CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

# Organometallic Compounds with Metal–Metal Bonds. XIV. Reactions of Cyclopentadienyldicarbonylcobalt with Halides and Organometallic Halides of Germanium(IV) and Tin(IV)[1]

BY RUDOLF KUMMER AND W. A. G. GRAHAM

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Tetrahalides of germanium and tin undergo reactions with $\pi$-$C_5H_5(CO)_2Co$ forming compounds of two types, $\pi$-$C_5H_5COX$-$CoMX_3$ and $\pi$-$C_5H_5COCo(MX_3)_2$ (M = Ge, Sn; X = Cl, Br, I). With the tetraiodides, only the first type is formed, while germanium tetrachloride forms only the second type. Organotin and germanium trihalides form similar compounds which show *two* terminal carbonyl stretching bands in cyclohexane solution; this is attributed to the presence of more than one conformer of the molecule.

## Introduction

Recent papers of this series have dealt with the oxidative elimination reaction of certain metal carbonyl derivatives in which metal–metal bonds to germanium or tin are formed. Examples are

$$\text{bipy}(CO)_4Mo + CH_3SnCl_3 \longrightarrow \text{bipy}(CO)_3ClMoSnCH_3Cl_2 + CO^{2}$$

$$(OC)_5Fe + SnX_4 \longrightarrow (OC)_4XFeSnX_3 \longrightarrow (OC)_4Fe(SnX_3)_2{}^{1}$$

It was pointed out some years ago that $C_5H_5Co(CO)_2$ bore both a formal resemblance and a strong chemical similarity to $Fe(CO)_5$.[3] This similarity has recently been extended to include reactions of both compounds with the halogens, in which derivatives such as $C_5H_5Co(CO)I_2$ were formed as analogs of the long known tetracarbonyl dihalides of iron.[4,5] It thus seemed possible that halides of germanium(IV) and tin(IV), recently shown to react with $Fe(CO)_5$,[1] might react also with $C_5H_5Co(CO)_2$. This proved to be the case, and we report in the present paper our study of the reaction, which gave rise to many new compounds of relatively high stability.

## Experimental Section

All reactions and crystallizations were carried out under a nitrogen atmosphere, mainly by the use of Schlenk-tube techniques. Some representative preparations are described later in this section. **Infrared spectra** were obtained using a Perkin-Elmer Model 337 grating spectrometer, with scale expansion and calibration with gaseous CO and DBr as previously described.[6] Cyclohexane was used when solubility permitted, or otherwise dichloromethane. **Proton nmr spectra** were recorded using Varian A-60 or HA-100 instruments in the solvent indicated. **Mass spectra** were taken with an Associated Electrical Industries MS-9 spectrometer, using direct introduction of the solid samples. Tin- and germanium-containing fragments were readily identified by the characteristic pattern of stable isotopes. **Conductivities** were measured using a Phillips Type PR-9500 conductivity bridge and a cell with cell constant 0.28 $cm^{-1}$. Acetone was used as the solvent, allowance being made for conductivity of the solvent in the calculations. **Microanalyses** were performed by Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany, and by the microanalytical laboratory of this department with results as given in Tables I and II. The colors of the compounds are given and reaction conditions also summarized in Tables I and II. No melting points or decomposition temperatures are listed because most of the compounds decompose gradually over a considerable range (10–40°).

**Materials.**—Benzene was dried over sodium–lead alloy and dichloromethane by distillation from $P_2O_5$. Acetone was purified by distillation from sodium carbonate and potassium permanganate. All solvents were saturated with nitrogen. $C_5H_5Co(CO)_2$, $SnCl_4$, $GeCl_4$, $GeBr_4$, and $C_6H_5SnCl_3$ were commercially available and were used without further purification. The following compounds were prepared by the procedure of the reference cited: $GeI_4$,[7] $SnBr_4$,[7] $SnI_4$,[7] $CH_3SnCl_3$,[8] $CH_3SnBr_3$,[9] $CH_3SnI_3$,[9] $C_6H_5GeCl_3$,[10] $C_6H_5GeI_3$,[11] $C_6H_5SnBr_3$,[12] and $C_6H_5SnI_3$.[12]

