of C_2H_4 are also found (≤10%), suggesting a small contribution from the outer-sphere oxidation of $^\bullet C_2H_5$.

Introduction

The occurrence of reactions between such free radicals as I$^\bullet$, HO$^\bullet$, SO$_4^{\bullet-}$, and $^\bullet CH_3$ and pentaamminehalocobalt(III) complexes was first reported by Haim and Taube,[1] who found nearly quantitative formation of $Co(H_2O)_6^{2+}$. The studies with methyl radicals were of an exploratory nature; no kinetic data were sought, and the organic products were not determined. They postulated that the reaction of methyl radicals might occur by the equation

$$(NH_3)_5CoX^{2+} + {}^\bullet CH_3 + 5H_3O^+ \rightarrow$$
$$Co_{aq}^{2+} + CH_3X + 5NH_4^+ \quad (1)$$
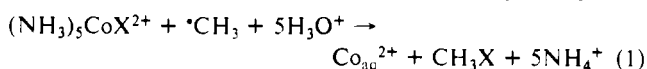
Our goal in this work has been to conduct kinetic measurements by means of laser flash photolysis, to determine the products

formed, and to examine the mechanism of this reaction. We have done this for the ethyl radical, which gives less volatile products than methyl. The source of $C_2H_5^\bullet$ is the photohomolysis of ethylcobalt complexes, $C_2H_5Co(dmgH)_2OH_2$ (mostly) and $C_2H_5Co(cyclam)OH_2^{2+}$ (occasionally).[2,3] The laser flash provides the method by which the radicals are produced in a short time (<1 μs) and at concentration levels high enough to be kinetically useful.

Because the Co(III) and Ru(III) complexes to be examined in this study possess relatively small molar absorptivities in the visible region, a competing chromophore is required as a probe

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(3) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1989**, *28*, 4319. The abbreviations are dmgH$^-$ = the monoanion of 2,3-butanedione dioxime and cyclam = 1,4,8,11-tetraazacyclotetradecane.

to follow the kinetics. This probe must react rapidly with alkyl radicals, must have a large molar absorptivity in the low-energy visible spectral region, and must not undergo thermal reactions with either the ethylcobalt precursor or the transition-metal substrate complex.

Our search[4] for a kinetic probe led us to ABTS^{2-} (2,2'-azino-bis(3-ethylbenzothiazoline-6-sulfonate)), which is readily oxidized

ABTS^{2-}
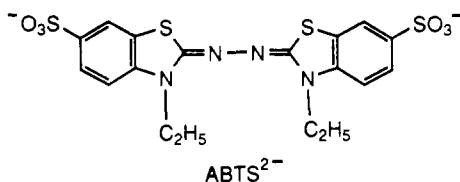
to ABTS$^{\bullet-}$. The radical is quite persistent, with a lifetime of many weeks, and brightly colored.[5] Wolfenden and Willson were the first to employ ABTS$^{\bullet-}$ as a kinetic probe, following the reactions of alcohols, organic acids, and amino acids with free radicals generated by pulse radiolysis.[6] More recent studies have further demonstrated the spectroscopic utility of ABTS$^{\bullet-}$ as a scavenger of reactive intermediates,[7] as an indicator for the determination of enzymatic activity,[8] and as a kinetic probe in competition reactions.[9] We also used hexachloroiridate(IV) ion as a probe in one instance to verify the ABTS$^{\bullet-}$ method. Rate constants thus obtained were compared with relative rates measured in competition studies by product ratios.

Experimental Section

Reagents. The cobalt(III)[10–18] and ruthenium(III)[19] complexes were prepared by literature procedures, as were the metal polypyridyl complexes.[20,21] The ethylcobalt radical precursors, $C_2H_5Co(dmgH)_2L$ (L = H_2O[22] or pyridine[23]) and $[C_2H_5Co([14]aneN_4)H_2O](ClO_4)_2$[24] were also prepared by published procedures. Commercial sources provided $(NH_4)_2ABTS$ (Sigma) and $(NH_4)_2[IrCl_6]$ (Aldrich). Stock solutions of reagents were prepared as needed and kept in the dark. All solutions were prepared from distilled water, which was purified by passage through a Milli-Q Millipore reagent water system. For our purposes the most efficient way to prepare ABTS$^{\bullet-}$ was to mix solutions of ABTS^{2-} and Ce(IV) is nearly equal volume and concentration but with a slight deficiency of cerium(IV) so that further oxidation to give the neutral ABTS species was avoided, along with any possible reaction chemistry of cerium(IV). Solutions of $(H_2O)_5CrC_2H_5^{2+}$ were prepared from Cr^{2+} and *tert*-amyl hydroperoxide.[25] These solutions were ion exchanged on
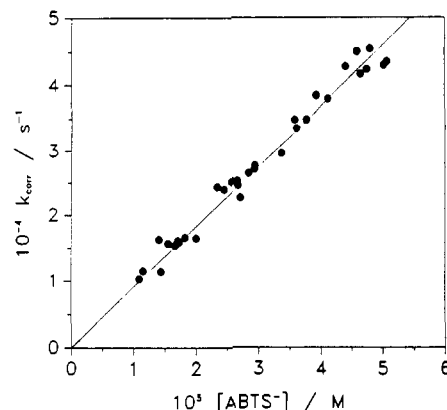
Figure 1. Plot of kinetic data for the reaction of $C_2H_5{}^{\bullet}$ with ABTS$^{\bullet-}$ (eq 3). The slope of the line represents the rate constant k_A.
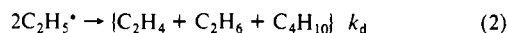
Sephadex SP-25 in an ice-jacketed column and used immediately after the organochromium fraction emerged from the column.

