

unremarkable. The thermal motion of some of the atoms is relatively large in amplitude (see Table IV and the figures); this undoubtedly lowers the accuracy of some of the bond distances and angles, particularly those toward the periphery of the molecule. The N-C(methyl) distances of 1.496 (6) and 1.509 (5) Å are slightly longer than the N-C distance of 1.474 Å in methylamine.¹⁶ The C-O distances average to 1.142 (10) Å and the mean C-C(phenyl) distance is 1.396 (26) Å. The variation in the distances in the phenyl ring is substantially greater than would be expected on the basis of the tabulated esd's. This problem stems primarily from the short C(7)-C(8) distance and may well be related to the high thermal motion of the phenyl carbon atoms. Three of the four Mn-C-O angles are somewhat nonlinear.

To summarize, a detailed comparison of the three closely related complexes Mn(bza), Mn(dma), and Mn(mca) has revealed many similarities among their structures, including

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parallel trends in Mn-C(carbonyl) distances and nearly identical Mn-C(sp²) distances. Significant differences are also observed; many of these may be attributed to hybridization differences at the N atom or to constraints associated with the chelate rings present in two of the complexes. It would be of interest to determine whether the relatively small variations in Mn-C(carbonyl) distances we see may be correlated with trends in chemical reactivity. One might ask, for example, whether the substitutional lability of the various carbonyl groups in a given complex parallels the observed trends in bond distances. One could also inquire whether the generally shorter Mn-C(carbonyl) bonds in Mn-(bza) are associated with a lesser tendency of this complex to undergo carbonyl exchange or substitution reactions.

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Crystal and Molecular Structure of Tris(tetracarbonylcobalt)indium(III), In[Co(CO)₄]₃

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Tris(tetracarbonylcobalt)indium(III) crystallizes in the monoclinic space group $P2_1/n$ with 4 molecules in a unit cell of dimensions $a = 18.834$ (8), $b = 6.806$ (3), $c = 16.606$ (7) Å, and $\beta = 113.91$ (4)°. Using a data set of 1898 observed reflections collected by counter methods with an automated diffractometer and corrected for absorption, the structure was solved by Patterson and Fourier techniques and refined to a final R of 0.067. The structure consists of discrete molecules of In[Co(CO)₄]₃ with approximate C_{3h-6} symmetry. The average In-Co bond distance of 2.594 (3) Å is not consistent with $d\pi-p\pi$ bonding between the empty valence p orbital of the indium and the filled d orbitals of the cobalt. The coordination geometry about the cobalt resembles the approximate trigonal bipyramid observed in other Co(CO)₄ derivatives except that the indium is displaced from an axial position toward two of the equatorial carbonyl groups. From a comparison with other In(III) structures, it is suggested that this displacement reflects primarily a In-C interaction rather than a steric effect although the latter effect may also be important.

Introduction

Compounds containing heteronuclear metal-metal bonds between the elements of groups IIb and IVa and transition metal carbonyl derivatives have been the subject of extensive synthetic, physical, and structural studies.¹⁻⁶ Similar investigations with elements of group IIIa have been restricted for the most part to synthetic studies. The structures of M[Co(CO)₄]₃,⁷ M[Mn(CO)₅]₃⁸⁻¹⁰ (M = In or Tl), and Tl[(h₅-C₅H₅)Mo(CO)₃]₃¹¹ have been inferred as trigonal planar in

solution from limited spectroscopic characterizations. Since no crystal structure data were available for these systems, we have determined the structure of In[Co(CO)₄]₃ and found that the trigonal planar structure suggested for this compound in solution is retained in the solid state. This molecule constitutes one of the rare examples of three-coordinate indium(III).

Experimental Section

Tris(tetracarbonylcobalt)indium(III) was prepared by the reaction of 5 g of Hg[Co(CO)₄]₂ in 30 ml of toluene under nitrogen with an excess of a 1% indium amalgam. Following 6 hr of stirring, the amalgam was removed and the solution filtered, concentrated to a volume of 10 ml, and cooled to -78°. The red crystals which formed were filtered from the solvent, washed with 10 ml of cold pentane, and dried *in vacuo*. *Anal.* Calcd for In[Co(CO)₄]₃: C, 23.0; H, 0.0; In, 18.3. Found: C, 22.9; H, 0.0; In, 18.2.