**Preparation of $C_5H_5COICoSnI_3$.**[13]—To a stirred solution of tin(IV) iodide (6.3 g, 10 mmol) in 30 ml of benzene was added $C_5H_5Co(CO)_2$ (1.6 ml, 2.24 g, 12.4 mmol). The reaction mixture was allowed to stand at room temperature for several hours after the vigorous evolution of carbon monoxide had ceased. Addition of *n*-pentane to the solution followed by cooling afforded shiny black crystals of product (5.5 g, 70% yield). The analytical sample was recrystallized from dichloromethane–petroleum ether, washed with petroleum ether (bp 30–60°), and dried under vacuum. The crystalline compound is stable toward air and light. It is soluble in dichloromethane, tetrahydrofuran, acetone, and benzene, slightly soluble in cyclohexane, and almost insoluble in petroleum ether.

**Preparation of $C_5H_5COICoGeC_6H_5I_2$.**—Reaction between $C_5H_5Co(CO)_2$ (0.5 ml, 0.7 g, 3.9 mmol) and $C_6H_5GeI_3$ (1.6 g, 3.0 mmol) was carried out in boiling benzene for 5 days. The solution was filtered and evaporated to dryness, and the residue was washed with petroleum ether. The residue was then extracted with three 20-ml portions of $CH_2Cl_2$ which were combined and concentrated to 10 ml. Addition of 5 ml of petroleum ether and cooling in a refrigerator afforded a black crystalline product which was washed with pentane and dried under vacuum to give 0.5 g of the product (24% yield).

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(1) Part XIII: R. Kummer and W. A. G. Graham, *Inorg. Chem.*, in press.

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(3) R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3593 (1961).

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(6) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *id.*, **5**, 2217 (1966).

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(13) We write the molecular formulas of these compounds so as to imply which ligands are associated with each metal atom and to emphasize the metal–metal bond.

TABLE I

REACTION CONDITIONS, ANALYTICAL DATA, AND CARBONYL STRETCHING FREQUENCIES FOR COMPOUNDS OF THE TYPE $C_5H_5COXCoMX_3$

| | | | Analyses, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | Calcd | | | | Found | | | |
| Compound[a] | Prepn[b] | $\nu_{CO}$, cm$^{-1}$ [c] | C | H | O | X | C | H | O | X |
| $C_5H_5COClCoSnCl_3$ | 25°[f] | 2086[d] | 17.5 | 1.2 | 3.9 | 34.4 | 17.4 | 1.6 | 3.7 | 34.3 |
| $C_5H_5COBrCoSnBr_3$ | 25°[f] | 2076[d] | 12.2 | 0.8 | 2.7 | 54.1 | 12.6 | 0.7 | 2.6 | 53.8 |
| $C_5H_5COICoSnI_3$ | 25°[f] | 2062[d,e] | 9.3 | 0.7 | 2.1 | 65.2 | 9.2 | 0.9 | 1.9 | 64.9 |
| $C_5H_5COBrCoGeBr_3$ | 25°[f] | 2083[d] | 13.2 | 0.9 | 2.9 | 58.7 | 13.1 | 1.0 | 3.0 | 58.4 |
| $C_5H_5COICoGeI_3$ | 25°[f] | 2066 | 9.8 | 0.7 | 2.2 | 69.3 | 9.6 | 0.6 | ... | 69.7 |
| $C_5H_5COBrCoSnC_6H_5Br_2$ | 40°, 40 hr | 2060 w, 2048 s | 24.5 | 1.7 | 2.7 | 40.8 | 24.4 | 1.6 | 2.6 | 40.7 |
| $C_5H_5COBrCoSnCH_3Br_2$ | 55°, 6 hr | 2061 w, 2045 s | 16.0 | 1.5 | 3.0 | 45.6 | 16.2 | 1.5 | 3.2 | 45.6 |
| $C_5H_5COICoSnCH_3I_2$ | 70°, 3 hr | 2053 w, 2037 s | 12.6 | 1.2 | 2.4 | 57.1 | 12.5 | 1.0 | 2.2 | 57.4 |
| $C_5H_5COICoSnC_6H_5I_2$ | 60°, 3 hr | 2052 w, 2041 s | 19.8 | 1.4 | 2.2 | 52.3 | 19.7 | 1.4 | ... | 56.0 |
| $C_5H_5COICoGeC_6H_5I_2$[g] | Reflux, 5 days | 2059 w, 2049 s | 21.1 | 1.5 | 2.3 | 55.8 | 21.6 | 1.1 | 2.6 | 56.5 |

