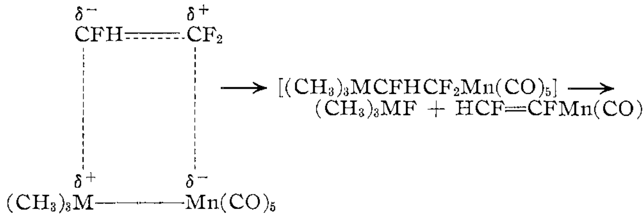
and, in addition, different substituents on the olefin lead to very different products. The fact that there is, as yet, no good evidence for the formation of polyadducts containing, for example, the $M(C_2F_4)_nMn$ unit (M = Ge or Sn) reinforces further our previous suggestion[3] that a free-radical process is unlikely. Moreover, we have very recently found[16] that the course of these reactions of olefins with metal–metal bonded compounds is dependent on the polarity of the solvent medium. An ionic or four-center type of mechanism therefore seems more probable, and for these the direction and degree of polarity of the M–Mn bonds (M = Ge or Sn) are among the most important controlling factors. The polarity $(CH_3)_3M^{\delta+}\text{–}Mn^{\delta-}(CO)_5$ (M = Ge or Sn), together with a fluorine atom migration, is consistent with the reactions of both the germanium and tin derivatives with trifluoroethylene



$$\overset{\delta-}{CFH}\text{---}\overset{\delta+}{CF_2} \;/\; \overset{\delta+}{(CH_3)_3M}\text{---}\overset{\delta-}{Mn(CO)_5} \longrightarrow [(CH_3)_3MCFHCF_2Mn(CO)_5] \longrightarrow (CH_3)_3MF + HCF{=}CFMn(CO)_5$$

However, if this polarity is the determining factor, then these reactions involve essentially the attack of the $Mn(CO)_5^-$ anion on the olefin. Such reactions have been studied recently,[17] and one would then anticipate that the Ge–Mn and Sn–Mn compounds would behave similarly. Clearly, however, these two compounds behave very differently with, for example, chlorotrifluoroethylene, so that the above type of argument is not sufficient in itself. It is conceivable that bonds such as Ge–Mn and Sn–Mn have a very low degree of intrinsic polarity or that some degree of polarity is induced by the specific reagent or reaction conditions. The direction of polarity may even be reversed under appropriate circumstances, and this may be elucidated by further studies. Certainly the infrared spectra of $(CH_3)_3GeMn(CO)_5$ and $(CH_3)_3SnMn(CO)_5$ indicate a different polarity for the Ge–Mn and Sn–Mn bonds. On the other hand, the over-all energy changes of these reactions must be important, and consideration must also be given to the relative bond energies of Ge–C, Sn–C, Ge–X, and Sn–X (X = halogen) bonds.

Acknowledgments.—We are grateful for the financial support of the National Research Council of Canada, in the form of research grants (to H. C. C.), and of a National Research Council postdoctoral fellowship (to J. D. C.). J. H. T. acknowledges gratefully the award of a University of British Columbia graduate fellowship, and we express our thanks to Ethyl Corp., Detroit, Mich., for gifts of chemicals.

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[16] A. D. Beveridge and H. C. Clark, unpublished results.

[17] P. W. Jolly, M. I. Bruce, and F. G. A. Stone, *J. Chem. Soc.*, 5830 (1965).

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

Organometallic Compounds with Metal–Metal Bonds. III. Tetracarbonylcobalt Derivatives of Gallium, Indium, and Thallium[1]

BY D. J. PATMORE AND W. A. G. GRAHAM

Received May 20, 1966

Twelve compounds having Ga–Co, In–Co, or Tl–Co bonds have been prepared by halide displacement with $Co(CO)_4^-$ or by unusual "insertion" reactions. In the latter, $Co_2(CO)_8$ reacts in tetrahydrofuran (THF) with InBr or GaX_2 (X = Cl, Br) affording $BrIn[Co(CO)_4]_2\cdot THF$ or $X_2GaCo(CO)_4\cdot THF$. Also described are the types $XGa[Co(CO)_4]_2\cdot THF$ and $In[Co(CO)_4]_3$, and acetylacetonate (acac) derivatives such as $(acac)Ga[Co(CO)_4]_2$. The number of strong infrared carbonyl stretching frequencies compares well with expectations based on symmetry.

