mechanism.[16] The stereochemistry of the reaction of the anion with the *R,S* isomer does not change appreciably with change in reagent ratio and the trans/cis product ratio is essentially constant at >95% trans. In the case of the *rac* isomer a complex variation of product ratio with reagent ratio exists. High stereoselectivity is observed only at low dibromide/ complex ratios. When the dibromide/complex ratio is greater than 1:2 (i.e., whenever the complex is not in substantial excess), the reaction is not selective and in fact *trans*-3-hexene can be 50–60% of the 3-hexene yield. The reason for the change in product ratio with reagent ratio is not clear but two possibilities are (1) a mechanistic change or (2) an alteration[17] of the iron reagent under the experimental conditions. We prefer the latter possibility since it might also explain the very low conversion to 3-hexene observed at these conditions.[17]

The data presented indicate both the $C_3H_5Fe(CO)_2$-$P(C_6H_5)_3^-$ anion and the $C_3H_5Fe(CO)_2P(C_6H_5)$ radical are effective debromination agents for vicinal organic dibromides under mild, aprotic conditions. Both reagents debrominate but do not dehydrohalogenate. Under appropriate conditions the debromination reaction of the anion can be highly stereoselective and proceed in high yield.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Research Corporation for the support of this research.

Registry No. I, 12098-67-8; II, 59388-96-4; η^3-C_3H_5Fe-$(CO)_2P(C_6H_5)_3Br$, 59388-97-5; *rac*-3,4-dibromohexane, 16230-28-7; (R,S)-3,4-dibromohexane, 16230-27-6; *trans*-3-hexene, 13269-52-8; *cis*-3-hexene, 7642-09-3.

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(11) P. A. Wegner and B. Mills, unpublished data. For example, during the same time period, the coupling of benzyl bromide by zinc to form bibenzyl in tetrahydrofuran at ambient conditions proceeds to 80% conversion when catalyzed by η^3-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ (200/1 substrate/catalyst ratio) compared to 16% conversion for the uncatalyzed reaction.
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(17) A possible sequence of reactions of the anion which would be compatible with the data assumes a relatively slow reaction of $C_3H_5Fe(CO)_2$-$P(C_6H_5)_3^-$ with the *rac*-3,4-dibromohexane. A reaction product would be η-$C_3H_5Fe(CO)_2P(C_6H_5)_3Br$ which could react rapidly with remaining anion to form the radical $C_3H_5Fe(CO)_2P(C_6H_5)_3$ and Br^-. The radical does not debrominate stereospecifically and also produces more 1,5-$Fe(CO)_3[P(C_6H_5)_3]_2$ during its reactions. The (R,S)-3,4-dibromohexane may not be susceptible to the same set of reactions since this isomer may react more rapidly with the $C_3H_5Fe(CO)_2P(C_6H_5)_3^-$. Differences of this type in the rate of reactivity of *R,S* and *rac* isomers have been previously observed.[16]

Contribution from Chemistry Department 1, H. C. Ørsted Institute,
DK 2100 Copenhagen Ø, Denmark

Oxidation of Some Tris(2,2'-bipyridyl)- and Tris(1,10-phenanthroline)osmium(II) Salts by Thallium(III) in Aqueous Acid
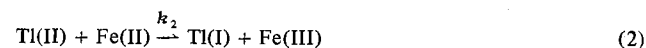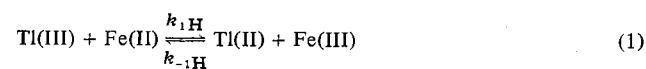
GWYNETH NORD[1]

The oxidation rate of $Os(bpy)_3^{2+}$ and of $Os(phen)_3^{2+}$ by Tl(III) is first order in each of the reactants and increases with decrease in H^+ concentration. For $Os(bpy)_3^{2+}$ the rate constants at 25 °C are 16.6 $dm^3\ mol^{-1}\ s^{-1}$ in 1 M $HClO_4$ + 0.4 M $NaClO_4$, 0.26 $dm^3\ mol^{-1}\ s^{-1}$ in 1.05 M HNO_3 + 0.31 M $NaNO_3$, and 0.054 $dm^3\ mol^{-1}\ s^{-1}$ in 0.453 M H_2SO_4 + 0.535 M Na_2SO_4. The decrease in rate with change in medium is attributed to the formation of unreactive Tl(III) anion complexes. The H^+ dependence is attributed to the more rapid reaction of $TlOH^{2+}$. The oxidation of $Os(phen)_3^{2+}$ was measured in nitrate media only and is faster than that of $Os(bpy)_3^{2+}$. *k* at 25 °C in 1.05 M HNO_3 + 0.31 M $NaNO_3$ is 2.68 $dm^3\ mol^{-1}\ s^{-1}$. Activation parameters are given for the reactions of both of the Os complexes, and the changes in these with change of ligand are discussed in terms of an intermediate formed by attack of $TlOH^{2+}$ on a carbon atom of the ligand.