[a] All compounds are black; decomposition temperatures are poorly defined. [b] All reactions are in benzene solution; temperature and time are listed. [c] Carbonyl stretching frequency in cyclohexane solution except as noted. [d] In dichloromethane solution. [e] At 2058 cm$^{-1}$ in cyclohexane. [f] Reaction complete (CO evolution ceases) in <15 min. [g] Molecular weight: calcd, 683; found, 701 (osmometric in $CH_2Br_2$).

TABLE II

REACTION CONDITIONS, ANALYTICAL DATA, AND CARBONYL STRETCHING FREQUENCIES FOR COMPOUNDS OF THE TYPE $C_5H_5COCo(MX_3)_2$

| | | | | Analyses, % | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | Calcd | | | | Found | | | |
| Compound[a] | Color | Prepn[b] | $\nu_{CO}$, cm$^{-1}$ [c] | C | H | O | X | C | H | O | X |
| $C_5H_5COCo(GeCl_3)_2$[e] | Yellow | B, reflux, 4 hr | 2079 | 14.1 | 1.0 | 3.2 | 41.7 | 14.0 | 1.1 | 3.4 | 41.4 |
| $C_5H_5COCo(GeBr_3)_2$ | Yellow-brown | T, 110°, 3 hr | 2075 | 9.3 | 0.7 | 2.1 | 61.7 | 8.7 | 0.7 | 2.5 | 60.7 |
| $C_5H_5COCo(SnCl_3)_2$ | Yellow | B, reflux, 4 hr | 2069 | 12.0 | 0.8 | 2.7 | 35.3 | 12.3 | 0.8 | 3.4 | 35.7 |
| $C_5H_5COCo(SnBr_3)_2$ | Orange-brown | B, reflux, 6 hr | 2064 | 8.3 | 0.6 | 1.8 | 55.2 | 8.5 | 0.4 | 2.4 | 55.7 |
| $C_5H_5COCo(GeC_6H_5Cl_2)_2$ | Yellow | T, 110°, 2 days | 2043 | 36.5 | 2.6 | 2.7 | 23.9 | 36.7 | 2.6 | ... | 24.1 |
| $C_5H_5COCo(SnCH_3Cl_2)_2$ | Yellow | B, 55°, 5 days | 2033<br>2057 w, 2032 s[d] | 17.1 | 2.0 | 2.9 | 25.3 | 17.4 | 1.8 | 3.2 | 24.8 |
| $C_5H_5COCo(SnCl_3)SnC_6H_5Cl_2$ | Yellow | B, 50°, 7 hr | 2060 | 22.4 | 1.6 | 2.5 | 27.5 | 21.9 | 2.0 | 3.0 | 27.6 |
| $C_5H_5COCo(SnCl_3)SnC_2H_3Cl_2$ | Yellow | B, 50°, 3 hr | 2051 | 16.2 | 1.4 | 2.7 | 29.9 | 16.1 | 1.2 | ... | 29.3 |
| $C_5H_5COCo(SnCH_3Br_2)_2$ | Yellow | T, 110°, 24 hr | 2031<br>2050 w, 2031 s[d] | 13.0 | 1.5 | 2.2 | 43.3 | 13.7 | 1.5 | 2.4 | 43.7 |