Introduction

Many compounds are now known in which a transition metal is covalently bonded to silicon, germanium, tin, or lead.[2] Cases in which a transition metal is bonded to an element of main group III are, by contrast, few in number.[3] In an early paper on mixed-metal carbonyls, Hieber and Teller[6] obtained the compounds $In[Co(CO)_4]_3$, $Tl[Co(CO)_4]_3$, and $TlCo(CO)_4$ by direct reaction of the finely divided metals under vigorous conditions (200°, 200 atm). There was some evidence for the occasional formation in trace amounts of a

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[1] Presented in part at the Symposium on the Metal–Metal Bond in Inorganic Chemistry, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966. Abstracts, paper H70.

[2] For leading references, see previous papers of this series: (a) H. R. H. Patil and W. A. G. Graham, *Inorg. Chem.*, **5**, 1401 (1966) (part I); (b) D. J. Patmore and W. A. G. Graham, *ibid.*, **5**, 1405 (1966) (part II).

[3] With the exception of boron, metal–metal bonding of any kind involving main group III elements is rare. A gallium–gallium bond exists in GaS,[4] while an aluminum–aluminum covalent bond is believed to occur in $Al_4B[N(CH_3)_2]_3(CH_3)_6$.[5]

[4] H. Hahn and G. Frank, *Z. Anorg. Allgem. Chem.*, **278**, 340 (1955).

[5] E. P. Schram, Abstracts, 151st National Meeting of the American Chemical Society, Pittsburgh, Pa., March 1966, paper H9.

[6] W. Hieber and U. Teller, *Z. Anorg. Allgem. Chem.*, **249**, 43 (1942).

TABLE I

ANALYTICAL DATA AND PHYSICAL PROPERTIES

Compd[a]	Mp,[b] °C	Color	% calcd						% found					
			C	H	O	X[c]	M[d]	Co	C	H	O	X[c]	M[d]	Co
$Cl_2GaCo(CO)_4\cdot THF$	56–60	White	25.1	2.1	20.9	18.5	...	...	24.7	2.1	20.1	19.0	...	...
$Br_2GaCo(CO)_4\cdot THF$	82–87	Pale yellow	20.3	1.7	16.9	33.8	14.7	12.4	19.3	1.8	15.1	34.3	14.2	15.7
$Br(acac)GaCo(CO)_4$	65–68	Pale yellow	25.8	1.7	22.9	19.1	...	...	25.6	2.0	21.2	19.8	...	...
$ClGa[Co(CO)_4]_2\cdot THF$	66–70	Lemon-yellow	27.8	1.6	27.8	6.9	13.5	22.7	26.0	1.7	25.8	7.5	14.3	23.8
$BrGa[Co(CO)_4]_2\cdot THF$	82–85 dec	Lemon-yellow	25.6	1.4	25.6	14.2	...	...	24.2	1.1	24.3	14.9	...	...
$(acac)Ga[Co(CO)_4]_2$	51–53°	Yellow	30.6	1.4	31.3	0.0	...	...	29.1	1.2	30.9	0.0	...	...
$BrIn[Co(CO)_4]_2\cdot THF$	72–75	Bright yellow	23.7	1.3	...	13.1	...	...	23.4	1.1	...	13.9	...	...
$(acac)In[Co(CO)_4]_2$	28–32	Bright yellow	28.0	1.4	28.0	...	...	...	28.1	1.6	29.1	...	...	...
$[BrIn[Co(CO)_4]_2]_x$	140–150 dec	Orange	17.9	0.0	23.8	14.8	21.4	21.9	17.7	0.1	23.8	15.1	23.9	18.9
$Br_3In_3Co_4(CO)_{16}$	148–152 dec	Orange	15.3	0.0	20.2	18.9	27.2	18.6	15.4	0.3	19.9	19.2	27.0	18.6
$In[Co(CO)_4]_3$	92–94	Red	23.0	0.0	30.6	0.0	...	...	22.1	1.3	27.7	0.0	...	...
$Tl[Co(CO)_4]_3$	61–65 dec	Dark red	20.1	0.0	26.8	...	...	24.7	20.4	0.2	25.2	...	...	24.2

[a] acac represents the acetylacetonate group $C_5H_7O_2$. [b] In sealed, evacuated capillary, uncorrected. [c] X = Cl or Br. [d] M = Ga, In, or Tl.