Kinetics. Control experiments were done to explore the photohomolysis of $C_2H_5Co(dmgH)_2OH_2$. The loss in concentration of this complex during a typical laser flash was 6.5 ± 1.5 μM, determined by the absorbance change at 440 nm ($\epsilon = 1350$ L mol^{-1} cm^{-1}). This measurement was done at [H$^+$] = 1.0 M, where the cobalt(II) complex Co(dmgH)$_2$-(OH$_2$)$_2$ very rapidly demetalates. The formation of the cobalt(II) product was then examined at pH 7, where it is stable (ϵ_{440} = 3500 L mol^{-1} cm^{-1}). The increase in [Co(dmgH)$_2$(OH$_2$)$_2$] was 5.1 ± 0.9 μM, which matches the loss in ethylcobalt complex within experimental error.

Laser flash photolysis experiments were performed by means of the previously described system.[26] The reactions were monitored under argon by following the increase of transmittance at an absorption maximum of the particular chromophore: ABTS$^{\bullet-}$ (ϵ_{650} = 1.0 × 10^4 L mol^{-1} cm^{-1}) and IrCl$_6^{2-}$ (ϵ_{487} = 4.09 × 10^3 L mol^{-1} cm^{-1}). It should be noted that the spectrum of ABTS$^{\bullet-}$ has a relatively transparent window, 440–500 nm, permitting the photolysis of the ethyl complex.

The digitized absorbance–time values were analyzed by a nonlinear least-squares program and were found to fit first-order kinetics: $D_t = D_\infty + (D_0 - D_\infty) \exp(-k_\psi t)$, where D = absorbance. The simplicity of this treatment is really an approximation, since the actual situation should require an additional second-order component. The validity of this approximation is explained in the following paragraphs.

When no Co(III) complex is present, the ethyl radical disappears by two pathways. One is its self-reaction, eq 2, which proceeds at a known rate (k_d = 1.2 × 10^9 M^{-1} s^{-1})[27] and yields ethane, ethylene, and butane in a relative ratio 1:1:2.3, consistent with that previously reported for ethyl radicals in aqueous solution.[28] The other is the reaction of $C_2H_5{}^{\bullet}$ with the excess of ABTS$^{\bullet-}$, eq 3.

$$2C_2H_5{}^{\bullet} \rightarrow \{C_2H_4 + C_2H_6 + C_4H_{10}\} \quad k_d \qquad (2)$$

$$C_2H_5{}^{\bullet} + ABTS^{\bullet-} \rightarrow [ABTS\text{-}C_2H_5]^{2-} + H^+ \quad k_A \qquad (3)$$

$$-d[C_2H_5{}^{\bullet}]/dt = 2k_d[C_2H_5{}^{\bullet}]^2 + k_A[C_2H_5{}^{\bullet}][ABTS^{\bullet-}] \qquad (4a)$$

Given the value of the rate constants involved, and the concentration range of ABTS$^{\bullet-}$ used, the first reaction makes a very small contribution to the reaction rate, although one that is not entirely negligible. If one approximates [C$_2$H$_5{}^{\bullet}$] as a constant or average value, eq 4a reduces to a pseudo-first-order kinetic expression, eq 4b. The value of [C$_2$H$_5{}^{\bullet}$] used

$$k_\psi = 2k_d[C_2H_5{}^{\bullet}]_{av} + k_A[ABTS^{\bullet-}] \qquad (4b)$$

in eq 4b is the average[29] of the initial and final values; although the

(4) The methyl viologen radical cation, which had been successful as a kinetic probe in our applications[2,3] could not be used in the present system because it reacts with the Co(III) and Ru(III) substrates.