Space Group and Unit Cell. A needlelike crystal was mounted in a Lindemann capillary and $h0l-h2l$ Weissenberg levels and $0kl$ and $hk0$ precession levels were collected. These photographs displayed $2/m$ diffraction symmetry. From the systematic absences ($h0l, l = 2n + 1; 0k0, k = 2n + 1$) the space group was identified as $P2_1/c$ (No. 14). In order to work in a more nearly orthogonal unit cell, the space group $P2_1/n$ was used in subsequent steps. The unit cell dimensions were determined from measurements from the different crystals used in data collection using an Enraf-Nonius Inc. CAD-4 automated diffrac-

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tometer with Mo radiation (λ 0.70926 Å) filtered through 2 mils of Zr foil. An incident beam collimator of 0.8 mm at a takeoff angle of 4.0° was used with a receiving aperture located 173 mm from the crystal. The pulse height analyzer was set to admit approximately 95% of the diffracted intensity. Following optical centering of a needlelike crystal mounted along the b axis in a Lindemann tube, a minimum of 10 reflections was located. These reflections were widely separated in reciprocal space and were located at as high a 2θ value ($\sim 40^\circ$) as possible consistent with obtaining reasonable intensity. Accurate values of 2θ , ω , κ , and ϕ were determined by scanning ω , κ , and 2θ and locating the peak at the average positions of the half-heights. A 3 mm wide aperture, a narrow horizontal slit, and a narrow vertical slit, respectively, were used in these scans. Following X-ray centering of the crystal, the reflection-centering process was repeated, and the unit cell dimensions were determined from a least-squares fit of the angular settings. Both the alignment procedures and the least-squares fit used programs supplied by the manufacturer. The $P2_1/n$ unit cell parameters, determined from measurements before and after data collection from each of three crystals, were $a = 18.834$ (8), $b = 6.806$ (3), $c = 16.606$ (7) Å, and $\beta = 113.91$ (4) $^\circ$. The numbers in parentheses are the root mean square of the deviations from the average of the six determinations. The density calculated with $Z = 2$ is 1.07 g ml $^{-1}$ and with $Z = 4$, 2.13 g ml $^{-1}$. Since crystals of $\text{In}[\text{Co}(\text{CO})_4]_3$ float in HCB_3 ($\rho = 2.92$ g ml $^{-1}$) and sink in CCl_4 ($\rho = 1.56$ g ml $^{-1}$), the value of Z was taken as 4. An exact density was not determined since the compound dissolved in or reacted with water and all common organic media. With $Z = 4$ all atoms are in the general positions of the space group.

Data Collection and Reduction. Three crystals were used to obtain a data set due to decomposition of the compound in the X-ray beam. The crystals of dimensions $0.18 \times 0.40 \times 0.20$ mm, $0.12 \times 0.28 \times 0.16$ mm, and $0.20 \times 0.42 \times 0.22$ mm along the a , b , and c directions, respectively, were mounted along the long axis (b) in Lindemann capillaries. Following alignment of each crystal as indicated above, intensity data was collected using the θ - 2θ scanning technique with variable scanning rates over a 2θ range of $1.6 + \tan \theta$ centered about the average peak position. The aperture was set at 4 mm high by 3 mm wide. The reflections in a quadrant of reciprocal space were collected in the region $4^\circ < 2\theta < 60^\circ$. Very few observed reflections were found above $2\theta = 45^\circ$. Each reflection was first scanned rapidly at a rate of $20.1^\circ \text{ min}^{-1}$ with a background count for one-fourth of the scan time at each end of the scan to determine its approximate intensity. If this intensity was not sufficient to accumulate a minimum of 100 counts above background using a 180-sec slow scan (a net intensity to background ratio of about 2:1) the reflection was considered unobserved, the results of the fast scan were recorded, and the next reflection was processed. The observed reflections were scanned twice at a slower rate necessary to accumulate the desired net count. The intensities of those reflections for which the results of the two scans were statistically different were redetermined. The maximum rate for the slower scan was set at $6.7^\circ \text{ min}^{-1}$ with the majority of reflections counted at this rate. The intensities of 90% of these reflections were well above the minimum net count required. The counting electronics of the diffractometer correct for coincidence loss up to 50,000 counts sec $^{-1}$. All reflection maxima were well below this rate so no attenuators were required. Background counts were made for one-fourth of the scan time at both ends of each slow scan. The 022, 905, and 400 reflections from each crystal were monitored alternately every 20 min, and when these reflections were reduced to 90% of their initial intensity, data collection from that particular crystal was terminated.