TABLE II

INFRARED SPECTRA[a]

Compd[b]	Point group	No. of ν(CO) predicted	ν(CO), cm^{-1}, obsd
$Cl_2GaCo(CO)_4\cdot THF$	C_s	4	2095 ms, 2058 w, 2035 ms, 2021 w, sh, 2012 s, 2000 s
$Br_2GaCo(CO)_4\cdot THF$	C_s	4	2096 ms, 2060 w, 2036 ms, 2019 w, sh, 2012 s, 2001 s
$Br(acac)GaCo(CO)_4$	C_s	4	2096 m, 2052 w, 2035 ms, 2031 w, sh, 2013 s, 2001 ms
$ClGa[Co(CO)_4]_2\cdot THF$	C_s	8	2095 m, 2077 s, 2039 wm, 2031 m, 2022 m, 2010 s, 2000 s, 1990 m, sh
$BrGa[Co(CO)_4]_2\cdot THF$[c]	C_s	8	2094 m, 2077 s, 2040 wm, 2032 ms, 2024 ms, 2012 s, 2004 s, 1992 m, sh, 1980 m
$(acac)Ga[Co(CO)_4]_2$	C_{2v}	7	2094 m, 2076 s, 2027 m, sh, 2020 s, 2010 s, 2000 s, 1988 ms
$BrIn[Co(CO)_4]_2\cdot THF$	C_s	8	2092 m, 2076 s, 2030 m, 2022 m, 2009 s, 2003 s, 1991 m, sh, 1982 m, sh
$(acac)In[Co(CO)_4]_2$	C_{2v}	7	2094 w, 2076 s, 2027 w, 2020 m, 2003 s,[d] 1991 m, sh, 1959 vw
$[BrIn[Co(CO)_4]_2]_x$			2092 m, 2076 s, 2070 m, sh, 2040 m, 2029 ms, 2020 ms, 2008 s, sh, 2003 s
$Br_3In_3Co_4(CO)_{16}$			2097 w, sh, 2089 s, 2055 m, 2035 m, 2025 ms, 2012 ms, 2000 wm, sh
$In[Co(CO)_4]_3$[c]	C_{3v}(?)	7	2092 w, 2076 m, 2069 s, 2042 w, 2025 w, sh, 2002 s, 1978 w, sh
$Tl[Co(CO)_4]_3$[c]	C_{3v}(?)	7	2069 s, 2057 w, sh, 2044 w, sh, 2040 wm, 2030 w, sh, 2022 wm, 2007 s, 1990 w, sh

[a] In cyclohexane solution. [b] acac represents the acetylacetonate group $C_5H_7O_2$. [c] Compound decomposing in cell, spectrum not of pure compound. [d] Band is asymmetric, probably doublet.

gallium–cobalt carbonyl, but this could not be isolated. In their solubility and volatility, these compounds resembled the polynuclear metal carbonyls, and structures were proposed having carbonyl bridges between the two metal atoms.[6] Such speculation was reasonable, bearing in mind that infrared spectroscopy had not yet emerged as a means of distinguishing bridging and terminal carbonyl groups; nor had the concept of an unsupported covalent metal–metal bond gained credence. More recently, Nöth has prepared a number of compounds in which boron is bonded to manganese,[7] iron,[7] cobalt,[8] and platinum.[8]

Our previous investigation[2b] of the "insertion" of tin(II) halides and germanium(II) iodide into metal–metal bonds led us to attempt a similar reaction with indium(I) bromide. The latter reagent reacted with cobalt carbonyl, forming indium–cobalt bonds.[9] We report here the details of this reaction and of a more general study of cobalt carbonyl derivatives of gallium, indium, and thallium.

Experimental Section

All reactions were carried out under a nitrogen atmosphere, and solid products were handled with minimum exposure to air. Tetrahydrofuran (THF) was purified by distillation from lithium aluminum hydride. Sodium tetracarbonylcobaltate(–I) solutions were prepared by stirring a THF solution of dicobalt octacarbonyl over excess 1% sodium amalgam. Indium(I) bromide was prepared by heating indium(III) bromide with metallic indium[10] and purified by vacuum distillation. Gallium dihalides were prepared by heating equimolar amounts of metallic gallium and the mercuric halide.[11]

Microanalyses (Table I) were performed by Alfred Bernhardt Mikroanalytisches Laboratorium, Mülheim, Germany, or by Pascher Mikronalytisches Laboratorium, Bonn, Germany.

Infrared spectra (Table II) were measured with a Perkin-Elmer 337 grating spectrometer. Spectra were recorded on a Texas Instruments Servo-Riter recorder so that 100 cm^{-1} corresponded to about 13 cm of chart paper. Bands of gaseous CO and DBr were superimposed on each spectrum for calibration purposes, and carbonyl stretching frequencies were determined by interpolation. The deviation of duplicate spectra did not exceed 1 cm^{-1}, and this is believed to represent the accuracy of the measurements relative to the calibration gases.[12] Typical spectra are shown in Figures 1–4 to indicate band shapes and relative intensities.

