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Reactions of Bis(organo)(chelate)cobalt Complexes with Electrophiles

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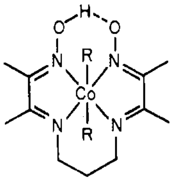
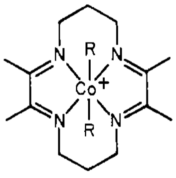
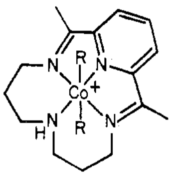
Kinetics studies were conducted on the electrophilic methyl-transfer reaction of $(CH_3)_2Co$(chelate) with three electrophilic reagents, $(H_2O)_2Co$(chelate)$^+$, H_3O^+, and $C_6H_5Hg^+$. The mechanisms of these reactions are discussed in terms of the factors which influence the reactivity.

Introduction

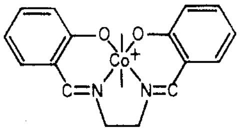
Reactions in which alkyl groups are transferred from a high-valent metal complex, such as a Co^{III} or Cr^{III} complex, have in recent years provoked a great deal of interest.[1-3] Despite the ready cleavage[3-9] of the Co–C bond in materials such as $CH_3Co(dmgH)_2H_2O$[10] by the electrophile Hg^{2+}, a surprising number of other reagents including the electrophiles H_3O^+, CH_3Hg^+, and $C_6H_5Hg^+$ are essentially unreactive toward cleavage of the Co–C bond.[11] In this paper we report the results of kinetic studies of a particular group of bis(organo)(chelate)cobalt(III) complexes,[13] structures I–III, with electrophilic reagents.

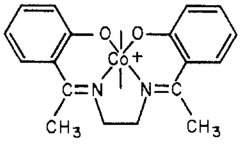

I
$R_2Co(dpnH)$

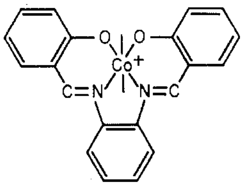

II
$R_2Co(tim)^+$


III
$R_2Co(cr)^+$

The reactions considered here occur with transfer of a (formal) carbanion to the reagents $(H_2O)_2Co$(chelate)$^+$ (structures IV–VI),[14,15] $C_6H_5Hg^+$, and H_3O^+, as in eq 1–3


IV
$(H_2O)_2Co(salen)^+$


V
$(H_2O)_2Co(Me_2salen)^+$


VI
$(H_2O)_2Co(saloph)^+$

$$(CH_3)_2Co(dpnH) + (H_2O)_2Co(chel)^+ = CH_3Co(dpnH)H_2O^+ + CH_3Co(chel)H_2O \qquad (1)$$

$$(CH_3)_2Co(dpnH) + C_6H_5Hg^+ = CH_3Co(dpnH)H_2O^+ + C_6H_5HgCH_3 \qquad (2)$$

$$(CH_3)_2Co(dpnH) + H_3O^+ = CH_3Co(dpnH)H_2O^+ + CH_4 \qquad (3)$$

(using $(CH_3)_2Co(dpnH)$ as a sample reactant).

Results

Reactions of Dimethylcobalt Complexes with H^+. Monomethylcobalt complexes are not dealkylated by H^+, even under forcing conditions, in contrast to the ready decomposition by acidolysis of the dimethyl complexes to the corresponding monomethyl complex and methane, as shown in eq 3. The reactions of $(CH_3)_2Co(dpnH)$ and $(CH_3)_2Co(tim)^+$ with excess H^+ show a first-order dependence on the concentration of the dimethylcobalt complex, the value of k_{obsd} so determined being linear in $[H^+]$ as shown in Figure 1. The data depicted refer to 25 °C, μ = 0.10 M (maintained with $LiClO_4$), in THF–H_2O (1:1 v/v). The rate law is given by eq 4, with k_H

$$-d[(CH_3)_2Co(chel)]/dt = k_H[(CH_3)_2Co(chel)][H^+] \qquad (4)$$

= 4.5 ± 0.2 and 0.27 ± 0.01 $dm^3\ mol^{-1}\ s^{-1}$ for $(CH_3)_2Co(dpnH)$ and $(CH_3)_2Co(tim)^+$, respectively. The reaction of the former complex shows a small salt and solvent dependence, k_H being 6.8 $dm^3\ mol^{-1}\ s^{-1}$ at μ = 0.002–0.01 M (in 1:1 H_2O–THF solutions of $HClO_4$ of nonconstant ionic strength) and 40 $dm^3\ mol^{-1}\ s^{-1}$ in CH_3OH–H_2O (1:1 v/v).