[a] Decomposition temperatures are poorly defined. [b] B = benzene; T = toluene. [c] In dichloromethane except as noted. [d] In cyclohexane. [e] Exact mass of molecular ion: calcd for $^{12}C_6{}^{1}H_5{}^{16}O_1{}^{35}Cl_5{}^{37}Cl_1{}^{72}Ge_1{}^{74}Ge_1{}^{59}Co_1$, 509.6202; found, 509.6202.

**Preparation of $C_5H_5COCo(GeCl_3)_2$.**—Dicarbonyl-π-cyclopentadienylcobalt (0.4 ml, 0.56 g, 3.1 mmol) and germanium(IV) chloride (0.8 ml, 1.44 g, 6.7 mmol) were refluxed in 20 ml of benzene for 4 hr. The precipitate of $CoCl_2$ (0.17 g) was filtered off and the solution was concentrated to 5 ml. Slow addition of pentane and cooling caused immediate formation of yellow crystals (0.4 g, 51% yield). An analytical sample was prepared by an additional crystallization from benzene–pentane and sublimation at 130° (0.1 mm). The compound is stable to air and light, moderately soluble in $CH_2Cl_2$, $CHCl_3$, tetrahydrofuran, and benzene, but completely insoluble in cyclohexane and petroleum ether.

**Preparation of $C_5H_5COCo(SnCl_3)(SnC_2H_3Cl_2)$.**—A solution of $C_5H_5Co(CO)_2$ (0.6 ml, 0.84 g, 4.65 mmol) and vinyltin trichloride (2 ml) in 30 ml of benzene was heated at 40–50° for 3 hr. Cobalt(II) chloride was then filtered off and the solution was concentrated to 5 ml. Addition of 5 ml of *n*-pentane afforded yellow crystals of product which were washed with *n*-pentane and dried under vacuum.

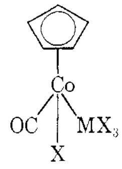
Addition of more *n*-pentane to the mother liquor yielded additional crystals which were shown by infrared analysis to be a mixture of the above product and $C_5H_5COCo(SnCl_3)_2$.

**Preparation of $[C_5H_5bipyCoSnI_3]I$.**—A solution of $C_5H_5COICoSnI_3$ (0.78 g, 1 mmol) in 20 ml of benzene was treated with 2,2′-bipyridyl (0.2 g, 1.3 mmol). There was immediate and vigorous gas evolution, accompanied by formation of a dark purple precipitate. After stirring for 2 hr at room temperature, the product was filtered, washed with benzene, dichloromethane, and ether, and dried under vacuum. The yield was almost quantitative. Recrystallization was not feasible owing to the low solubility of the product in all solvents examined.

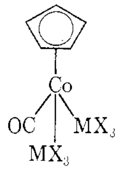
*Anal.* Calcd for $[C_5H_5C_{10}H_8N_2CoSnI_3]I$: C, 19.9; H, 1.5; N, 3.1; I, 56.0. Found: C, 20.6; H, 1.6; N, 3.3; I, 58.0.

## Results and Discussion

Cyclopentadienyldicarbonylcobalt has been found to react with tetrahalides of germanium and tin forming products of two general types: $C_5H_5COXCoMX_3$ and $C_5H_5COCo(MX_3)_2$, where M = Ge or Sn and X = halogen. These possess one or two metal–metal bonds, respectively, and are listed in Tables I and II. The conductivity data of Table III establish that these are neutral, molecular species to which structures I and II may be assigned. The reaction leading to compounds of type I can be written