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(29) The [C$_2$H$_5{}^{\bullet}$] can be obtained from the loss of absorbance of ABTS$^{\bullet-}$ in each experiment, after allowance for the percent of reaction going by the ABTS$^{\bullet-}$ pathway. This approach uses an iterative procedure for k_A, but the refinement is a simple one in that self-reaction represents such a small part of the total rate.

magnitude of the term $2k_d[C_2H_5^\bullet]_{av}$ changes greatly during the course of the run, it is still small ($\leq 5\%$) relative to the second term since these experiments were designed to have $[ABTS^{\bullet-}]_0 \geq 10$ $[C_2H_5^\bullet]_0$. Thus this method is valid despite the fact that $C_2H_5^\bullet$ decays totally during the experiment. Thus a plot of k_ψ vs $[ABTS^{\bullet-}]$ is expected to be linear, with a small intercept representing the contribution of the self-reaction. Rate constants corrected for the self-reaction, k_{corr}, were obtained by using an iterative process employing eq 5 until a reproducible value for k_A was obtained. The plot of k_{corr} versus $[ABTS^{\bullet-}]$ is shown in Figure 1, and

$$k_{corr} = k_\psi - 2k_d \frac{k_\psi[ABTS^{\bullet-}]_{lost}/2}{k_A[ABTS^{\bullet-}]_{av}} = k_A[ABTS^{\bullet-}]_{av} \quad (5)$$

leads to a value of $k_A = (9.2 \pm 0.2) \times 10^8$ L mol^{-1} s^{-1}. The validity of this method was verified by using a numerical integration program, KINSIM,[30] to generate values of $[ABTS^{\bullet-}]$ as a function of time using the specified rate constants. First-order analyses of these simulated data agreed with the treatment implied by eq 4b.

The main experiments for the Co(III) reactions were carried out analogously, except now there is an additional reaction (eq 6)[31] and a third term in the rate law (eq 7). In this case both of the excess con-

$$C_2H_5^\bullet + L_5Co^{III}X \rightarrow C_2H_5X + L_5Co^{II} \quad k_{Co} \quad (6)$$
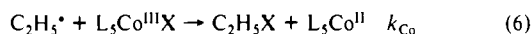
$$k_\psi = 2k_d[C_2H_5^\bullet]_{av} + k_A[ABTS^{\bullet-}] + k_{Co}[L_5CoX] \quad (7)$$

centrations, $ABTS^{\bullet-}$ and $L_5Co^{III}X$, were varied. The data were analyzed by a plot of k_{corr} (eq 8) versus [Co(III)], having subtracted the k_d and k_A terms at each $[ABTS^{\bullet-}]$.

$$k_{corr} = k_\psi - 2k_d[C_2H_5^\bullet]_{av} - k_A[ABTS^{\bullet-}] = k_{Co}[L_5Co^{III}X] \quad (8)$$

$$k_{corr} = k_\psi - 2k_d \frac{k_\psi[ABTS^{\bullet-}]_{lost}/2}{k_A[ABTS^{\bullet-}]_{av}} - k_A[ABTS^{\bullet-}]_{av} \quad (9)$$

A further correction was necessary in the data analysis for Co-(dmg$_2$H$_3$)Cl$_2$ and Co(dmgH)$_2$(H$_2$O)Cl, in that these complexes have significant absorption at 650 nm, with $\epsilon = 20$ and 15 L mol^{-1} cm^{-1}, respectively. Allowance for this absorbance contribution was made in the calculation of the initial $ABTS^{\bullet-}$ concentration (eq 10). The same

$$[ABTS^{\bullet-}]_i = \frac{Abs_{total} - \{[CoCl]_i \, \epsilon(CoCl)_{650}\}}{\epsilon(ABTS^{\bullet-})_{650}} \quad (10)$$

was true when $[IrCl_6^{2-}]$ was followed at 487 nm; allowance was made for both C$_2$H$_5$Co(dmgH)$_2$OH$_2$ ($\epsilon_{487} = 5.0 \times 10^2$ L mol^{-1} cm^{-1}) and $(NH_3)_5$CoBr^{2+} ($\epsilon_{487} = 32$ L mol^{-1} cm^{-1}).

Gas Chromatography. The reaction products were determined by use of a Hewlett-Packard Model 5790 gas chromatograph with a 3390A integrator. Alkyl halides were determined on Carbopak and OV-101 columns, and ethylene was determined on a VZ10 column.