Dihalo(tetracarbonylcobalt)gallium(III) Tetrahydrofuranate, $X_2GaCo(CO)_4\cdot THF$. Method i.—Gallium dichloride, $Ga[GaCl_4]$ (7.2 g, 25.6 mmoles), was added to THF (50 ml) cooled to –80°, and the mixture was allowed to warm to room temperature with vigorous stirring. A solution of $Co_2(CO)_8$ (8.5 g, 25.0 mmoles) in 50 ml of THF was then added and the mixture was stirred at

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(7) H. Nöth and G. Schmid, *Angew. Chem. Intern. Ed. Engl.*, **2**, 623 (1963); *J. Organometal. Chem.*, **5**, 109 (1966).

(8) G. Schmid and H. Nöth, *Z. Naturforsch.*, **20b**, 1008 (1965).

(9) D. J. Patmore and W. A. G. Graham, *Chem. Commun.*, 591 (1965).

(10) G. Brauer, "Handbook of Preparative Inorganic Chemistry," Vol. 1, 2nd ed, Academic Press Inc., New York, N. Y., 1963, p 861.

(11) R. C. Carlston, E. Griswold, and J. Kleinberg, *J. Am. Chem. Soc.*, **80**, 1532 (1958).

(12) International Union of Pure and Applied Chemistry, "Tables of Wavenumbers for the Calibration of Infrared Spectrometers," Butterworth & Co. Ltd., London, 1961.

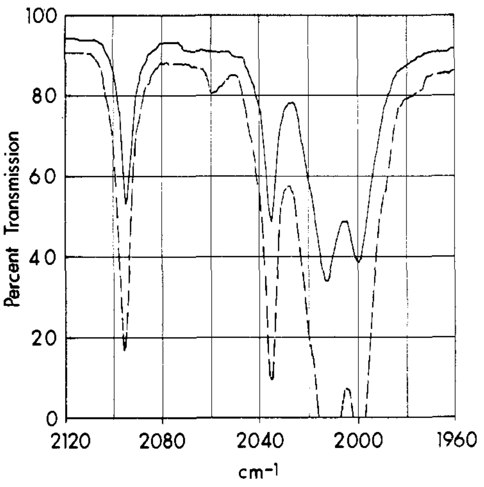


Figure 1.—Infrared spectrum (carbonyl stretching region) of $Br_2GaCo(CO)_4 \cdot THF$: upper solid curve, *ca.* 1 mg/ml of cyclohexane; lower dashed curve, *ca.* 10 mg/ml of cyclohexane.

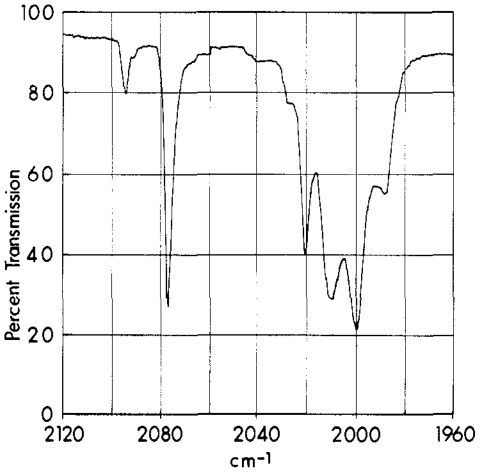


Figure 2.—Infrared spectrum of $(acac)Ga[Co(CO)_4]_2$; *ca.* 1 mg/ml of cyclohexane.

room temperature for 30 min. After removal of THF at reduced pressure, the residue was extracted with 25 ml of *n*-pentane to remove excess $Co_2(CO)_8$, and then with 600 ml of *n*-pentane. The latter extract on concentration to about 50 ml and cooling to −80° afforded white needles (6.6 g, 50%) which were recrystallized from *n*-pentane. **Dibromo(tetracarbonylcobalt)gallium(III) tetrahydrofuranate** and **diiodo(tetracarbonylcobalt)gallium(III) tetrahydrofuranate** were prepared in identical fashion from $Ga[GaBr_4]$ and $Ga[GaI_4]$, respectively. The iodo derivative could not be obtained in a sufficiently pure state for analysis owing to its instability.