I



II

$$C_5H_5(CO)_2Co + MX_4 \longrightarrow C_5H_5COXCoMX_3 + CO$$

TABLE III

CONDUCTIVITIES[a]

| Compound | Concn, m*M* | Conductance, ohm$^{-1}$ cm$^2$ mole$^{-1}$ |
|---|---|---|
| $C_5H_5COICoSnI_3$ | 0.61 | 2.7 |
| $C_5H_5COClCoSnCl_3$ | 1.17 | 6.6 |
| $C_5H_5COICoSnC_6H_5I_2$ | 0.71 | 1.3 |
| $C_5H_5COCo(GeBr_3)_2$ | 0.75 | 7.6 |
| $C_5H_5COCo(SnCH_3Cl_2)_2$ | 0.68 | 3.2 |
| $[C_5H_5bipyCoSnI_3]I$ | 0.47 | 135 |

[a] In acetone at room temperature (25°). These compounds show little change of conductivity after observation times of 5–10 min except for $C_5H_5COICoSnI_3$, for which a steady increase was observed.

Under more vigorous conditions with excess $MX_4$, the over-all reaction is

$$2C_5H_5(CO)_2Co + 2MX_4 \longrightarrow C_5H_5COCo(MX_3)_2 + 3CO + CoX_2 + \{C_5H_5\}$$

The reaction in this case would presumably involve the initial formation of compounds of type I. High yields of recovered cobalt(II) halides in these reactions make it unnecessary to postulate phosgene formation to balance the equation, and the course of the reaction is quite similar to that established for the reactions of iron pentacarbonyl.[1] The reactions also proceed with a number of organogermanium and organotin halides, giving rise to products of special interest from a spectroscopic standpoint.

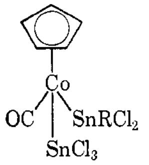
Compounds of type I, $C_5H_5COXCoMX_3$ or $C_5H_5COXCoMRX_2$ (where R is an organic group), form black, air-stable crystals soluble in chloroform, dichloromethane, tetrahydrofuran, acetone, and benzene, but insoluble in petroleum ether. Iodo derivatives are more soluble than the chloro compounds, and are in some cases sufficiently soluble in cyclohexane to obtain useful infrared spectra. The tetrahalogeno compounds show the expected single carbonyl stretching band in the infrared spectrum, but the spectrum of the organo derivatives is more complex and will be discussed later.

Useful structural information comes from the nmr spectrum of $C_5H_5COBrCoSnCH_3Br_2$ in $CDCl_3$. A sharp resonance at $\tau$ 4.53 indicates the diamagnetism of the compound and is assigned to the $\pi$-cyclopentadienyl ring protons. A second sharp peak at $\tau$ 8.30 with characteristic methyl–tin spin-coupling satellites shows that the methyl group has remained on the tin atom $J(^{117,119}Sn–CH_3)$ = 56 cps, with the peaks of the two isotopes not resolved. The ratio of intensities of the absorptions due to the two kinds of protons is 5:3.

Compounds of type II, $C_5H_5COCo(MX_3)_2$ or $C_5H_5COCo(MRX_2)_2$, having two metal–metal bonds, form yellow to orange-brown crystals which appear to be completely stable to light and air. They are of lower solubility than compounds of type I, but have a similar low conductivity and normally show a single terminal carbonyl band (see below, however). The nmr spectrum of $C_5H_5COCo(SnCH_3Br_2)_2$ in $CDCl_3$ exhibits strong bands at $\tau$ 4.58 ($C_5H_5$) and $\tau$ 8.26 ($CH_3$) in the expected 5:6 ratio; satellites of the methyl resonance corresponding to $J(^{117,119}Sn–CH_3)$ = 50 cps (unresolved) are observed.