Relative rate constants were determined for pairs of metal complexes by a competition method in which $C_2H_5^\bullet$ was photochemically generated in mixtures of $L_5Co^{III}Cl$ and $L_5Co^{III}Br$ complexes or the ruthenium(III) analogues. The ratio C_2H_5Cl/C_2H_5Br was determined gas chromatographically, and the relative rate constants were calculated as in eq 11.

$$\frac{k_{Cl}}{k_{Br}} = \frac{[C_2H_5Cl]_\infty}{[C_2H_5Br]_\infty} \frac{[L_5Co^{III}Br]_{av}}{[L_5Co^{III}Cl]_{av}} \quad (11)$$

These studies were performed by placing an anaerobic 1-cm quartz cuvette, filled to capacity with the desired combination of reagents, before a Pyrex-filtered sunlamp for 3 min. Photolysis was continued until C$_2$H$_5$Co(dmgH)$_2$OH$_2$ was completely destroyed. This method was employed for solutions at pH 2, to lessen decomposition of the GC column at high acid concentrations.

Results and Discussion

Cobalt(III) Complexes. These reactions were studied in deaerated 0.50 M H$_2$SO$_4$. Typical concentrations are ~ 20 μM C$_2$H$_5$Co(dmgH)$_2$OH$_2$, 19–37 μM ABTS$^{\bullet-}$, and a variable Co(III) concentration, depending on the value of k_{Co} and the solubility of the complex. For Co(NH$_3$)$_5$Br^{2+}, for example, the concentration ranged from (0.50 to 5.0) $\times$ 10^{-3} M, and for others the Co(III) concentrations lay in a range where a measurable effect on k_ψ

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(31) Equation 6 is an approximate representation, in that C$_2$H$_4$ is also formed in minor amount (see text).
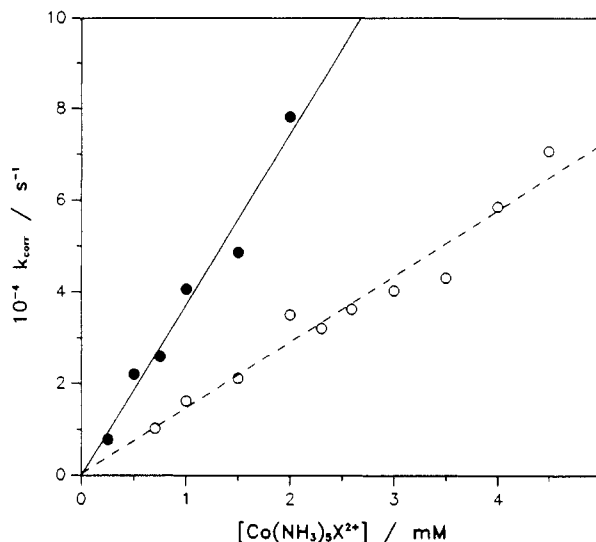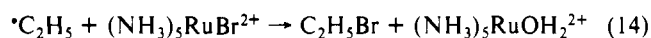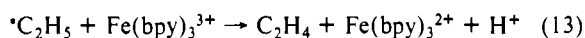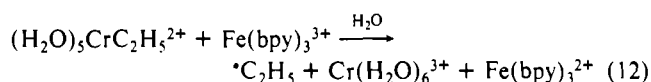

Figure 2. Plot of k_{corr} (eq 8) vs the concentration of the cobalt(III) complexes. Data are shown for (NH$_3$)$_5$CoN$_3^{2+}$ (filled circles) and for (NH$_3$)$_5$CoSCN^{2+} (open circles).

Table I. Summary of Rate Constants[a] for Reduction of Cobalt(III) Complexes by Ethyl Radicals

| | $K_{Co}/10^6$ L mol^{-1} s^{-1} | |
Co(III) complex	laser flash photolysis[b]	product ratio[d]
Co(NH$_3$)$_5$Cl^{2+}	<0.3	0.018
Co(NH$_3$)$_5$Br^{2+}	2.6 (3.0)[c]	
Co(NH$_3$)$_5$N$_3^{2+}$	37.	
Co(NH$_3$)$_5$SCN^{2+}	14.	
Co(NH$_3$)$_5$NCS^{2+}	<0.2	
Co(NH$_3$)$_5$OH$_2^{3+}$	<0.2	
Co(NH$_3$)$_5$F^{2+}	<0.2	
Co(NH$_3$)$_5$CN^{2+}	<0.4	
trans-Co(en)$_2$Cl$_2^+$	~0.6	
cis-Co(en)$_2$Cl$_2^+$	<0.2	
cis-Co(en)$_2$(H$_2$O)Cl^{2+}	<0.3	
ClCo(dmgH)$_2$H$_2$O	2.3	3
Co(dmgH)$_2$Cl$_2^-$	10.5	6
BrCo(dmgH)$_2$NCCH$_3$	160	
Co(dmgH)$_2$Br$_2^-$	530	