Method ii.—Dibromo(tetracarbonylcobalt)gallium(III) tetrahydrofuranate, $Br_2GaCo(CO)_4 \cdot THF$, was prepared by treating a THF solution of $GaBr_3$ (3.09 g, 10 mmoles) with $NaCo(CO)_4$ (10 mmoles) in THF at room temperature. After stirring for 5 min, solvent was removed at reduced pressure and the residue was extracted with *n*-pentane. Evaporation of this extract gave the product (4.1 g, 87%) which afforded pale yellow crystals on crystallization from *n*-pentane at −80°. The dichloro derivative was also prepared by this method.

Bromo(tetracarbonylcobalt)gallium(III) Acetylacetonate, Br(acac)GaCo(CO)$_4$.—A solution of 1.0 g (3.3 mmoles) of thallium(I) acetylacetonate in THF was added to a well-stirred solution of 1.6 g (3.4 mmoles) of $Br_2GaCo(CO)_4 \cdot THF$ in THF at room temperature. The cream-colored precipitate of TlBr was filtered off, and THF was removed *in vacuo* from the filtrate. The residue was extracted with *n*-pentane, and the solution was evaporated to a small volume. Cooling in Dry Ice deposited star-shaped crystals, which on recrystallization from *n*-pentane at −80° gave the product as pale yellow plates in 25% yield.

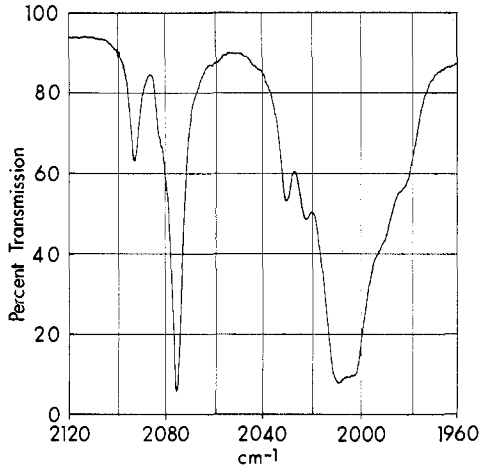


Figure 3.—Infrared spectrum of $BrIn[Co(CO)_4]_2 \cdot THF$; *ca.* 1 mg/ml of cyclohexane.

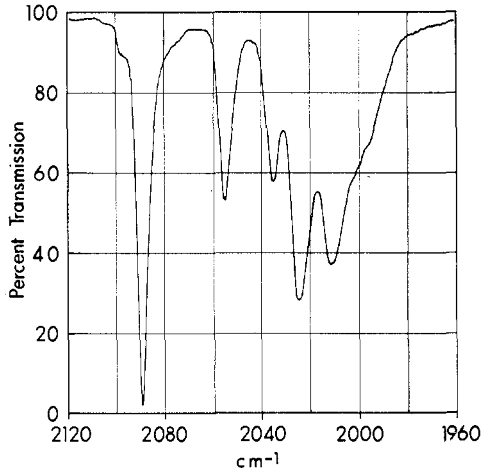


Figure 4.—Infrared spectrum of $Br_3In_3Co_4(CO)_{16}$; *ca.* 2 mg/ml of cyclohexane.

Chlorobis(tetracarbonylcobalt)gallium(III) Tetrahydrofuranate, ClGa[Co(CO)$_4$]$_2$·THF.—Gallium(III) chloride (1.73 g, 9.8 mmoles) in THF was added to a stirred THF solution of $NaCo(CO)_4$ (20 mmoles) prepared from 3.4 g of $Co_2(CO)_8$ (10 mmoles). After 15 min, THF was removed under reduced pressure and the residue was extracted with *n*-pentane (60 ml). Cooling to −80° afforded the product as lemon-yellow crystals which were recrystallized from *n*-pentane in 25% yield.

Bromobis(tetracarbonylcobalt)gallium(III) Tetrahydrofuranate, BrGa[Co(CO)$_4$]$_2$·THF.—A THF solution of 11 mmoles of $NaCo(CO)_4$ was added to 4.6 g of $Br_2GaCo(CO)_4 \cdot THF$ (9.7 mmoles) in THF at 0° with stirring. After 10 min THF was removed *in vacuo* and the residue was extracted with 100 ml of *n*-pentane which was then cooled to −80°. The crystals thus formed were recrystallized from *n*-pentane affording the product as lemon-yellow needles in 60% yield.