Integrated intensities, I , were obtained using the expression $I = C - 2B$ where C is the total count collected during the two slower scans and B is the sum of the background counts. A standard deviation was assigned to each measured intensity using the expression $\sigma(I) = [C + 4B]^{1/2}$. The faces of each crystal were measured using a microscope with a micrometer eyepiece, and an absorption correction was applied.¹² For $\mu = 38.1 \text{ cm}^{-1}$, the transmission factors ranged from 0.504 to 0.633 for crystal 1, from 0.585 to 0.668 for crystal 2, and from 0.625 to 0.777 for crystal 3. Following correction for Lorentz-polarization effects¹³ the data were divided into groups within which the intensities of the control reflections did not vary by more than 2%. The various groups were then adjusted to a common scale by the method of Rae¹⁴ using the control reflections and 50 strong common reflections collected from each crystal. Of the 2811

resulting reflections, the 1898 considered observed were used in the solution and refinement of the structure.

Solution and Refinement. The position of the indium atom was located from a Patterson map,¹⁵ and the cobalt, carbon, and oxygen atoms were located on two subsequent Fourier maps. R_1 ($R_1 = \sum |F_o - F_c| / \sum |F_o|$) converged to 0.111 after four cycles of least-squares refinement¹⁶ of the scale factor, atomic positions, and isotropic temperature factors. Three subsequent cycles of weighted refinement of all parameters with anisotropic temperature factors (suggested by the appearance of a difference Fourier map) for all atoms reduced R_1 to 0.067 and R_2 ($R_2 = [\sum w|F_o - F_c|^2]^{1/2} / [\sum w|F_o|^2]^{1/2}$) to 0.061. Because of storage limitations in our computer, each cycle of anisotropic refinement consisted of refinement of three blocks of parameters, each block containing the parameters of the indium and one of the $\text{Co}(\text{CO})_4$ groups. Weights were assigned as $w = 1/\sigma^2$ where σ , the error in F_o , was obtained from the expression $\sigma = \{0.5/F_o\}[\sigma(F_o^2)^2 + (0.03F_o^2)^2]^{1/2}$. The value 0.03 was chosen to minimize the variation in $\sum w|F_o - F_c|$ with respect to $(\sin \theta)/\lambda$ and intensity.¹⁷ The scattering factors for In^0 , Co^0 , C^0 , and O^0 were those of Ibers¹⁸ with real and imaginary anomalous scattering corrections¹⁹ applied for In and Co. No correction for extinction was applied.

Final shifts in parameters were less than 0.1 times their respective standard deviations. The standard deviation of an observation of unit weight was 1.23. Using the last phased set of data, a difference Fourier map showed no peaks larger than about 1 electron Å $^{-1}$, and these peaks were within 0.9 Å of the cobalt atoms. The final atomic positional parameters are listed in Table I and anisotropic thermal parameters are given in Table II. Bond distances and angles may be found in Table III. A table of structure factors may be found in the microfilm edition.²⁰

Description of the Structure

The structure of $\text{In}[\text{Co}(\text{CO})_4]_3$ contains discrete molecules (Figure 1) in which each indium is surrounded by three $\text{Co}(\text{CO})_4$ groups in a trigonal-planar arrangement. The average In-Co bond length is 2.594 (3) Å with Co-In-Co angles averaging 119.8 (6) $^\circ$. The geometry about each cobalt atom resembles the approximate trigonal bipyramid observed in other $\text{Co}(\text{CO})_4$ derivatives³ except that the indium is displaced from an axial position toward two of the equatorial carbonyl groups. The deviations of the atoms in the molecule from a plane through the three cobalt atoms are listed in Table IV. These values illustrate the essential planarity of the InCo_3 unit, the axial CO groups of each $\text{Co}(\text{CO})_4$ unit, and one of the equatorial CO groups of each $\text{Co}(\text{CO})_4$ unit. The remaining two equatorial carbonyls of each $\text{Co}(\text{CO})_4$ are disposed above and below the plane. The point group symmetry of the molecule approximates C_{3h} -6.

Within the $\text{Co}(\text{CO})_4$ groups the Co-C distances average 1.75 (6) Å, and the C-O distances, 1.17 (3) Å. The axial carbon atoms, C(ax), are equidistant from the equatorial carbon atoms, C(eq), with the C(ax)-C(eq) distances averaging 2.63 (4) Å. The In-Co-C(ax) angles and In-C(ax) distances re-

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Table I. Atomic Positional Parameters for $\text{In}[\text{Co}(\text{CO})_4]_3^a$