Reactions of Dimethylcobalt Complexes with Diaquocobalt(III) Complexes. Costa and co-workers[15] first reported the alkyl-transfer reaction shown in eq 1. These reactions occur with the indicated 1:1 stoichiometry and proceed essentially to completion for the diaquocobalt(III) complexes of the chelates saloph, salen, and Me_2salen. The reactions with vitamin B_{12a} are very slow and with $(H_2O)_2Co(dmgH)_2^+$ and $(H_2O)_2Co(dpnH)^{2+}$ apparently do not proceed at all, with the only observable process in the latter instance being the slower acidolysis reaction of the dialkyl complex by reaction with the low level of hydrogen ion added to the solution to repress acid dissociation of the diaquo complexes. In the case of the three diaquo complexes which do undergo the methyl-transfer reactions, the diaquocobalt complexes of saloph, salen, and Me_2salen, the reaction, when studied under conditions with a large excess of the diaquo ion, follows pseudo-first-order kinetics. The values of k_{obsd} show a linear dependence[16] upon $[(H_2O)_2Co(chel)^+]$, as depicted for typical reactions in Figure 2, in accord with eq 5. The rate constants are summarized

$$-d[Me_2Co(chel)]/dt = k[(H_2O)_2Co(chel)^+][Me_2Co(chel)] \qquad (5)$$

in Table I.

Reactions of Dimethylcobalt Complexes with Organomercury Cations. In contrast to the negligibly slow reactions of monoalkylcobalt complexes with RHg^+ (R = Me, Ph), the reactions in eq 2 occur very rapidly. In fact, many of the combinations attempted proved too rapid for stopped-flow kinetic studies even at exceptionally low concentrations; thus, the second-order rate constants (25 °C, 1:1 THF–H_2O) are >ca. 10^7 $dm^3\ mol^{-1}\ s^{-1}$ for the reactions of phenylmercuric ion and the complexes $(C_6H_5)_2Co(dpnH)$, $(C_2H_5)_2Co(cr)^+$, and $(n\text{-}C_3H_7)_2Co(cr)^+$. Products of reaction are as shown in eq 2 (verified by NMR for $(CH_3)_2Co(dpnH) + Hg(CH_3)^+$: see Experimental Methods), and reactions occur according to the indicated 1:1 stoichiometry (verified by spectrophotometric titration). The reactions were studied with a large (≥10:1) excess of $C_6H_5Hg^+$ at 25 °C in 1:1 v/v THF–H_2O and followed pseudo-first-order kinetics under these conditions. The linear dependence of the pseudo-first-order rate constant

Table I. Summary of Second-Order Rate constants,[a] k ($dm^3\ mol^{-1}\ s^{-1}$), for the Reactions of Dimethylcobalt Complexes with Various Electrophiles.

Electrophile	$(CH_3)_2Co(dpnH)$ in 1:1 CH_3OH-H_2O	$(CH_3)_2Co(dpnH)$ in 1:1 $THF-H_2O$	$(CH_3)_2Co(tim)$ in 1:1 $THF-H_2O$
H_3O^+	40	4.5 ± 0.2	0.27 ± 0.01
$(H_2O)_2Co(saloph)^+$	$(2.9 \pm 0.3) \times 10^3$	$(1.13 \pm 0.02) \times 10^3$	$(1.03 \pm 0.16) \times 10^3$
$(H_2O)_2Co(salen)^+$		$(1.73 \pm 0.05) \times 10^4$	$(1.33 \pm 0.21) \times 10^4$
$(H_2O)_2Co(Me_2salen)^+$		$(2.9 \pm 0.3) \times 10^4$	$(1.64 \pm 0.13) \times 10^4$
$C_6H_5Hg^+$ [b]		ca. 2×10^6	$(1.3 \pm 0.3) \times 10^5$

[a] At 25 °C, $\mu = 0.10$ M ($LiClO_4$). [b] Other reactions of $C_6H_5Hg^+$ have rate constants of $(2.1 \pm 0.3) \times 10^5$ for $(CH_3)_2Co(cr)^+$ and $(2.0 \pm 0.2) \times 10^4$ for $(C_6H_5CH_2)_2Co(dpnH)$.

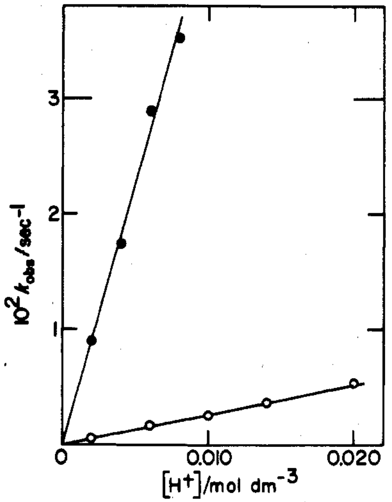


Figure 1. Linear dependence of the rate of reaction of dimethylcobalt complexes with H^+ illustrated for $(CH_3)_2Co(dpnH)$ (filled circles) and $(CH_3)_2Co(tim)^+$ (open circles) at 25 °C and $\mu = 0.10$ M ($LiClO_4$) in $THF-H_2O$ (1:1 v/v).