Earlier work[2] on the oxidation of the tris(2,2'-bipyridyl)[3] complex of Os(II) by Tl(III) in 3 M[4] aqueous $HClO_4$–$NaClO_4$ purported to show that this reaction occurred by a mechanism which was analogous to that established[5] for the Tl(III)–Fe(II) reaction

$$Tl(III) + Fe(II) \underset{k_{-1}H}{\overset{k_1H}{\rightleftharpoons}} Tl(II) + Fe(III) \qquad (1)$$

$$Tl(II) + Fe(II) \overset{k_2}{\rightarrow} Tl(I) + Fe(III) \qquad (2)$$

However, in contrast to that found for the preceding mechanism, the oxidation rate of Os(II) was reported to increase with increasing H^+ concentration. Later[6] the same effect was reported for the Tl(III)–Ru(bpy)$_3^{2+}$ reaction. We find that this anomalous acid dependence arises from side reactions and present here data for what we believe to be the true thermal

rates. In our interpretation of the new experimental results we use recent work[7,8] on Tl(II) and also the fact that for at least one other redox reaction[9,10] the relative rates of bpy and phen complexes are known to be determined by the type of ligand and not by the overall free energy change.

Experimental Section

All chemicals were analytical grade or were prepared by published methods.[2,11] $Os(bpy)_3(ClO_4)_2$ and $Os(phen)_3(ClO_4)_2$ were repeatedly recrystallized from redistilled water until reproducible rates were observed. Stock solutions of the sulfate and nitrate were prepared from the perchlorates by repeated absorption and elution using columns of SP Sephadex Type C-25 from Pharmacia, Uppsala, Sweden.

Rates were followed by measuring the decrease of color at or near the maximum absorbance of the Os(II) complexes. Both conventional and stopped-flow spectrophotometries were used. Because of the high molar absorbances, measurements could be made only with very dilute solutions.

Table I. Oxidation of Tris(2,2'-bipyridyl)osmium(II) by Thallium(III) Perchlorate, at an Ionic Strength of 1.40 mol dm^{-3} with $HClO_4$ and $NaClO_4{}^a$

$[H^+]$, mol dm^{-3}	k, dm^3 mol^{-1} s^{-1}	Temp, °C	$\alpha_{TlOH^{2+}}$
1.392	12.0	25.0	0.058
0.965	18.0	25.0	0.062
0.750	21.9	25.0	0.103
0.537	29.8	25.0	0.138
1.400	2.5	0.0	0.046
0.800	4.4	0.0	0.079
0.600	6.1	0.0	0.101

^{a} [Tl(III)] = 2 × 10^{-5}–5 × 10^{-4} mol dm^{-3}; [Os(bpy)$_3{}^{2+}$] = 3 × 10^{-5}–8 × 10^{-5} mol dm^{-3}; $\alpha_{TlOH^{2+}}/(1 - \alpha_{TlOH^{2+}}) = K_h/[H^+]$; K_h(25 °C) = 0.086; K_h(0 °C) = 0.068.

Table II. Oxidation of Tris(2,2'-bipyridyl)osmium(II) by Thallium(III) Perchlorate at an Ionic Strength of 3.0 mol dm^{-3} with $HClO_4$ and $NaClO_4$ at 25 °C

$[H^+]$, mol dm^{-3}	k, dm^3 mol^{-1} s^{-1}	$\alpha_{TlOH^{2+}}$	$[H^+]$, mol dm^{-3}	k, dm^3 mol^{-1} s^{-1}	$\alpha_{TlOH^{2+}}$
2.94	6.6	0.024	0.765	11.5	0.087
1.52	8.5	0.046	0.511	12.7	0.125
1.30	8.1	0.053	0.270	19.0	0.213
1.27	9.5	0.054	0.257	18.8	0.221
1.02	10.0	0.067	0.100	26.5	0.422^a

^{a} See Figure 2. In most other cases [Tl(III)] > [Os(bpy)$_3{}^{2+}$] and therefore K was calculated from the measured pseudo-first-order rate constants k_m using $k = k_m/2$[Tl(III)]. α_{OH} was calculated using $K_h = 0.073$; see also footnote to Table I.

It was also necessary to choose conditions where neither photochemical nor side reactions (a, b, and c below) contributed to the rate.

(a) Both photochemical and thermal oxidations[12] of Os(bpy)$_3{}^{2+}$ and of Os(phen)$_3{}^{2+}$ occur in concentrated solutions of $HClO_4$, of H_2SO_4, and of HNO_3 in the absence of Tl(III). This restricted the studies using conventional spectrophotometry to acid concentrations less than about 1.5 M. For higher acid concentrations, measurements under pseudo-first-order conditions (excess Tl(III)) were made with a stopped-flow apparatus. Measurements at acid concentrations less than about 0.5 M were limited to second-order conditions by the low solubility of hydrated Tl(III) oxide. There was no photochemical contribution to the rates given in the tables.

(b) The title reactions were found to be strongly catalyzed by Os(bpy)$_2$Cl$_2{}^+$. As this could be introduced into the Os(II) complex during the preparation in spite of rigorous purification, we felt that it was necessary to explore this reaction.