Atom	x	y	z
In	0.28275 (7)	0.64253 (16)	0.51306 (8)
Co1	0.35947 (13)	0.49613 (34)	0.66878 (14)
Co2	0.13385 (13)	0.69158 (36)	0.45698 (17)
Co3	0.35440 (13)	0.77669 (33)	0.42042 (15)
C1a	0.3979 (9)	0.3467 (27)	0.6059 (12)
O1a	0.4307 (8)	0.2449 (23)	0.5778 (11)
C1b	0.3867 (12)	0.7315 (30)	0.6868 (12)
O1b	0.4126 (12)	0.8955 (26)	0.7077 (11)
C1c	0.2690 (10)	0.4426 (33)	0.6714 (10)
O1c	0.2111 (8)	0.4091 (28)	0.6790 (8)
C1d	0.4168 (9)	0.3911 (29)	0.7691 (15)
O1d	0.4558 (10)	0.3182 (28)	0.8354 (9)
C2a	0.1336 (9)	0.4303 (29)	0.4585 (9)
O2a	0.1340 (8)	0.2574 (24)	0.4542 (10)
C2b	0.1713 (10)	0.8386 (24)	0.5507 (12)
O2b	0.1890 (9)	0.9358 (25)	0.6132 (10)
C2c	0.1272 (10)	0.8019 (30)	0.3608 (13)
O2c	0.1192 (8)	0.8772 (26)	0.2929 (9)
C2d	0.0316 (12)	0.7048 (31)	0.4387 (13)
O2d	-0.0304 (8)	0.7188 (31)	0.4283 (12)
C3a	0.4448 (10)	0.7370 (28)	0.5103 (12)
O3a	0.5034 (7)	0.7105 (26)	0.5712 (9)
C3b	0.3108 (13)	0.9896 (31)	0.4264 (12)
O3b	0.2755 (9)	1.1366 (26)	0.4269 (12)
C3c	0.3044 (13)	0.5940 (33)	0.3585 (16)
O3c	0.2703 (10)	0.4660 (29)	0.3061 (9)
C3d	0.3942 (9)	0.8652 (31)	0.3439 (12)
O3d	0.4172 (8)	0.9088 (31)	0.2932 (9)

^a In fractions of the unit cell edges. Numbers in parentheses are the estimated standard deviations of the last significant figure.

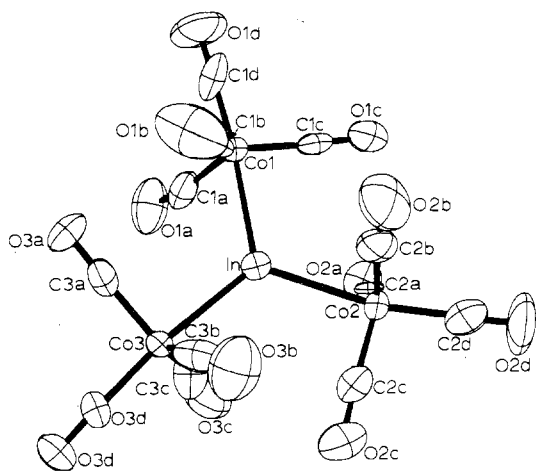


Figure 1. Molecular structure of $\text{In}[\text{Co}(\text{CO})_4]_3$ with the atoms represented by the 50% probability contour of the thermal ellipsoids. Labels correspond to those in Tables I-IV.

flect the displacement of the indium atom from the axis of the trigonal-bipyramidal cobalt coordination shell toward the two carbonyl groups which lie above and below the molecular plane. The In-Co-C(ip) angles average $90.0 (17)^\circ$ where C(ip) represents the in-plane carbon atom. The In-Co-C(op) angles average $80.1 (23)^\circ$. The In-C(ip) and In-C(op) distances average $3.13 (5)$ and $2.86 (7) \text{ \AA}$, respectively. The average In-Co-C(ax) angle is $172.2 (26)^\circ$.

The small but significant differences observed in the various In-Co-C angles and In-C distances (Table III) whose averages are given above probably reflect packing effects since the three $\text{Co}(\text{CO})_4$ groups in a given molecule have intermolecular nonbonded contacts which differ both in number and in distance. For example, two intermolecular contacts of less than 3.4 \AA are observed at 3.17 and 3.27 \AA for O1d; three at 3.26 , 3.28 , and 3.36 \AA for O2d; and three at 2.99 , 3.26 , and 3.36 \AA for O3d. Other nonbonded distances are

listed in Table III. A stereodrawing of the unit cell may be found in Figure 2.