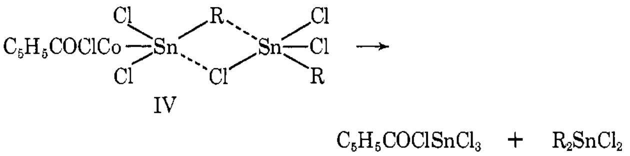
Many reactions of $C_5H_5Co(CO)_2$ have been explored to define the scope of the reaction. It is of interest that no carbonyl complex could be obtained from reactions with $SiCl_4$ or $SiBr_4$, although decomposition to $CoX_2$ was observed. Earlier attempts to extend the oxidative elimination reaction to silicon in the case of bipyMo(CO)$_4$ were likewise not successful,[2] and the surprisingly sharp distinction between silicon on the one hand and germanium and tin on the other in these reactions is again illustrated.[14] Germanium(IV) chloride does not react at all at lower temperatures, while at higher temperatures the only product was $C_5H_5COCo(GeCl_3)_2$. Some reaction was observed with $(C_6H_5)_2SnI_2$ at higher temperatures but the only product isolated was the known $C_5H_5COCoI_2$.[3,4]

Unusual behavior was found for $C_6H_5SnCl_3$ and $C_2H_3SnCl_3$, which afforded only three-metal compounds of a mixed type III. This partial disproportionation resembles those observed in the dithiahexanetetracarbonylmolybdenum series[15] and with iron pentacarbonyl.[1] The high acceptor strength of tin in these two compounds and the more labile nature of the vinyl and phenyl groups might make them uniquely susceptible to disproportionation by way of an intermediate such as IV. In the subsequent step the three-metal complex III would form, and further disproportionation at this stage may be restricted by steric effects or by some type of intramolecular coordination process as in V.

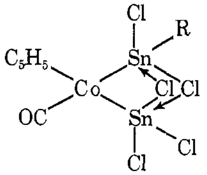


III

III, R = $C_6H_5$, $CH_2$=CH



IV



V

With $GeI_4$, $C_6H_5GeI_3$, $SnI_4$, $CH_3SnI_3$, and $C_6H_5SnI_3$, only two-metal complexes were formed, even under the most vigorous reaction conditions.

The reaction of $C_5H_5COICoSnI_3$ with 2,2′-bipyridyl proceeds with vigorous evolution of carbon monoxide to form a purple-blue compound. Elemental analysis

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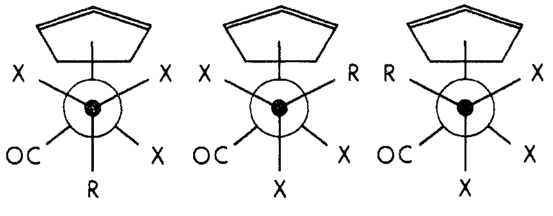
[14] In unpublished research, W. Jetz has prepared the compound $C_5H_5COCo(SiCl_3)_2$ by another method. It is a stable compound, indicating that the failure of $SiCl_4$ to react as expected is the result of kinetic factors in the reaction rather than product instability.

[15] R. Kummer and W. A. G. Graham, *Inorg. Chem.*, in press.

and the high conductivity in acetone (135 ohm$^{-1}$ cm$^2$ mol$^{-1}$) establish that the compound should be formulated as $[C_5H_5bipyCoSnI_3]^+I^-$. A high degree of insolubility in all solvents made it impossible to carry out metathetical reactions (for example with $NH_4^+PF_6^-$) by which the constitution of the cation could have been confirmed. The reaction with bipyridyl is quite analogous to that observed earlier with $C_5H_5COCoI_2$.[3,4]

**Infrared Spectra.**—As pointed out above, compounds of the type $C_5H_5COXCoMX_3$ and $C_5H_5COCo(MX_3)_2$ exhibit the single carbonyl stretching fundamental expected for monocarbonyl molecules. However, the spectra of the organic derivatives $C_5H_5COXCoMRX_2$ and $C_5H_5COCo(MRX_2)_2$, when it is possible to use cyclohexane as solvent, show an unexpected feature in the form of a *second weaker band at higher frequency*. The separation of the two bands ranges from 10 to 20 cm$^{-1}$, and they are not resolved in dichloromethane.