[a] At 23 $\pm$ 2 °C, with an estimated precision of $\pm 20\%$. [b] With ABTS$^{\bullet-}$ as chromophore in 0.50 M H$_2$SO$_4$. [c] With IrCl$_6^{2-}$ as chromophore. [d] Relative to $k = 2.6 \times 10^6$ L mol^{-1} s^{-1} for Co(NH$_3$)$_5$Br^{2+} in 0.010 M HClO$_4$.

was to be found. Typical results for two complexes, Co-(NH$_3$)$_5$N$_3^{2+}$ and Co(NH$_3$)$_5$SCN^{2+}, are presented in Figure 2, where the linear dependence of k_{corr} upon cobalt concentration, as in eq 8, is shown. The slope of each line gives the value of k_{Co}, which is listed in Table I. The precision of individual values is estimated to be about 20%, in view of the subtractions involved in calculating k_{corr}. All of these values are pH independent in the range 0–7.

For Co(NH$_3$)$_5$Br^{2+} separate determinations of k_{Co} were made with ABTS$^{\bullet-}$ and IrCl$_6^{2-}$ as chromophores. The agreement of the two values of k_{Co}, 2.6 $\times$ 10^6 and 3.0 $\times$ 10^6 L mol^{-1} s^{-1}, is within the experimental error and assists in confirming the correctness of the procedures adopted.

The method fails for certain of the cobalt complexes whose values of k_{Co} are low. Roughly speaking, we are unable to determine a rate constant smaller than about 5 $\times$ 10^5 L mol^{-1} s^{-1}, although the actual limit depends on the compound, given the solubility limit of different complexes. Upper limits on the rate constant for a number of slowly reacting compounds are also shown in Table I.

The product ratio method applied to Co(NH$_3$)$_5$Cl^{2+} relative to Co(NH$_3$)$_5$Br^{2+} affords a ratio $k_{Cl}/k_{Br} = 6.4 \times 10^{-3}$. This in turn yields $k_{Cl} = 1.8 \times 10^4$ L mol^{-1} s^{-1}, a value much smaller than the laser technique is capable of measuring. The product ratio

method was also applied to two of the chlorocobaloxime complexes. The rate constants were in only fair agreement with the flash photolytically determined (Table I), although the agreement was sufficiently close to suggest that both procedures are correct in concept and execution.

Ruthenium(III) Complexes. Kinetic studies were limited to one complex, $Ru(NH_3)_5Br^{2+}$. Studies were carried out with $IrCl_6^{2-}$ as chromophore. From the data at low ruthenium concentration, a rate constant of 1.6×10^7 L mol^{-1} s^{-1} was estimated. At higher concentrations k_ψ decreased with increasing [Ru(III)], until precipitation occurred. Trials with ABTS^{-} were completely unsuccessful, with k_{obs} inexplicably decreasing with [Ru(III)] from the outset.

A second approach was taken in which the thermal reaction between $(H_2O)_5CrC_2H_5^{2+}$ and $Fe(bpy)_3^{3+}$ was used to provide the source of ethyl radicals (eq 12). The radical then competes between a reaction with $Fe(bpy)_3^{3+}$ (eq 13) and that with $(NH_3)_5RuBr^{2+}$ (eq 14).

$$(H_2O)_5CrC_2H_5^{2+} + Fe(bpy)_3^{3+} \xrightarrow{H_2O}$$
$$\cdot C_2H_5 + Cr(H_2O)_6^{3+} + Fe(bpy)_3^{2+} \quad (12)$$

$$\cdot C_2H_5 + Fe(bpy)_3^{3+} \rightarrow C_2H_4 + Fe(bpy)_3^{2+} + H^+ \quad (13)$$

$$\cdot C_2H_5 + (NH_3)_5RuBr^{2+} \rightarrow C_2H_5Br + (NH_3)_5RuOH_2^{2+} \quad (14)$$

Reaction solutions were prepared with the concentrations 0.13 mM $(H_2O)_5CrC_2H_5^{2+}$, 0.40 mM $Fe(bpy)_3^{3+}$, 5.0 mM $(NH_3)_5RuBr^{2+}$, and 0.10 M $HClO_4$. The reaction was run in a septum-sealed 1-cm spectrophotometer cell filled to capacity to minimize the vapor space above the solution. In each of three trials the concentration of ethyl bromide produced was 3.0×10^{-5} M (determined by gas chromatography with a column calibrated with standard solutions of C_2H_5Br). This corresponds to 23% of the total ethyl radicals reacting with the ruthenium complex as in eq 11. With $k_{13} = 9.2 \times 10^8$ L mol^{-1} s^{-1} (see below), this yields a rate constant for reaction 14, $k_{RuBr} = 2.2 \times 10^7$ L mol^{-1} s^{-1}.