Discussion

The structure of tris(tetracarbonylcobalt)indium(III) is an example of three-coordinate trigonal-planar indium(III), a geometry which is rare for this element. Most indium(III) compounds exhibit coordination numbers of 4 or more as a result of bridging by one or more ligands²¹⁻²⁴ or coordination of additional ligands.^{25,26} The indium of $\text{In}[\text{Co}(\text{CO})_4]_3$, however, is bonded to only three $\text{Co}(\text{CO})_4$ groups with an average In-Co distance of $2.594 (3) \text{ \AA}$ and Co-In-Co angle of $119.8 (6)^\circ$. The shortest intermolecular distance between the indium of one molecule and the atoms of a second molecule is an In-O distance of $3.71 (2) \text{ \AA}$. This distance is much longer than the calculated single-bond distance of 2.40 \AA . The radius of 0.80 \AA for an oxygen of a carbonyl group was derived from the Al-O distance of 2.00 \AA in $[\text{Fe}(h^5\text{-C}_5\text{H}_5)(\text{CO})\text{Al}(\text{C}_2\text{H}_5)_3]_2$ ²⁷ and an aluminum radius of 1.20 \AA derived from $\text{Al}_2(\text{CH}_3)_6$.²³ The axial covalent radius of 1.61 \AA for a trigonal-bipyramidal indium(III) was obtained from the $2.712\text{-}\text{\AA}$ In-P distance in $\text{InCl}_3[\text{P}(\text{C}_6\text{H}_5)_3]_2$ ²⁴ and a phosphorus radius of 1.10 \AA .²⁸

The In-Co bonds in $\text{In}[\text{Co}(\text{CO})_4]_3$ are shorter than might be expected from the sum of the single-bond covalent radii of indium and cobalt. In many other compounds containing bonds between transition metal carbonyl fragments and post-transition metals the metal-metal distances also appear shorter than those predicted from the sum of the single-bond covalent radii of the metals. For example, the metal-metal bonds of $\text{Hg}[\text{Co}(\text{CO})_4]_2$,²⁹ $\text{Zn}[\text{Co}(\text{CO})_4]_2$,³⁰ $(h^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{HgCo}(\text{CO})_4$,³¹ $\text{Br}_3\text{In}_3\text{Co}_4(\text{CO})_{15}$,³² $\{\text{N}(\text{C}_2\text{H}_5)_4\}\{\text{Br}_2\text{In}[\text{Co}(\text{CO})_4]_2\}$,³³ $\text{X}_3\text{SiCo}(\text{CO})_4$ ($\text{X} = \text{H}$,³⁴ F ,³⁵ Cl)³⁶, and $(\text{C}_6\text{H}_5)_3\text{GeCo}(\text{CO})_3\text{P}(\text{C}_6\text{H}_5)_3$ ³⁷ are some $0.1\text{-}0.2 \text{ \AA}$ ³⁸⁻⁴⁰ short-

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Table II. Anisotropic Thermal Parameters (\AA^2) for $\text{In}[\text{Co}(\text{CO})_4]_3 \times 10^3$

Atom	U_{11}^a	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
In	39.5 (6)	73.1 (6)	38.7 (6)	-0.6 (6)	15.1 (4)	3.2 (6)
Co1	35.6 (19)	57.0 (13)	30.7 (14)	-0.9 (11)	11.5 (11)	5.1 (12)
Co2	27.8 (13)	58.7 (14)	42.2 (17)	3.8 (10)	15.0 (12)	6.3 (12)
Co3	34.4 (13)	62.3 (14)	34.4 (14)	-3.9 (11)	15.9 (12)	9.2 (12)
C1a	36 (10)	67 (11)	79 (14)	4 (9)	12 (9)	15 (10)
O1a	75 (10)	104 (10)	175 (16)	21 (9)	74 (11)	-16 (11)
C1b	93 (16)	81 (13)	38 (12)	9 (11)	40 (11)	10 (10)
O1b	234 (21)	94 (11)	118 (14)	-55 (12)	93 (13)	-24 (10)
C1c	49 (12)	141 (17)	24 (9)	-4 (12)	4 (8)	14 (10)
O1c	75 (10)	189 (15)	51 (8)	8 (11)	28 (8)	16 (10)
C1d	31 (10)	82 (12)	111 (19)	-6 (10)	18 (11)	0 (13)
O1d	120 (14)	172 (17)	62 (9)	50 (13)	0 (9)	36 (11)
C2a	39 (12)	90 (14)	9 (8)	12 (9)	3 (8)	11 (9)
O2a	73 (12)	96 (11)	98 (14)	4 (9)	29 (9)	0 (9)
C2b	72 (12)	62 (10)	55 (12)	24 (9)	26 (11)	19 (9)
O2b	121 (14)	141 (14)	116 (13)	9 (11)	68 (12)	-50 (12)
C2c	51 (10)	111 (14)	62 (13)	19 (11)	17 (11)	15 (13)
O2c	79 (9)	151 (13)	66 (9)	2 (11)	10 (8)	19 (10)
C2d	79 (14)	100 (14)	71 (14)	32 (14)	25 (12)	32 (12)
O2d	54 (9)	185 (16)	204 (19)	28 (12)	75 (11)	52 (15)
C3a	56 (10)	83 (11)	66 (13)	-6 (10)	42 (11)	0 (11)
O3a	39 (8)	179 (15)	70 (9)	8 (10)	-3 (7)	32 (10)
C3b	110 (20)	74 (12)	50 (12)	-9 (13)	33 (12)	15 (11)
O3b	93 (12)	109 (13)	149 (16)	-14 (11)	44 (11)	-8 (12)
C3c	66 (16)	99 (16)	141 (24)	-4 (13)	53 (16)	-7 (17)
O3c	129 (15)	169 (16)	79 (12)	-52 (14)	54 (11)	-26 (12)
C3d	45 (10)	111 (14)	68 (13)	-6 (11)	30 (9)	24 (12)
O3d	76 (10)	256 (21)	91 (10)	-24 (12)	38 (9)	81 (14)