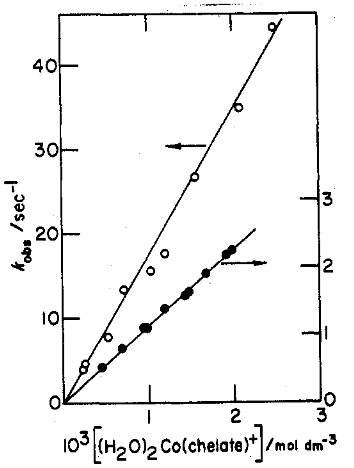


Figure 2. Variation of k_{obsd} with $[(H_2O)_2Co(saloph)^+]$ (open circles) and $[(H_2O)_2Co(salen)^+]$ (filled circles) in reactions with $(CH_3)_2Co(dpnH)$ at 25 °C and $\mu = 0.10$ M ($LiClO_4$) in $THF-H_2O$ (1:1 v/v).

upon $[C_6H_5Hg^+]$ is consistent with a second-order reaction; the kinetic data are summarized in Table I.

Discussion

Each of the reactions follows a second-order rate expression, supporting a mechanism in which there is a direct transfer of the carbanion in a transition state formed by the bimolecular interaction of the dialkylcobalt complex with the electrophile. The reaction rates for a given $R_2Co(chel)$ complex with the different electrophiles follow the order $C_6H_5Hg^+ > (H_2O)_2Co(chel)^+ > H_3O^+$.

An interesting aspect of the mechanism of reaction of the diaquocobalt complex arises from a consideration of the process by which a $Co-H_2O$ bond is cleaved. This necessarily occurs during the overall process, presumably in forming an alkyl-bridged transition state, yet the rate of $Co-H_2O$ substitution in the diaquocobalt(III) chelate complexes has been thought to be very slow.[17] Although the evidence is hardly compelling, certain results do suggest that the rate of axial ligand substitution in aquocobalt(III) chelates may not, in fact, be as slow as is generally supposed. Although $L_2Co^{III}(dmgH)_2$ complexes undergo slow substitution of L,[17] vitamin B_{12a} substitutes quite rapidly, the rate constants for anation by uninegative entering groups being ca. $10^3\ dm^3\ mol^{-1}\ s^{-1}$ at 25 °C.[18] *If* the complexes $(H_2O)_2Co^{III}(chel)^+$ for chel = saloph, salen, and Me_2salen undergo ligand substitution at rates comparable to vitamin B_{12}, this would explain not only the rapidity of the methyl-transfer rates found here but also the fact that each of the dimethyl complexes reacts with a given diaquo complex at virtually the same rate, a coincidence supporting our contention that alkyl transfer to the diaquo complexes may be controlled by a substitution process.

In contrast to the high rates of reaction 2 for the indicated chelates, the complex $(H_2O)_2Co(dmgH)_2^+$, for which substitution is known to occur very slowly,[17] does not react to any measurable extent with the dimethyl complexes under these conditions, nor does the structurally similar $(H_2O)_2Co(dpnH)^{2+}$ undergo the methylation reaction. The failure to react does not seem to us to reflect a fundamental deficiency on the part of these two diaquo complexes but may merely result from the low rates of $Co-H_2O$ substitution, in which case decomposition of the dimethyl complexes with H_3O^+ predominates, by default as it were.

We made some attempts to confirm this postulated substitution-limited methyl transfer, attempting to evaluate the rate of anation of $(H_2O)_2Co(salen)^+$ by SCN^-. Unfortunately the degree of complexation and/or the accompanying spectral change was so small as to preclude this determination. Our suggested mechanism thus remains unconfirmed in this regard.

The methylation of the organomercury cations by the dimethylcobalt complexes constitutes an example of the formation of a bis(organo)mercurial by alkyl transfer from cobalt to mercury. Previous workers[6,12] have alluded to the formation of $Hg(CH_3)_2$ by reaction of $HgCH_3^+$ and methylcobalamin, but details were not given. Model complexes such as $CH_3Co(dmgH)_2H_2O$ and related monomethylorganocobalt compounds do not react with CH_3Hg^+,[4,7,9] and the suggestion has been offered by Dodd and Johnson[19] that the formation of $Hg(CH_3)_2$ in marine organisms may in fact result not from the direct methylation of $HgCH_3^+$ by methylcobalamin but rather from the displacement to the right of the symmetrization reaction of eq 6. In any event, the bisorganomercurials are

$$2CH_3Hg^+ = Hg(CH_3)_2 + Hg^{2+} \tag{6}$$

formed readily in reaction 2; certainly no substitution barrier, at least, is offered by $RHgH_2O^+$, whose substitution reactions are quite rapid.[20]