Still another approach was taken, this time based on product ratios. First, $(NH_3)_5RuCl^{2+}$ and $(NH_3)_5CoBr^{2+}$ were used together. From the ratio of ethyl chloride to ethyl bromide and the known rate constant for $Co(NH_3)_5Br^{2+}$, a value of $k_{RuCl} = 6 \times 10^6$ L mol^{-1} s^{-1} was determined. Then a second competition was run, with $(NH_3)_5RuCl^{2+}$ and $(NH_3)_5RuBr^{2+}$. This gave product ratios such that $k_{RuCl}/k_{RuBr} = 0.094$, from which $k_{RuBr} = 7 \times 10^7$ L mol^{-1} s^{-1}. This double comparison is the least precise of the three methods used, however, and the most probable value is $k_{RuBr} = 2 \times 10^7$ L mol^{-1} s^{-1}.

Product Analysis. For several of the cobalt and ruthenium complexes GC measurements were made to determine the product(s) formed. These experiments were run by the slow photolysis of $C_2H_5Co(dmgH)_2py$ in the presence of excess metal complex, thereby eliminating the radical self-reactions and their products. In each case the alkyl halide was detected in at least 90% yield. Specifically, the percents of the original concentrations of ethyl cobaloxime found as ethyl halides are as follows: $Co(NH_3)_5Cl^{2+}$, >90%; $Co(NH_3)_5Br^{2+}$, >95%; $Ru(NH_3)_5Br^{2+}$, >93%; $Ru(NH_3)_5Cl^{2+}$, >90%; $Co(dmgH)_2Cl_2^-$, >90%, and $ClCo(dmgH)_2OH_2$, >90%. Control experiments showed that the identity of the counterion was immaterial. Similar experiments were also carried out for $Co(NH_3)_5SCN^{2+}$. Both C_2H_5SCN and C_2H_5NCS were used as GC standards. Only C_2H_5SCN was formed; C_2H_5NCS was not detected.

In the case of each halide, however, a small amount of C_2H_4 was also detected amounting by difference to an estimated 5-10%. Ethylene is not the result of self-reactions, except possibly in the case of $Co(NH_3)_5Cl^{2+}$, where the reaction rate is very low, because ethane and butane are absent. We attribute C_2H_4 formation to a parallel outer sphere oxidation reaction.

$$\cdot C_2H_5 + M^{III}L_5X \rightarrow C_2H_4 + M^{II}L_5 + X^- + H^+ \quad (15)$$
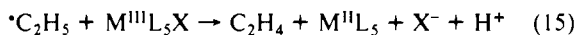
Other Reactions of C_2H_5. During the course of this work the rate constants for other substrates, particularly certain chromophores and chromogens we did use or attempt to use, were

Table II. Rate Constants[a] for the Reactions of Ethyl Radicals with Various Substrates

compound	k/L mol^{-1} s^{-1}	ref
ABTS^{-}	9.2×10^8	this work
MV^{+}	1.2×10^9	this work
	1.0×10^9	b
IrCl$_6^{2-}$	2.8×10^9	this work
	3.1×10^9	c
Fe(phen)$_3^{3+}$	1.5×10^9	this work
	1.0×10^9	d
Fe(bpy)$_3^{3+}$	9.2×10^8	this work[e]
Cr(bpy)$_3^{3+}$	1.8×10^7	this work

[a] In aqueous solution at 23 ± 2 °C with $C_2H_5Co(dmgH)_2OH_2$ as the source of $\cdot C_2H_5$. [b] Reference 2, in which $C_2H_5Co([14]aneN_4)OH_2^{2+}$ was used. [c] Reference 32, by pulse radiolysis. [d] Reference 33, by pulse radiolysis. [e] With $C_2H_5Co([14]aneN_4)OH_2^{2+}$ as the source of $\cdot C_2H_5$, to avoid thermal reactions.

measured. The substrates are ABTS^{-}, MV^{+}, IrCl$_6^{2-}$, Fe(bpy)$_3^{3+}$, Fe(phen)$_3^{3+}$, and Cr(bpy)$_3^{3+}$. The rate constants are given in Table II. Values had appeared in the literature for three compounds, IrCl$_6^{2-}$,[32] Fe(phen)$_3^{3+}$,[33] and MV$^+$.[2] Our values are in good agreement.