^a The form of the approximation is $f = f_0 \exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ where $\beta_{ij} = U_{ij}(2\pi^2 a_i^* a_j^*)$.

Table III. Interatomic Distances and Angles for $\text{In}[\text{Co}(\text{CO})_4]_3$

Interatomic Distances within the Molecule (\AA)							
In-Co1	2.597 (3)	In··C2a	2.96 (2)	C1a-O1a	1.15 (2)	C1d··C1a	2.61 (3)
In-Co2	2.595 (3)	In··C2b	2.77 (2)	C1b-O1b	1.21 (3)	C1d··C1b	2.63 (3)
In-Co3	2.590 (3)	In··C2c	3.19 (2)	C1c-O1c	1.17 (2)	C1d··C1c	2.62 (2)
Co1-C1a	1.81 (2)	In··C3a	3.14 (2)	C1d-O1d	1.16 (3)	C2d··C2a	2.60 (3)
Co1-C1b	1.68 (2)	In··C3b	2.92 (2)	C2a-O2a	1.18 (3)	C2d··C2b	2.69 (3)
Co1-C1c	1.76 (2)	In··C3c	2.78 (2)	C2b-O2b	1.16 (2)	C2d··C2c	2.69 (3)
Co1-C1d	1.73 (2)	In··O1a	3.72 (1)	C2c-O2c	1.19 (2)	C3d··C3a	2.68 (3)
Co2-C2a	1.79 (2)	In··O1b	3.60 (2)	C2d-O2d	1.11 (3)	C3d··C3b	2.61 (3)
Co2-C2b	1.74 (2)	In··O1c	3.87 (1)	C3a-O3a	1.17 (2)	C3d··C3c	2.58 (3)
Co2-C2c	1.72 (2)	In··O2a	3.67 (2)	C3b-O3b	1.20 (3)	O1c··C2a	3.35 (2)
Co2-C2d	1.83 (2)	In··O2b	3.50 (2)	C3c-O3c	1.21 (3)	O1c··C2b	3.52 (2)
Co3-C3a	1.77 (2)	In··O2c	4.04 (1)	C3d-O3d	1.13 (2)	O2c··C3b	3.47 (3)
Co3-C3b	1.69 (2)	In··O3a	3.90 (1)	In··C1a	2.90 (2)	O2c··C3c	3.74 (3)
Co3-C3c	1.65 (2)	In··O3b	3.64 (2)	In··C1b	2.83 (2)	O3a··C1a	3.37 (2)
Co3-C3d	1.82 (2)	In··O3c	3.56 (1)	In··C1c	3.06 (2)	O3a··C1b	3.44 (2)
Bond Angles (deg)							
Co1-In-Co2	119.44 (8)	C2b-Co2-C2c	115 (1)	Co3-C3a-O3a	178.1 (17)	In-Co1-C1b	79.6 (7)
Co1-In-Co3	120.88 (8)	C2a-Co2-C2d	92.4 (8)	Co3-C3b-O3b	175.9 (17)	In-Co1-C1c	87.1 (7)
Co2-In-Co3	119.31 (9)	C2b-Co2-C2d	98.0 (9)	Co3-C3c-O3c	172.9 (20)	In-Co1-C1d	174.8 (6)
Co1-C1a-O1a	170.0 (16)	C2c-Co2-C2d	98.6 (10)	Co3-C3d-O3d	175.3 (16)	In-Co2-C2a	82.8 (5)
Co1-C1b-O1b	173.8 (17)	C3a-Co3-C3b	114 (1)	C1a-Co1-C1b	118 (1)	In-Co2-C2b	76.4 (6)
Co1-C1c-O1c	175.6 (14)	C3a-Co3-C3c	121 (1)	C1a-Co1-C1c	121 (1)	In-Co2-C2c	92.9 (7)
Co1-C1d-O1d	178.5 (19)	C3b-Co3-C3c	121 (1)	C1b-Co1-C1c	116 (1)	In-Co2-C2d	168.6 (7)
Co2-C2a-O2a	175.5 (15)	C3a-Co3-C3d	96.4 (8)	C1a-Co1-C1d	95 (1)	In-Co3-C3a	90.0 (6)
Co2-C2b-O2b	173.2 (16)	C3b-Co3-C3d	96.1 (9)	C1b-Co1-C1d	101 (1)	In-Co3-C3b	83.3 (8)
Co2-C2c-O2c	177.1 (16)	C3c-Co3-C3d	96.1 (10)	C1c-Co1-C1d	97 (1)	In-Co3-C3c	78.4 (8)
Co2-C2d-O2d	177.8 (20)	In-Co1-C1a	80.4 (5)	C2a-Co2-C2b	124 (1)	In-Co3-C3d	173.2 (6)
				C2a-Co2-C2c	117 (1)		