Experimental Methods

The following compounds were prepared by literature methods or slight modifications thereof: $dpnH_2$,[21] $[I_2Co(dpnH)]$,[22]

$[(CH_3)_2Co(dpnH)]$,[23] $[(CH_3)Co(dpnH)H_2O]ClO_4$,[22] $[(C_6H_5)_2Co(dpnH)]$,[24] $[C_6H_5Co(dpnH)H_2O]ClO_4$,[24] $[(C_6H_5)(CH_3)Co(dpnH)]$,[24] $[(H_2O)_2Co(dpnH)](ClO_4)_2$,[22] $[(CH_3)_2Co(tim)]ClO_4$,[25] $[CH_3Co(tim)H_2O](ClO_4)_2$,[25] $[(H_2O)_2Co(salen)]ClO_4$,[26] $[CH_3Co(salen)H_2O]$,[26] $[(H_2O)_2Co(Me_2salen)]ClO_4$,[25] $[CH_3Co(Me_2salen)H_2O]$,[26] $[(H_2O)_2Co(saloph)]ClO_4$,[26] $[CH_3Co(saloph)H_2O]$,[26] $[(CH_3)_2Co(cr)](BPh_4)$.[25]

Lithium perchlorate was prepared from the carbonate and was recrystallized twice. Tetrahydrofuran was distilled from $LiAlH_4$ immediately before use to eliminate peroxides. Reagent grade phenylmercuric nitrate, perchloric acid, and methanol were used without purification.

Kinetic determinations were carried out spectrophotometrically, utilizing a Cary Model 14 recording instrument for slower reactions and stopped-flow instruments (Canterbury SF-3A and Durrum D-110) for the faster reactions.

The NMR spectrum of products taken after mixing solutions of $(CH_3)_2Co(dpnH)$ and CH_3HgOAc shows that the Co–CH_3 resonance (δ 0.06) has disappeared and a new peak (δ 0.27) has formed, corresponding to $Hg(CH_3)_2$.[27] There are also produced a peak at δ 0.39 corresponding[28] to OAc^- coordinated trans to Co–CH_3 and peaks at δ 2.26 and 2.33 corresponding to the C–CH_3 resonances of dpnH.

Registry No. $(CH_3)_2Co(dpnH)$, 33569-60-7; $(CH_3)_2Co(tim)^+$, 47100-11-8; $(CH_3)_2Co(cr)^+$, 47176-21-6; $(C_6H_5CH_2)_2Co(dpnH)$, 36542-14-0; $(H_2O)_2Co(saloph)^+$, 49858-56-2; $(H_2O)_2Co(salen)^+$, 54194-54-6; $(H_2O)_2Co(Me_2salen)^+$, 58281-52-0; $C_6H_5Hg^+$, 23172-37-4; H_3O^+, 13968-08-6.

References and Notes

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(10) dmgH represents the monoanion of dimethylglyoxime; bis(dimethylglyoximato)cobalt complexes are referred to as cobaloximes.

(11) Exceptions to this broad generalization are, of course, to be found: benzylcobaloxime reacts with concentrated sulfuric acid [C. W. Fong and M. D. Johnson, unpublished observations as cited in ref 1a, p 70], and a methyl group is apparently transferred to $HgCH_3^+$ by more reactive methylcobalt complexes.[12]

(12) R. E. Di Simone, M. W. Penley, L. Charbonneau, S. G. Smith, J. M. Wood, H. A. O. Hill, J. M. Pratt, S. Risdale, and R. J. P. Williams, *Biochim. Biophys. Acta*, **304**, 851 (1973); see also ref 1a, pp 76–77.

(13) The uninegative ligand dpnH shown in structure I represents the monoanion of 3,3'-(trimethylenediimino)bis(butan-2-one oximato), the uncharged ligand tim in structure II is 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene, and the ligand cr in structure III is 2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.11]heptadeca-1(17),2,11,13,15-pentaene.

(14) The dinegative ligands in structures IV–VI are given the respective designations salen [*N,N'*-ethylenebis(salicylideniminato)], Me_2salen [*N,N'*-ethylenebis(7,7'-dimethylbissalicylideniminato)], and saloph [*N,N'*-*o*-phenylenebis(salicylideniminato)].

(15) G. Costa, G. Mestroni, and C. Cocevar, *Chem. Commun.*, 706 (1971).

(16) In the reaction of $(CH_3)_2Co(dpnH)$ with $(H_2O)_2Co(saloph)^+$, acidolysis occurs as a minor parallel reaction. The rate constants depicted for this reaction in Figure 2 have been corrected for this effect: $k_{cor} = k_{obsd} - k_H[H^+]$, the corrections being in the range of 3–15%, average 7.5%.

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(19) See ref 1a, pp 76–77.

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