(c) The well-known tendency for Tl(III) to promote loss of coordinated chloride led us also to investigate the possibility of side reactions arising from hydrolyzed products of Os(bpy)$_2$Cl$_2{}^+$.

Results

The stoichiometry was always

$$Tl(III) + 2Os^{II}L_3{}^{2+} = Tl(I) + 2Os^{III}L_3{}^{3+} \qquad (3)$$
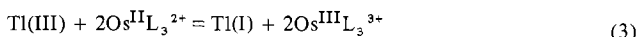
In all cases reported in Tables I–III, contributions from side reactions were negligible (see below for details of these) and the reactions were strictly first order in each of the two reactants. Figures 1 and 2 illustrate this and clearly show that there is no indication of a reverse reaction path. The sec-
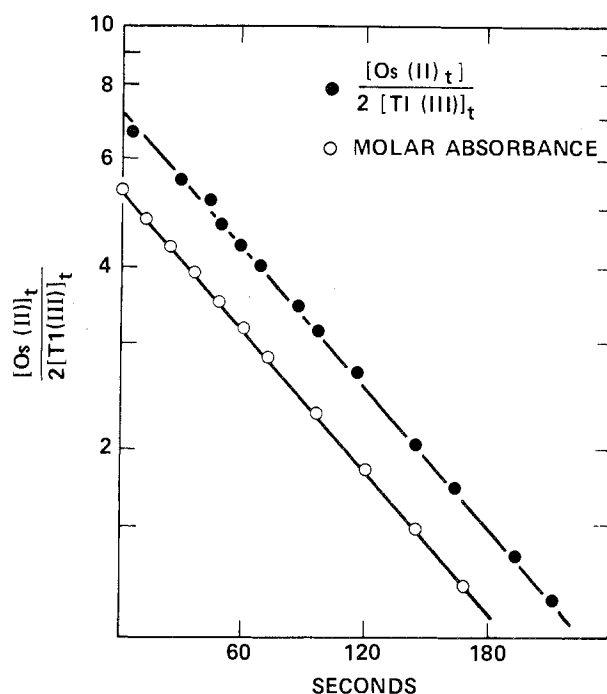

Figure 1. Semilogarithmic plots for the oxidation of OsL$_3{}^{2+}$ by Tl(III): open circles, molar absorbance (λ 480 nm) vs. time at 25 °C; [Os(bpy)$_3{}^{2+}$] = 2.23 × 10^{-4} M, [Tl(III)] = 5.79 × 10^{-3} M, [H$^+$] = 0.453 M, [SO$_4{}^{2-}$] = 0.997 M; pseudo-first-order plot; closed circles, [Os(phen)$_3{}^{2+}$]/2[Tl(III)] vs. time at 25 °C; [Os(phen)$_3{}^{2+}$] = 1.009 × 10^{-4} M, [Tl(III)] = 7.586 × 10^{-5} M, [H$^+$] = 0.54 M, [NO$_3{}^-$] = 1.26 M; second-order plot.
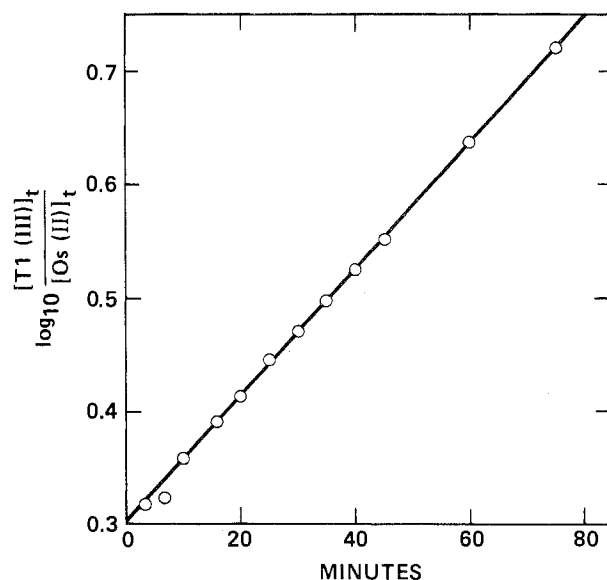
Figure 2. Second-order plot for the oxidation of Os(bpy)$_3{}^{2+}$ by Tl(III); [Os(bpy)$_3{}^{2+}$] = 5.87 × 10^{-6} M, [Tl(III)] = 1.122 × 10^{-5} M ([Os(bpy)$_3{}^{2+}$] calculated from intercept 5.61 × 10^{-6} M), [H$^+$] = 0.10 M, NaClO$_4$ = 3.0 M, temperature 25 °C.