Selected Intermolecular Nonbonding Distances (\AA) and Symmetry Operations

In··O3b	3.71	$x, -1 + y, z$	O2a··O3b	2.99	$x, -1 + y, z$
O1a··O3d	2.99	$1 - x, 1 - y, 1 - z$	O2a··C2b	3.20	$x, -1 + y, z$
O1a··O3b	3.03	$x, -1 + y, z$	O2a··O2b	3.26	$x, -1 + y, z$
O1a··C3d	3.11	$1 - x, 1 - y, 1 - z$	O2a··O2d	3.28	$-x, 1 - y, 1 - z$
O1a··C3b	3.14	$x, -1 + y, z$	O2b··C1d	3.32	$1/2 - x, 1/2 + y, 3/2 - z$
O1a··O3a	3.20	$1 - x, 1 - y, 1 - z$	O2b··C1c	3.33	$1/2 - x, 1/2 + y, 3/2 - z$
O1a··C3a	3.23	$1 - x, 1 - y, 1 - z$	O2c··O3c	3.19	$1/2 - x, 1/2 + y, 1/2 - z$
O1a··O1b	3.32	$x, -1 + y, z$	O2d··C2a	3.36	$-x, 1 - y, 1 - z$
O1b··O1a	3.32	$x, 1 + y, z$	O3a··O3d	3.36	$1 - x, 2 - y, 1 - z$
O1c··O2b	3.20	$1/2 - x, -1/2 + y, 3/2 - z$	O3b··O3c	2.98	$x, 1 + y, z$
O1c··O2d	3.26	$-x, 1 - y, 1 - z$	O3b··C1a	3.26	$x, 1 + y, z$
O1c··O2b	3.37	$x, -1 + y, z$	O3c··C3d	3.17	$1/2 - x, -1/2 + y, 1/2 - z$
O1d··O2a	3.17	$1/2 + x, 1/2 - y, 1/2 + z$	O3c··O3d	3.26	$1/2 - x, -1/2 + y, 1/2 - z$
O1d··O2b	3.27	$1/2 - x, -1/2 + y, 3/2 - z$			

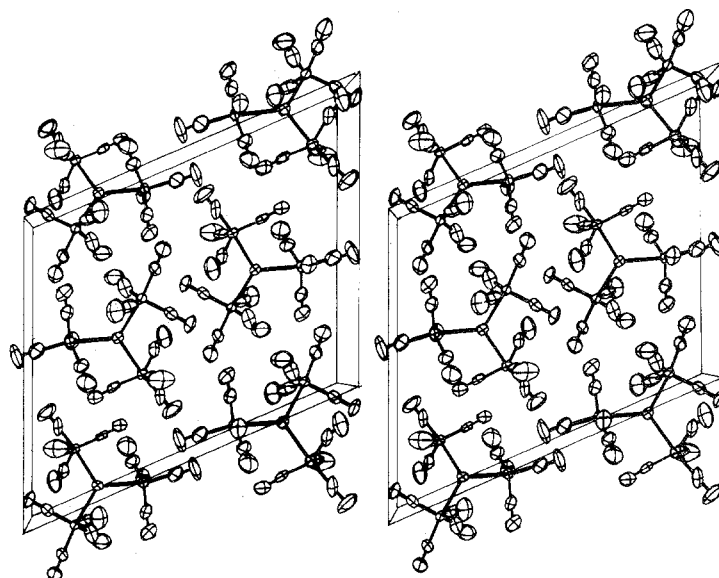


Figure 2. A stereoscopic packing diagram of $\text{In}[\text{Co}(\text{CO})_4]_3$ viewed normal to the XZ plane. One unit cell is outlined.