To account for the appearance of two carbonyl stretching bands in a molecule possessing a single carbonyl group, it is necessary to assume that more than one isomer is present. We believe that the isomerism in this case is of conformational origin and that these compounds provide further novel examples of an effect only recently recognized in these laboratories.[16] Thus, for molecules of the $C_5H_5COXCoMRX_2$ type, Newman projections of the three possible staggered conformations are shown in VI, VII, and VIII. Both metal atoms are regarded for this purpose as four-coordinate and tetrahedral, although it is more common in coordination chemistry to regard the π-cyclopentadienyl ligand as occupying three coordination positions. The fact that only two bands are observed could mean that the concentration of one conformer is very low, or that two of the conformers (for example, VI and VIII) have almost identical carbonyl frequencies.



VI VII VIII

## Conclusions

Bonds between cobalt and germanium or tin have been formed in several ways: displacement reactions,[17] the insertion of $SnX_2$ or $GeX_2$ into cobalt carbonyl,[18] and what is presumably a cleavage reaction involving $MX_4$ and cobalt carbonyl.[19] The experiments reported in this paper describe an important new method for the synthesis of cobalt–germanium and cobalt–tin bonds, namely, the oxidative elimination reaction with appropriate halides of germanium(IV) and tin(IV). As later papers in this series will show, these cyclopentadienylcarbonylcobalt derivatives are valuable intermediates in the synthesis of more complex metal–metal-bonded species.

**Acknowledgment.**—We thank the National Research Council of Canada for support of this work.

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[18] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, **5**, 1405 (1966).

[19] D. J. Patmore and W. A. G. Graham, *ibid.*, **6**, 981 (1967).

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF ALBERTA, EDMONTON, ALBERTA, CANADA

# Kinetic Study of the Alkaline Hydrolysis of Sulfato and Sulfamato Complexes of Pentaamminecobalt(III)

BY LUISA L. PO AND ROBERT B. JORDAN

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The rate of hydrolysis of $(NH_3)_5CoSO_4^+$ was found to be first order in hydroxide ion. The rate constant is $4.9 \times 10^{-2}$ $M^{-1}$ sec$^{-1}$ at 25° ($\mu = 1.00$ $M$ NaClO$_4$) and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are 26.3 kcal mole$^{-1}$ and 24.6 cal mole$^{-1}$ deg$^{-1}$, respectively. The rate law for hydrolysis of the sulfamato complex has the form $-d \ln [\text{complex}]/dt = k' + k''[OH^-]$. The rate constant (25°, $\mu = 1.00$ $M$ NaClO$_4$), activation enthalpy, and entropy, respectively, for $k'$ are $8.65 \times 10^{-7}$ sec$^{-1}$, 25.8 kcal mole$^{-1}$, and $-3.5$ cal mole$^{-1}$ deg$^{-1}$ and for $k''$ are $2.5 \times 10^{-7}$ $M^{-1}$ sec$^{-1}$, 41.2 kcal mole$^{-1}$, and 46 cal mole$^{-1}$ deg$^{-1}$. The $k'$ path is attributed to the reaction $(NH_3)_5CoNH_2SO_3^{2+} + OH^-$, and the $k''$ path, to the $(NH_3)_5CoNHSO_3^+ + OH^-$ reaction. The acid dissociation constant ($K_1$) of $(NH_3)_5CoNH_2SO_3^{2+}$ has been measured at low ionic strength and at 0, 13, and 25°, and also in 1 $M$ NaClO$_4$ at 25°. These results are used in the interpretation of the kinetics of the $k'$ path. The value of $K_1$ is also used to estimate the acid dissociation constant of coordinated ammonia.

## Introduction

The alkaline hydrolysis of cobalt(III)–ammine complexes has been widely studied and much of the recent evidence indicates that the S$_N$1CB mechanism best explains the results. This work has been summarized in several recent publications.[1,2]

[1] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, Inc., New York, N. Y., 1965, Chapter 3.

[2] N. S. Sutin, *Ann. Rev. Phys. Chem.*, **17**, 119 (1966).