Table III. Rates and Activation Parameters in Perchlorate, Sulfate, and Nitrate Solutions^a

Medium	Complex	k, dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
1.0 HClO$_4$ + 0.4 NaClO$_4$	Os(bpy)$_3{}^{2+}$	16.6	40 ± 4	−86 ± 10
1.05 HNO$_3$ + 0.31 NaNO$_3$	Os(bpy)$_3{}^{2+}$	0.26	46 ± 2	−102 ± 5
0.535 HNO$_3$ + 0.825 NaNO$_3$	Os(bpy)$_3{}^{2+}$	0.45	46 ± 2	−99 ± 10
0.453 H$_2$SO$_4$ + 0.535 Na$_2$SO$_4$	Os(bpy)$_3{}^{2+}$	0.054	82 ± 4	0 ± 6
0.277 H$_2$SO$_4$ + 0.721 Na$_2$SO$_4$	Os(bpy)$_3{}^{2+}$	0.10		
1.05 HNO$_3$ + 0.31 NaNO$_3$	Os(phen)$_3{}^{2+}$	2.7	37 ± 2	−113 ± 5
0.535 HNO$_3$ + 0.825 NaNO$_3$	Os(phen)$_3{}^{2+}$	5.9	37 ± 2	−106 ± 5

^{a} Concentrations of salt media given in mol dm^{-3}. [OsL$_3{}^{2+}$] = 5 × 10^{-5}–1 × 10^{-4} mol dm^{-3}; [Tl(III)] = 2 × 10^{-5}–9.1 × 10^{-3} mol dm^{-3}.

Table IV. Data Recalculated from Ref 2 Illustrating Increase of Discrepancy with Increasing Hydrogen Ion Concentration[a]

$[H^+]$, mol dm^{-3}	Temp, °C	k, dm^3 mol^{-1} s^{-1}
2.99	17.5	16.0
2.99	24.5	19.5
2.99	25.0	20.1 (7.6)
2.99	35.0	30.8
0.98	17.5	11.8
0.98	24.5	17.5
0.98	25.0	18.0 (10.1)
0.98	35.0	26.4
0.52	17.5	10.3
0.52	24.5	16.3
0.52	25.0	17.0 (13.2)
0.52	35.0	25.1

[a] New data are in parentheses. k values calculated from k_a, k_b, and K given in ref 2; values in parentheses, by extrapolation from new data given in Table II.

ond-order rate constants are given in Tables I–III; these were reproducible using different preparations of the complexes. The compositions of the solutions are given as footnotes to the tables.

Side reactions were only studied sufficiently for them to be eliminated.

We did not encounter the experimental difficulty described by Irvine[2] which he attributed to an impurity in the NaClO$_4$ and which resulted in a rapid initial oxidation of Os(bpy)$_3{}^{2+}$. In most cases we confirmed that extrapolated and calculated initial concentrations of reactants agreed within 2%. An exception was the very dilute solution of both reactants as stated in the caption to Figure 2; however, the discrepancy here also is within analytical error. In Table IV, we give the experimental second-order rate constants which were calculated using the rate and equilibrium constants given in ref 2 and which were used there to reform the data before it was reported. For comparison, we include some of the new data in the table. This illustrates that, as would be expected from the discussion under (a) above, the discrepancy between the earlier data and ours increases with increasing $[H^+]$ at constant $[ClO_4{}^-]$.

Very small concentrations of Os(bpy)$_2$Cl$_2{}^+$ catalyze the Tl(III)–OsL$_3{}^{2+}$ reaction significantly (see Figure 3 and Tables V and VI). With added catalyst, rates were no longer second order or pseudo first order throughout but increased after about 1 half-life in OsL$_3{}^{2+}$. The limiting rates (from the first linear portions of the plots), at constant [Tl(III)] and constant [OsL$_3{}^{2+}$] but with varying catalyst, obeyed eq 4 in which the first term is the rate in the absence of catalyst (see also Table
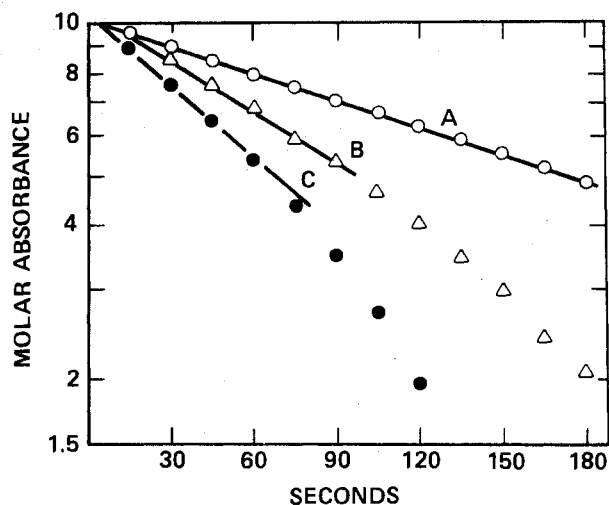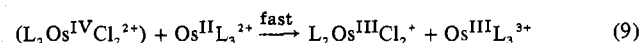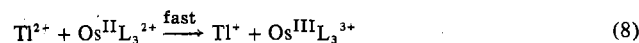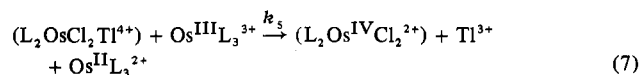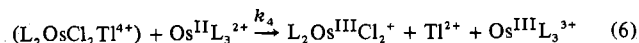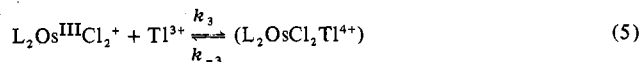