Bis(tetracarbonylcobalt)gallium(III) Acetylacetonate, (acac)Ga[Co(CO)$_4$]$_2$.—Thallium(I) acetylacetonate (1.28 g, 4.2 mmoles) in THF was added dropwise to a well-stirred solution of $Br_2GaCo(CO)_4 \cdot THF$ in THF at 0°. After filtering off the precipitated TlBr, the solution was evaporated *in vacuo*, and the residue was extracted with *n*-pentane. The pentane solution was evaporated to small volume and filtered to remove a small quantity of colorless crystalline material shown by infrared to contain the acetylacetone moiety, but no metal carbonyl groups. The filtered solution was evaporated completely to produce an oil which set to a mass of crystals. Recrystallization from *n*-pentane at −80° afforded pure product in 10% yield.

This compound was also prepared from $BrGa[Co(CO)_4]_2 \cdot THF$ and thallium(I) acetylacetonate using a similar procedure.

Reaction of $GaBr_3$ with Excess $NaCo(CO)_4$.—A THF solution of $GaBr_3$ (1.5 g, 4.85 mmoles) was added with stirring to a solution of 19.2 mmoles of $NaCo(CO)_4$ in tetrahydrofuran. After removal of solvent at reduced pressure, the residue was extracted with *n*-pentane and cooled to −80°. Recrystallization of the solid thus obtained gave lemon-yellow crystals of $BrGa[Co(CO)_4]_2 \cdot THF$, characterized by its infrared spectrum and melting point (yield 40%). Formation of $Ga[Co(CO)_4]_3$ was not observed.

Bromobis(tetracarbonylcobalt)indium(III) Tetrahydrofuranate, $BrIn[Co(CO)_4]_2 \cdot THF$.—(i) Finely powdered InBr (9.7 g, 50 mmoles) was stirred with a solution of 17.0 g of $Co_2(CO)_8$ (49.7 mmoles) in THF at room temperature. After 15 min all of the InBr had dissolved to form an orange solution. THF was removed *in vacuo* and the residue was extracted with *n*-pentane, which on cooling to −80° deposited orange-yellow crystals. Recrystallization from *n*-pentane at −80° afforded a product of yellow needles in 73% yield. Repeated recrystallization from pentane results in gradual loss of THF, which was shown by analytical results. Calcd mol wt: 608.7. Found: 607 (Mechrolab osmometer, benzene).

(ii) This compound was also prepared by reaction of $InBr_3$ and $NaCo(CO)_4$ (1:2 mole ratio) in THF at room temperature for 5 min. The solution was worked up as in (i) affording $BrIn[Co(CO)_4]_2 \cdot THF$ characterized by its infrared spectrum and melting point (yield 50%).

Bromobis(tetracarbonylcobalt)indium(III), $\{BrIn[Co(CO)_4]_2\}_x$.—$BrIn[Co(CO)_4]_2 \cdot THF$ (0.6075 g) was subjected to a pressure of 20 μ for 24 hr, after which a 12.2% loss in weight was observed (THF calcd for $BrIn[Co(CO)_4]_2 \cdot THF$, 11.8%). The yellow-orange powder thus produced was dissolved in benzene (200 ml), and the solution was filtered and concentrated at reduced pressure affording light orange crystals. Calcd mol wt for monomer: 536.6. Found: 508 (osmometer, acetone).

Tris(tetracarbonylcobalt)indium(III), $In[Co(CO)_4]_3$.—Indium tribromide (1.7 g, 4.8 mmoles) in THF was added to a stirred solution of 17.0 mmoles of $NaCo(CO)_4$ in the same solvent. Removal of THF under reduced pressure after 10 min, followed by extraction of the red residue with *n*-pentane, gave a red solution. Evaporation to dryness under reduced pressure, followed by several recrystallizations from *n*-pentane at −80°, afforded red crystals of product in 30% yield.

Tribromotriindiumtetracobalt Hexadecakiscarbonyl, $Br_3In_3Co_4(CO)_{16}$.—A benzene solution of 6.84 g of $Co_2(CO)_8$ (20 mmoles) was stirred for 12 hr at room temperature with 5.84 g of finely powdered InBr (30 mmoles). After filtering, the resultant orange solution was evaporated to small volume affording a 79% yield of orange crystalline product. It was purified by recrystallization from benzene, in which the solubility is of the order of 1%.

Tris(tetracarbonylcobalt)thallium(III), $Tl[Co(CO)_4]_3$.—(i) A solution of $TlCl_3$ (1.0 g, 3.2 mmoles) in THF was added to a well-stirred solution of 10 mmoles of $NaCo(CO)_4$ in the same solvent. Removal of THF under reduced pressure, followed by extraction with *n*-pentane, gave a deep red solution which deposited very deep red (almost black) crystals of product at −80° (yield 40%).