Varied products are formed in these reactions. With ABTS^{-}, for example, there is a readily detectable yield of C_2H_4, amounting to (very roughly) some 30% of the reaction. The balance consists of nonvolatile product(s), which we presume to be a species in which C_2H_5 has added to a carbon on the aromatic ring. A large amount of ethylene is formed in the reactions with Fe(phen)$_3^{3+}$ and Fe(bpy)$_3^{3+}$, as shown in eq 13. We cannot, however, go so far as to say ring addition products are absent. Kochi observed that the products from the reaction between CH$_3\cdot$ and Fe(phen)$_3^{3+}$ did not contain any measurable amount of alkyl-substituted phenanthroline.[33] With Cr(bpy)$_3^{3+}$, on the other hand, no ethane, ethylene, or butane is formed. A strong and readily detected chromium(II)–bipyridyl absorption at 560 nm is observed, which we interpret in terms of a ring-addition process, eq 16. Ethyl chloride is the major product of the reaction between $\cdot C_2H_5$ and IrCl$_6^{2-}$, although traces of ethylene are also detected.[32]

$$Cr(bpy)_3^{3+} + \cdot C_2H_5 \rightarrow Cr(bpy)_2(bpy-C_2H_5)^{2+} + H^+ \quad (16)$$
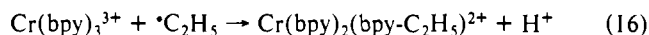
Reaction Mechanisms. The formation of C_2H_5X from the reactions of $L_5M^{III}X$ (M = Co, Ru; X = Cl, Br) directly substantiates an inner-sphere mechanism for these reactions. Thus the early supposition of Haim and Taube[1] has been proven correct. The rates follow the so-called "normal" order, with (F) < Cl < Br, for both the pentaamminehalo series and the dimethylglyoxime derivatives. The generally higher reactivity of the dimethylglyoxime complexes as compared to the pentaammines can be accounted for by the relative stabilities of the incipient Co(II) products in the transition state.

The formation of C_2H_5SCN from $Co(NH_3)_5SCN^{2+}$ also establishes as inner-sphere mechanism. The fact that the sulfur-bound product is formed and that C_2H_5NCS is completely absent indicate that the reaction proceeds entirely by an adjacent attack mechanism. We suggest that the relatively small size permits the more ready approach of $\cdot C_2H_5$ to the sulfur atom in the primary coordination sphere of cobalt. Of transition-metal complexes, only the very soft acid $Co(CN)_5^{3-}$ reacts analogously.[34,35]

We note the high reactivity of $Co(NH_3)_5SCN^{2+}$ ($k = 1.4 \times 10^7$ L mol^{-1} s^{-1}) as compared to $Co(NH_3)_5NCS^{2+}$ ($k < 2 \times 10^5$ L mol^{-1} s^{-1}). In effect the isothiocyanato complex does not react

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with $C_2H_5^{\cdot}$. The reactivity ratio is probably even higher than the upper limit suggests. For example, Fe^{2+}, V^{2+}, Cr^{2+}, and Co-$(CN)_5^{3-}$ have k_{SCN}/k_{NCS} ratios of $>4 \times 10^4$, 10^2, 10^4, and 10^{2-3}, respectively.[34,35]

The reactivity of $Co(NH_3)_5N_3^{2+}$ ($k = 3.7 \times 10^7$ L mol^{-1} s^{-1}) is somewhat higher than that of $Co(NH_3)_5SCN^{2+}$, whereas the opposite is true for the metal donors.[34,35] The product from the azido reaction was not established, and the higher reactivity toward ethyl radicals might possibly result from attack of $^{\cdot}C_2H_5$ on the $N=N$ bonds of coordinated azide ions.

The complexes $Ru(NH_3)_5X^{2+}$ (X = Cl, Br) are more reactive than their cobalt counterparts by factors of 300 (Cl) and 10 (Br). The greater reactivity of ruthenium was also observed in their reductions by α-hydroxyalkyl radicals.[36]

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Contribution from the Laboratoire de Chimie de Coordination CNRS, UP No. 8241 Liée par Conventions à l'Université Paul Sabatier et à l'Institut National Polytechnique, 205 Route de Narbonne, Toulouse Cedex, France, and the Department of Chemistry and Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Modification of the Reactivity of Polyhydrides with Lewis Acids. Synthesis and Reactivity of {IrH5[P(iC3H7)3]2}2Cu(CF3SO3). X-ray Crystal Structure of {IrH2(MeCN)2[P(iC3H7)3]2}(BF4)