Figure 3. Semilogarithmic plot of molar absorbance vs. time at 25 °C for the catalyzed oxidation of Os(bpy)$_3{}^{2+}$ by Tl(III); $[H^+]$ = $[ClO_4{}^-]$ = 1.51 M, [Os(bpy)$_3{}^{2+}$] = 7.66 × 10^{-5} M, [Tl(III)] = 1.42 × 10^{-4} M: A, [Os(bpy)$_2$Cl$_2{}^+$] = 0; B, [Os(bpy)$_2$Cl$_2{}^+$] = 0.805 × 10^{-5} M; C, [Os(bpy)$_2$Cl$_2{}^+$] = 1.61 × 10^{-5} M.

$$-d[OsL_3{}^{2+}]/dt = 2k\,[Tl(III)][OsL_3{}^{2+}]$$
$$+ 2k_{lim}\,[Tl(III)][OsL_3{}^{2+}][Os(bpy)_2Cl_2{}^+] \qquad (4)$$

V). In addition, we found that the first half-life (with respect to OsL$_3{}^{2+}$) decreased with increase in [Tl(III)]$_0$:[OsL$_3{}^{2+}$]$_0$ ratio, where the subscript zero denotes initial concentration. The reaction scheme shown in eq 5–9 which invokes both

$$L_2Os^{III}Cl_2{}^+ + Tl^{3+} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} (L_2OsCl_2Tl^{4+}) \qquad (5)$$

$$(L_2OsCl_2Tl^{4+}) + Os^{II}L_3{}^{2+} \overset{k_4}{\rightarrow} L_2Os^{III}Cl_2{}^+ + Tl^{2+} + Os^{III}L_3{}^{3+} \qquad (6)$$

$$(L_2OsCl_2Tl^{4+}) + Os^{III}L_3{}^{3+} \overset{k_5}{\rightarrow} (L_2Os^{IV}Cl_2{}^{2+}) + Tl^{3+}$$
$$+ Os^{II}L_3{}^{2+} \qquad (7)$$

$$Tl^{2+} + Os^{II}L_3{}^{2+} \overset{fast}{\longrightarrow} Tl^+ + Os^{III}L_3{}^{3+} \qquad (8)$$

$$(L_2Os^{IV}Cl_2{}^{2+}) + Os^{II}L_3{}^{2+} \overset{fast}{\longrightarrow} L_2Os^{III}Cl_2{}^+ + Os^{III}L_3{}^{3+} \qquad (9)$$

Os^{IV}(bpy)$_2$Cl$_2{}^{2+}$ and Os(bpy)$_2$Cl$_2$Tl^{4+} as reactive intermediates was considered. We have other evidence for the formation of a complex between Tl^{3+} and the catalyst (see catalyzed aquation below). Moreover, although the redox potential for the Os^{IV}(bpy)$_2$Cl$_2{}^{2+}$–Os^{III}(bpy)$_2$Cl$_2{}^+$ couple is

Table V. Limiting Rate Constants for the Os(bpy)$_2$Cl$_2{}^+$-Catalyzed Oxidation of Os(bpy)$_3{}^{2+}$ by Tl(III)[a]

[Os(bpy)$_3{}^{2+}$]	[Tl(III)]	[Os(bpy)$_2$Cl$_2{}^{2+}$]	Medium and temp	k,[d] dm^3 mol^{-1} s^{-1}	k_{lim},[d] dm^3 mol^{-2} s^{-1}
7.66 × 10^{-5}	1.42 × 10^{-4}	8 × 10^{-6},[b] 1.6 × 10^{-5} [b]	1.51 M HClO$_4$; 25 °C	17.1	1.65 × 10^6
1.90 × 10^{-4}	2.32 × 10^{-2}	2 × 10^{-6},[b] 4 × 10^{-6} [c]	0.45 M H$_2$SO$_4$ + 0.50 M Na$_2$SO$_4$; 15 °C	1.55 × 10^{-2}	2.7 × 10^4

[a] All concentrations given in mol dm^{-3}. [b] From second- or pseudo-first-order plots (linear for the first half-life in [Os(bpy)$_3{}^{2+}$]; see text. [c] From tangent to curved semilogarithmic plot of absorbance vs. time. [d] Defined in eq 4.