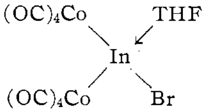
(ii) Thallium(I) acetylacetonate (1.0 g, 3.3 mmoles) in THF was added to 1.0 g of dicobalt octacarbonyl (2.8 mmoles) in the same solvent with stirring. The reaction mixture was initially at −80°. On warming to 0° the solution turned deep purple with evolution of CO. Removal of THF and extraction of the residue with *n*-pentane gave a deep red solution which deposited deep red crystals at −80°. Recrystallization from *n*-pentane gave product in 10% yield.

Discussion

The insertion reaction of tin(II) halides and germanium(II) iodide with cobalt carbonyl and related species provides a valuable route to a number of compounds having Co–Sn–Co and Co–Ge–Co linkages.[2b] It appeared that other reagents would undergo a similar reaction, provided that they were capable (a) of increasing their covalency and oxidation state by two units and (b) of forming stable covalent bonds with transition metals. A review of metal halides in terms of these criteria suggested that indium(I) halides should be suitable. The expectation was confirmed, and a suspension of indium(I) bromide in tetrahydrofuran reacted readily with cobalt carbonyl, dissolving to form an orange solution in accord with the equation

$$InBr + Co_2(CO)_8 \xrightarrow{THF} BrIn[Co(CO)_4]_2 \cdot THF$$

The product (I) forms yellow needles which are stable in air for short periods and readily lose tetrahydrofuran *in vacuo* or on repeated recrystallization from pentane to yield a much less soluble compound, presumably with a dimeric structure (II).



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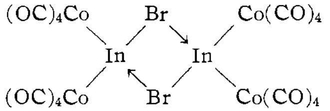

II

In benzene solution, InBr and $Co_2(CO)_8$ reacted much more slowly, forming an orange, crystalline compound assigned the empirical formula $Br_3In_3Co_4(CO)_{16}$ on the basis of complete elemental analysis. The infrared spectrum is shown in Figure 4. Further investigation of this compound is in progress, and speculation as to its structure will be deferred until more evidence has been accumulated.

Indium–cobalt bonds are also formed in the reaction of $InBr_3$ with $NaCo(CO)_4$, the product depending on the mole ratio of the reactants in accord with the equations

$$InBr_3 + 2NaCo(CO)_4 \xrightarrow{THF} BrIn[Co(CO)_4]_2 \cdot THF$$

$$InBr_3 + 3NaCo(CO)_4 \xrightarrow{THF} In[Co(CO)_4]_3$$

As indicated by the ease with which it loses tetrahydrofuran, the Lewis acidity of the monobromoindium derivative is rather low. When the bromine is replaced by a third electropositive $Co(CO)_4$ group, no isolable adduct is formed with tetrahydrofuran.

It seemed possible that gallium(I) would undergo a similar insertion reaction, providing that a suitable reactive compound embodying this unfamiliar oxidation state[13] could be found. Of the few compounds known to contain gallium(I), the gallium dihalides seemed most suitable. Their reaction with $Co_2(CO)_8$ yielded products of the type $X_2GaCo(CO)_4 \cdot THF$. The mechanism of this reaction is uncertain, and, indeed, the species present in tetrahydrofuran solutions of gallium(II) halides are a matter of conjecture. Although there is no question as to the formulation $Ga^+[GaCl_4]^-$ in the solid state, the isolation[14] of com-

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(13) N. N. Greenwood, *Advan. Inorg. Chem. Radiochem.*, **5**, 91 (1963).

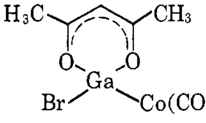
(14) F. M. Brewer, J. R. Chadwick, and G. Garton, *J. Inorg. Nucl. Chem.*, **23**, 45 (1961).

plexes such as [Ga(dioxane)$_2$]Cl from gallium dichloride in benzene suggests that species such as ClGa(THF)$_3$ and Cl$_3$Ga(THF) may be present. Then one could visualize a reaction sequence such as

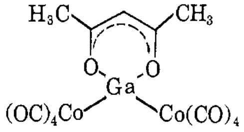
$$\mathrm{ClGa(THF)_3 + Co_2(CO)_8 \longrightarrow ClGa[Co(CO)_4]_2 \cdot THF}$$

$$\mathrm{ClGa[Co(CO)_4]_2 \cdot THF + Cl_3Ga \cdot THF \longrightarrow 2Cl_2GaCo(CO)_4 \cdot THF}$$

The dichlorogallium derivative forms white needles which rapidly deliquesce in air, giving rise to the characteristic odor of cobalt carbonyl hydride. The dibromo derivative Br$_2$GaCo(CO)$_4$·THF does not deliquesce, although both derivatives undergo rapid oxidation in air. Reaction of the latter with thallium(I) acetylacetonate affords compound III.