X. D. He,[†] J. Fernandez-Baeza,[†] B. Chaudret,[*,†] K. Folting,[‡] and K. G. Caulton[*,‡]

The reaction of $IrH_5(P^iPr_3)_2$ (**1**) with $[Cu(MeCN)_4]BF_4$ (2:1) in acetone yields $[IrH_2(MeCN)_2(P^iPr_3)_2]BF_4$ (**2**), characterized by spectroscopic methods and X-ray diffraction, in 46% yield. A similar reaction with $CuCF_3SO_3$ in CH_2Cl_2 yields $[IrH_5(P^iPr_3)_2]_2CuCF_3SO_3$ (**3**) in 91% yield. Compound **3** reacts rapidly with MeCN, D_2, and cyclopentadiene at 25 °C in CH_2Cl_2 to give respectively a 1:1 mixture of **1** and **2**, deuterated **3**, and $[CpIrH(P^iPr_3)_2]SO_3CF_3$ and shows a reduced relaxation time T_1 for the hydrides, compared to **1**.

Introduction

Since the first demonstration by Kubas et al. of the coordination of dihydrogen to a transition metal,[1] the chemistry of polyhydride derivatives has been dominated by the dilemma "classical or nonclassical"; i.e., are the so-called "polyhydrides" real hydrido derivatives or do they contain coordinated H_2?[2] The situation is probably not so clear, since in simple cases like $W(CO)_3$-$(PR_3)_2H_2$[1] and $CpRuL_2H_2^+$[3] the coexistence of dihydride and dihydrogen isomers has been demonstrated. We have reported recently a dynamic equilibrium between a dihydride and a dihydrogen complex.[4] Furthermore it is anticipated that slight modifications in the electron density on the metal can change the mode of bonding of the hydrogen ligands. The modification can be made in the phosphine substituents.[5] This behavior is also revealed by the protonation reaction[6]

$$IrH_5(PCy_3)_2 + H^+ \rightarrow [IrH_2(H_2)_2(PCy_3)_2]^+ \qquad (1)$$
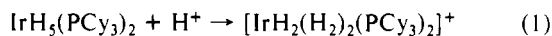
In this case, not only one hydrogen molecule is formed by protonation of a hydride ligand but a second one is formed by reductive coupling of two hydride ligands.

After the demonstration by one of us[7] and by Venanzi[8] that Lewis acid fragments can give adducts with polyhydrides, we have attempted to manipulate the free energy difference between hydrides and coordinated H_2 in complexes containing both type of ligands.[9] Although this goal has not yet been achieved, we succeeded there in observing exchange coupling between terminal and bridged hydride ligands. Nevertheless, coordination of a Lewis acid to a classical polyhydride is expected to reduce the electron density on the metal. A change in the structure and/or an increase in the reactivity of the polyhydride should normally result from this reaction. As a comparison to eq 1, we report in this paper the reaction of $IrH_5(PR_3)_2$ with copper salts and the chemical reactivity of one such adduct.

Experimental Section

All experiments were conducted under dry argon by using conventional Schlenk tube techniques. Infrared spectra were recorded as KBr disks or Nujol mulls with a Perkin-Elmer 983 grating spectrometer. ^1H and ^{31}P NMR spectra were recorded by using Bruker WH90, AC200, or WM250 NMR spectrometers. NMR integrations were measured either on one scan in concentrated solution or with a repetition delay of 1 min, to avoid incomplete and differential relaxation. Both methods gave results that agreed to within 10%. Microanalyses were performed by the "Centre de Microanalyse du CNRS" or in-house.

[IrH2(CH3CN)2(PiPr3)2]BF4 (2). To 500 mg, 0.97 mmol, of IrH_5-$(P^iPr_3)_2$[10] was added an acetone solution (20 mL) containing 161 mg, 0.48 mmol, of $[Cu(CH_3CN)_4]BF_4$. With stirring, $IrH_5(P^iPr_3)_2$ dissolved and a colorless solution was obtained in 5 min. After being stirred for 1 h, the resulting solution was concentrated to a small volume under reduced pressure and treated with 15 mL of hexane to precipitate white microcrystals, which were washed with hexane (3 × 5 mL). The product $[IrH_2(CH_3CN)_2(P^iPr_3)_2]BF_4$ was obtained in 46.5% yield (255 mg) based on Ir. Anal. Calcd for $IrP_2N_2BF_4C_{22}H_{50}$: C, 38.65; H, 7.37; N, 4.10. Found: C, 38.26; H, 7.77; N, 4.33. $IrH_5(P^iPr_3)_2$ (50% of initial quantity) may be recovered from the resulting filtrate.

Crystals suitable for X-ray diffraction studies may be obtained by cooling a saturated acetone solution to −20 °C.

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