Table VI. Catalyzed Oxidation of Os(bpy)$_3{}^{2+}$ in H$_2$SO$_4$[a]

[L$_3$Os^{2+}]	[Tl(III)]	[L$_2$OsCl$_2{}^+$]	$t_{1/2}$, s	k_3, dm^3 mol^{-1} s^{-1}	k_3(cor), dm^3 mol^{-1} s^{-1}
1.97 × 10^{-5}	5.79 × 10^{-3}	2.0 × 10^{-6}	109	5.4	5.2
1.02 × 10^{-5}	11.58 × 10^{-3}	2.0 × 10^{-6}	33	4.6	4.5
1.89 × 10^{-4}	23.16 × 10^{-3}	2.0 × 10^{-6}	247	5.7	4.3
1.89 × 10^{-4}	23.16 × 10^{-3}	4.0 × 10^{-6}	132	5.4	4.6
4.58 × 10^{-6}	11.58 × 10^{-3}	4.0 × 10^{-6}	7.1	4.7	4.7

[a] Concentrations given in mol dm^{-3}. $k_3 = 0.69[L_3Os^{2+}]_0(2t_{1/2}[Tl(III)]_0[L_2OsCl_2{}^+]_0)$; cf eq 12. k_3(cor) is calculated from the total rate minus the rate of uncatalyzed reaction in Table V. $[H^+] = 0.905$ M; $[SO_4{}^{2-}] = 0.998$ M; temperature is 15 °C.

not known, by analogy with known Ru couples[13] the oxidation to Os(IV) could well occur. As shown in Table VI, this scheme enabled us to correlate all of the data using eq 11 (vide infra). A steady-state treatment for the two intermediates (given in parentheses) leads to
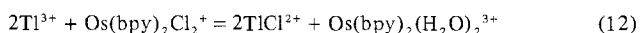
$$\frac{-d[L_3Os^{2+}]}{dt} = \frac{2k_4k_3[Os^{III}L_2Cl_2{}^+][Tl(III)][Os^{II}L_3{}^{2+}]}{k_{-3} + k_4Os^{II}L_3{}^{2+}] + k_5[Os^{III}L_3{}^{3+}]} \quad (10)$$

When k_{-3} is much less than the other terms in the denominator and when Tl(III) is in large excess over the other two reactants, then, if $k_4 = k_5$, the limiting rate with no added $L_3(Os^{III})^{3+}$ is

$$\frac{-d[L_3Os^{2+}]}{dt} = \frac{2k_3[Os^{III}L_2Cl_2{}^+][Tl(III)]_0[Os^{II}L_3{}^{2+}]_t}{[Os^{II}L_3{}^{2+}]_0} \quad (11)$$

We do not consider the mechanism depicted in eq 5–9 to be proven because we have only considered limiting rates. The buildup of the postulated intermediates could account for the observed deviations from the simple rate orders following the breakdown of this last assumption. The scheme, whether true or not, was useful as it enabled us to show that the catalyzed reaction has a very different rate law from the uncatalyzed and that therefore it could not have contributed to the rates given in Tables I–III.

The rate of acid hydrolysis of $(bpy)_2OsCl_2{}^+$ promoted by Tl^{3+} was studied spectrophotometrically in 0.5 M H_2SO_4 containing 0.5 M Na_2SO_4 by recording the rate of disappearance of the visible absorption at 392 nm. The maximum molar extinction coefficient, 3.95×10^3, was in excellent agreement with the literature value.[11] In the absence of Tl^{3+} there was no detectable hydrolysis in 48 h. With $[Tl^{3+}] = 0.83 \times 10^{-2}$ and 1.67×10^{-2} M and with $[Os(bpy)_2Cl_2{}^+] = 0.85 \times 10^{-4}$ and 1.70×10^{-4} M the stoichiometry was

$$2Tl^{3+} + Os(bpy)_2Cl_2{}^+ = 2TlCl^{2+} + Os(bpy)_2(H_2O)_2{}^{3+} \quad (12)$$

and the rate law was

$$-d[Os(bpy)_2Cl_2{}^+]/dt = k_{hyd}[Tl^{3+}][Os(bpy)_2Cl_2{}^+] \quad (13)$$

At 25 °C k_{hyd} is $(2.75 \pm 0.05) \times 10^{-3}$ dm^3 mol^{-1} s^{-1}. From this and data at 15 and 35 °C we calculate $\Delta H^\ddagger = 79$ kJ mol^{-1} and $\Delta S^\ddagger = -28$ J K^{-1} mol^{-1}. Comparison with rates in Table III shows that this reaction is too slow to have contributed to the rate of the Tl(III)–Os(bpy)$_3{}^{2+}$ reaction; it is however fast for a substitution reaction in an Os(III) complex. This supports the above postulate of an intermediate $((bpy)_2OsCl_2Tl^{4+})$ which in the presence of Os(bpy)$_3{}^{2+}$ would react according to eq 6 and in the absence of Os(bpy)$_3{}^{2+}$ would undergo aquation.

Discussion of the Tl(III)–OsL$_3{}^{2+}$ Reaction

The rate of the Tl^{III}–Os^{II}L$_3{}^{2+}$ reaction increases with decreasing $[H^+]$, decreases with change from $ClO_4{}^-$ to the more strongly complexing $NO_3{}^-$ and $SO_4{}^{2-}$ ions, and increases when Os(phen)$_3{}^{2+}$ replaces Os(bpy)$_3{}^{2+}$ (see Tables I–III).