III



IV

Monohalogenogallium derivatives resulted from the reaction (X = Cl or Br)

$$\mathrm{X_2GaCo(CO)_4 \cdot THF + NaCo(CO)_4 \longrightarrow XGa[Co(CO)_4]_2 \cdot THF + NaX}$$

Again, the chloro derivative was deliquescent; the bromo derivative was less stable thermally. The acetylacetone derivative IV was prepared from BrGa[Co(CO)$_4$]$_2$·THF and TlC$_5$H$_7$O$_2$ or, rather unexpectedly, from Br$_2$GaCo(CO)$_4$·THF and 2 moles of TlC$_5$H$_7$O$_2$. A reaction sequence that would account for these products might involve the initial formation of III, followed by its reaction with a second mole of TlC$_5$H$_7$O$_2$ to release Co(CO)$_4^-$.

$$\mathrm{Br_2GaCo(CO)_4 \cdot THF + TlC_5H_7O_2 \longrightarrow Br(acac)GaCo(CO)_4 + TlBr}$$

$$\mathrm{Br(acac)GaCo(CO)_4 + TlC_5H_7O_2 \longrightarrow [(acac)_2Ga]^+Co(CO)_4^- + TlBr}$$

$$\mathrm{Br(acac)GaCo(CO)_4 + Co(CO)_4^- \longrightarrow (acac)Ga[Co(CO)_4]_2 + Br^-}$$

By reaction of the gallium(III) halides with the stoichiometric quantity of NaCo(CO)$_4$, one or two halide ions can be displaced. Excess NaCo(CO)$_4$ does not displace the third halide group under our experimental conditions, and we did not obtain the tris(tetracarbonylcobalt)gallium compound.

Formally, the Tl(I)–Tl(III) system meets the requirements for insertion into Co$_2$(CO)$_8$. Thallium(I) halides were too insoluble to react, and the moderately soluble thallium(I) acetylacetonate was investigated. However, the product of the reaction was Tl[Co(CO)$_4$]$_3$ rather than the simple insertion product (acac)Tl[Co(CO)$_4$]$_2$. A possible sequence of reactions is

$$\mathrm{Tl^+acac^- + Co_2(CO)_8 \longrightarrow (THF)_{\mathit{x}}Co(acac)_2 + TlCo(CO)_4 + CO}$$

$$\mathrm{TlCo(CO)_4 + Co_2(CO)_8 \longrightarrow Tl[Co(CO)_4]_3}$$

Thallium(III) chloride and excess NaCo(CO)$_4$ gave the same product; in cyclohexane solution, this compound decomposed rather rapidly with formation of Co$_2$(CO)$_8$.

Infrared data are listed in Table II and representative spectra are shown in Figures 1–4. In those cases where the molecular symmetry can be inferred, assuming trigonal-pyramidal Co(CO)$_4$ groups, the observed number of strong carbonyl stretching bands is in accord with group theoretical predictions.

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Some Cobalt(III) Complexes of Glycine

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Two new cobalt(III) complexes containing monodentate glycine, *cis*-chloro(N-glycine)- and *cis*-chloro(N-glycinato)bis(ethylenediamine)cobalt(III) chloride, have been prepared and characterized *via* elemental analyses, conductivity measurements, and visible and infrared spectral data. The latter of these is isomeric with the well-known complex glycinatobis(ethylenediamine)cobalt(III) chloride and readily isomerizes to this complex in aqueous solution. The other new complex is an acid having a strength comparable to that of glycine hydrochloride.

Introduction

The complex glycinatobis(ethylenediamine)cobalt(III) chloride, [Co(en)$_2$(NH$_2$CH$_2$CO$_2$)]Cl$_2$, was prepared by Meisenheimer a number of years ago by the reaction of glycinate ion, NH$_2$CH$_2$CO$_2^-$, with *trans*-[Co(en)$_2$Cl$_2$]Cl in aqueous solution.[2] After characterizing the complex by means of elemental analysis and resolu-

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