The major Tl(III) species in the perchlorate solutions are Tl^{3+} and $TlOH^{2+}$. The acid dissociation constants for Tl^{3+} in the perchlorate media are known[14] so that the compositions of the solutions can be calculated. The $[H^+]$ dependence is adequately reproduced by considering the overall rate as due to two parallel reactions, eq 14 and 15, with Tl^{2+} rapidly

$$Tl^{3+} + OsL_3{}^{2+} \xrightarrow{k_0} Tl^{2+} + OsL_3{}^{3+} \quad (14)$$

$$TlOH^{2+} + OsL_3{}^{2+} \xrightarrow{k_1} Tl^{2+} + OsL_3OH^{2+} \quad (15)$$
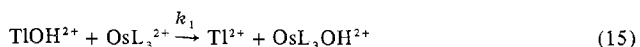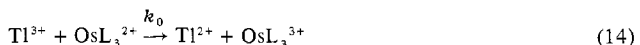
reacting further with $OsL_3{}^{2+}$. k_0 and k_1 are given in Table VII. The minor $[H^+]$-independent path (reaction 14) may occur by an outer-sphere reversible electron-transfer mech-

Table VII. k_0 and k_1 for the Tl(III)–Os(bpy)$_3{}^{2+}$ Reaction in Perchlorate Solution[a]

Ionic strength	Temp, °C	k_0, dm^3 mol^{-1} s^{-1}	k_1, dm^3 mol^{-1} s^{-1}	$k([H^+] = 1)$, dm^3 mol^{-1} s^{-1}
1.4	25	Small	214 ± 3	16.6
1.4	0	Small	56.8 ± 1.2	
3.0	25	6.2	63	10.0

[a] $k = k_1\alpha_{TlOH^{2+}} + k_0(1 - \alpha_{TlOH^{2+}})$ (see text); $\Delta H_1{}^\ddagger = 34$ kJ mol^{-1}; $\Delta S_1{}^\ddagger = -85$ J K^{-1} mol^{-1}.

anism. However, $E°$ for the Tl^{3+}–Tl^{2+} couple in this perchlorate medium is about 0.32 V[7] and $E°$ for the Os(bpy)$_3{}^{3+}$–Os(bpy)$_3{}^{2+}$ couple is 0.88 V[13] so that not only is $\Delta G°$ positive but also it is too large for the simplified Marcus electron-transfer theory[15] to be used to test this hypothesis. Certainly an outer-sphere electron transfer could not explain the differences in $\Delta H^\ddagger$ and $\Delta S^\ddagger$ when phen replaces bpy as is observed for the nitrate media.

We find that the large changes in rate and also the changes in activation parameters (see Table III) with change in *medium* can probably be attributed to removal of Tl(III) as nonreactive anion complexes. Thus, for the nitrate solutions, the decrease in rate over that in the corresponding perchlorate media can be quantitatively accounted for using the known[15] stability constants for Tl(III) and $NO_3{}^-$ and assuming that the stability constant for the $OsL_3{}^{2+}$–$NO_3{}^-$ complexes is nearly equal to that known for $TlOH^{2+}$–$NO_3{}^-$. Stability constants for the Tl^{III}–$SO_4{}^{2-}$ system are not as extensive, but by comparison with other metal ion sulfates, we find that a similar treatment here could also explain the data. Both $SO_4{}^{2-}$ and $NO_4{}^{2-}$ are known to catalyze some other redox reactions of Tl(III), but the present evidence suggests that in all media which we have studied, the composition of the transition state for the major reaction path is $(TlOHOsL_3{}^{4+})$.

If the first Os product, as in eq 15, is OsL_3OH^{2+}, then this may possibly resemble an intermediate of the same composition which has recently[10,16] been found to result from reaction of $OsL_3{}^{3+} + OH^-$ and we therefore propose that the role of the ligand in the reactive intermediate may be similar in both of the reactions and that in both cases the detailed mechanism may involve attack of a carbon atom of the ligand. Although such a mechanism has recently been proposed[17] to account for many diverse reactions (both substitution and redox) of bpy– and phen–metal complexes, quantitative data supporting this thesis are in most cases lacking, and in at least one case we found an alternative mechanism more satisfactory.[18,19] We therefore felt that our work on the Tl(III)–OsL$_3{}^{2+}$ reaction should be presented for publication at this time.

References and Notes

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and H$_2$SO$_4$ the oxidant is possibly O$_2$.

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Electron Transfer through Organic Structures. 21.
Reductions of Ortho-Substituted Benzoatocobalt(III) Derivatives[1]

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The reductions, by Cr^{2+}, of a series of 2-hydroxybenzoato derivatives of (NH$_3$)$_5$Co^{III} are compared with those of the 2-aminobenzoato analogues. Nearly all complexes in both series exhibit the rate law: rate = [Cr^{2+}][Co^{III}](k_0 + k_{-1}[H$^+$]$^{-1}$), in the range [H$^+$] = 0.01–1.0 M. Comparison of the distribution of Cr(III) products between chelate (VIII) and nonchelate (IX) with partition of the reduction into acid-independent and inverse-acid kinetic components extends to the 2-hydroxy complexes the three-path (chelated basic, chelated acidic, and nonchelated acidic) mechanism proposed earlier for the parent salicylato complex. Individual specific rates and the distribution between paths are quite insensitive to incorporation of ring substituents, but the inverse-acid path is seriously retarded for reactions proceeding through a seven- rather than a six-membered chelate. With 2-amino derivatives, all chelated product appears to be formed in the inverse-acid path; here, chelation cannot occur with the protonated reactant. Specific rates for the nonprotonated forms of the complexes (k_B's) lie between 2 and 64 M^{-1} s^{-1}. Values of k_B increase with basicity but are less intense functions of structure than are pK_A's. Comparison of such k_B's with analogous "rate constants" greater than 10^6 M^{-1} s^{-1} in the 2-hydroxy series provides further evidence that the latter values, which have been presumed to apply to direct reduction of the conjugate base (the o-O$^-$ form of the Co^{III} complex) are fictitiously high.

Shortly after the establishment of the inner-sphere mechanism for electron-transfer reactions between appropriately substituted metal centers,[2] indications appeared that reactions of this type could sometimes be markedly accelerated by development of chelation in the transition state.[3] The early reactions proceeding through chelated activated complexes utilized Cr^{2+} as the reductant,[4] and evidence is now at hand for chelation in inner-sphere reductions by Cu$^+$,[5] V^{2+},[6] Eu^{2+},[7] and Ti^{3+}.[8] Nevertheless, Cr^{2+} must be regarded as the most versatile of the known reducing centers in this respect, for it appears, under favorable conditions, to form chelates involving –COOH,[4b,9a] –COO$^-$,[4c] alcoholic –OH,[9b] phenolic –OH and –O$^-$,[9c] –SR,[9a] –SeR,[7a] and donor nitrogen from pyridine,[4c] pyrazine,[9d] pyrrole,[4c] and pyrazole[9e] rings.

The present study compares the reductions, by Cr^{2+}, of a series of 2-hydroxybenzoatocobalt(III) complexes with those of the 2-aminobenzoato analogues. Parallelism between the action of these structurally similar mediating groups is, in part, masked, by the much greater ease with which the amino substituents are protonated in our reaction media, and even after this difference is taken into account, dissimilarities between the two groups remain.

Experimental Section

Materials. Those cobalt(III) complexes not available from previous studies[8,9c] were prepared from aquopentaamminecobalt(III) perchlorate in water[4c] or the corresponding carbonato nitrate[4c] in diethylene glycol[5] as described. Crystallization of aminobenzoato derivatives from dilute HClO$_4$ gave tris(perchlorates), whereas crystallization from water generally gave bis(perchlorates). Aside from 8-hydroxy-1-naphthoic acid, which was prepared by the method of Birch and co-workers,[10] carboxylic acid ligands were Aldrich products and were used as received. Elemental analysis of complexes prepared here for the first time or those for which a check in purity was desired appear in Table I. Lithium perchlorate[5] and Cr(II) solutions[9e] were prepared as described. The cation-exchange resin

Table I. Analyses of Pentaamminecobalt(III) Perchlorates, RCo(NH$_3$)$_5$(ClO$_4$)$_2$

R	% calcd			% found		
	C	H	Co	C	H	Co^a
2-Hydroxy-3-methylbenzoato	19.44	4.50	11.9	19.54	4.25	12.1
2-Hydroxy-5-methylbenzoato	19.44	4.50	11.9	19.75	4.28	11.8
2-Aminobenzoato^b	14.55	3.84	10.2	14.56	3.81	10.0
2-Amino-3-methylbenzoato^b	16.23	4.06	10.0	16.50	4.20	10.1
2-Amino-4-chlorobenzoato	16.2	3.9		16.36	4.0	
2-Amino-4-chlorobenzoato^b	13.6	3.4		13.4	3.4	
2-Amino-5-chlorobenzoato^b	13.6	3.4		13.2	3.5	
4-Aminobenzoato^b	14.55	3.84	10.2	14.29	3.79	10.4

^{a} See ref 4. ^{b} Tris(perchlorates), obtained from recrystallization from dilute HClO$_4$.

Table II. pK_A Values of Some 2-Aminobenzoatopentaamminecobalt(III) Complexes, RCo(NH$_3$)$_5^{2+}$

R	p$K_A{}^a$
2-Aminobenzoato	3.74 ± 0.05
2-Amino-3-methylbenzoato	3.75 ± 0.10
2-Amino-4-methylbenzoato	3.85 ± 0.10
2-Amino-3,5-dichlorobenzoato	1.35 ± 0.10
2-Amino-4-chlorobenzoato	2.48 ± 0.05
2-Amino-5-chlorobenzoato	2.92 ± 0.10

^{a} Temperature was 25 °C; measurements were made in aqueous NaClO$_4$; μ = 1.0.

(Bio-Rad AG 50W-X2, 200–400 mesh) used in separations of reaction products was pretreated as described[11] and stored in 0.02 M HClO$_4$.

Rate Measurements. Rates were estimated from measurements of absorbance decreases on the Cary 14 recording spectrophotometer as described.[6b,7a,9] Measurements were made at 502 nm. Reactions were first order each in Co(III) and in Cr(II), but rate measurements were generally carried out under pseudo-first-order conditions with