Table IV. Atomic Displacements from a Plane^a through the Cobalt Atoms of $\text{In}[\text{Co}(\text{CO})_4]_3$

Atom	Distance, Å	Atom	Distance, Å
In	-0.009	C2c	0.016
C1a	-1.400	O2c	0.016
O1a	-2.261	O2d	0.078
C1b	1.535	O2d	0.167
O1b	2.656	C3a	0.272
C1c	-0.020	O3a	0.462
O1c	-0.028	C3b	1.401
C1d	-0.016	O3b	2.348
O1d	-0.050	C3c	-1.491
C2a	-1.592	O3c	-2.599
O2a	-2.683	C3d	-0.037
C2b	1.508	O3d	-0.151
O2b	2.518		

^a The equation of the plane is $-1.214X + 6.134Y + 6.955Z = 7.258$, relative to the unit cell axes in Å.

er than predicted. A variety of other similar compounds are discussed in ref 2-6.

A covalent radius for indium(III) in a trigonal-planar geometry may be calculated from the indium-carbon distance in trimethylindium.^{22,23} This compound crystallizes as a tetramolecular unit with bridging methyl groups. About each indium in the tetramer are located three methyl groups in a trigonal-planar arrangement with In-C distances averaging 2.22 (4) Å. Two other methyl groups are found at much greater distances (3.10 and 3.60 Å) from the indium and are located above and below the trigonal plane. Since the $\text{In}(\text{CH}_3)_3$ molecules in the tetramer are only very weakly associated ($\text{In}(\text{CH}_3)_3$ is monomeric in the gas phase⁴¹ and in solution⁴²), the methyl groups situated above and below the indium probably do not perturb the equatorial indium-methyl bonds to any significant extent. The equatorial In-C distances thus suggest an approximate sp^2 single-bond covalent radius of 1.45 (4) Å for indium(III) in a trigonal-planar environment. The covalent radius of the cobalt in a $\text{Co}(\text{CO})_4$ group has been variously described^{43,44} as 1.29-1.34 Å. Taking 1.45

Å as the radius of indium gives an expected single-bond distance of 2.74-2.79 Å for the In-Co bond, some 0.15-0.20 Å longer than that observed.

The shortness of the metal-metal bonds in compounds of the type listed above relative to the sums of covalent radii has been attributed to a combination of effects including (i) $d\pi-d\pi$ bonding between the filled d orbitals of the transition metal and the empty d orbitals of the posttransition metal,^{34,37} (ii) $d\pi-p\pi$ bonding between the filled d orbitals of the transition metal and the empty valence p orbitals, where available, of the posttransition metal,³⁹ (iii) an intramolecular interaction between the posttransition metal and the equatorial carbonyl groups of the metal carbonyl fragment,⁴⁵ and (iv) variation of the single-bond covalent radii of the metals with effective nuclear charge, hybridization, and effective electronegativity of the metals.^{46,47}

Explanations of the type i-iii are required if one assumes that the single-bond covalent radii of a posttransition metal and a transition metal are approximately invariant with substituent and that a radius derived from a bond length between two atoms with no d valence electrons is suitable for use in a bond in which one of the bonded atoms contains valence d electrons. It may be that this concept of a unique single-bond radius for metal is specious, and effects such as described in iv produce changes in the effective single-bond radius of metal atoms. As indicated in Table V, metals of groups II and IV exhibit covalent radii which vary by 0.07-0.23 Å. In Hg_2F_2 ⁴⁸ the Hg-Hg distance of 2.51 Å suggests a covalent radius of 1.25 Å for mercury in a linear two-coordinate geometry. A radius of 1.32 Å is suggested from the Hg-C distance of 2.09 Å in $\text{Hg}(\text{CH}_3)_2$.⁴⁰ Similar variations are observed from compound to compound with the other metals listed. Of particular interest is the variation in the Cl-Sn distance in the compounds of the type $\text{ClSnR}_2\text{R}'$. This distance varies from 2.31 Å ($\text{R} = \text{R}' = \text{Cl}$ ⁴⁹) to 2.54 Å ($\text{R} =$

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Table V. Variation of Covalent Radii with Substituent of Selected Metals

M-X	D(M-X), Å ^a	R(M), Å ^b	Compound
Hg-Hg	2.51	1.25	Hg ₂ F ₂ ^c
Hg-C	2.09	1.32	Hg(CH ₃) ₂ ^d
Si-C	1.867	1.10	CH ₃ SiH ₃ ^e
Si-H	1.48	1.18	CH ₃ SiH ₃ ^e
Si-Si	2.352	1.17	Si(diamond str) ^e
Si-C	1.84 (1.5)	1.07	CH ₃ SiF ₃ ^e
Ge-C	1.945	1.17	CH ₃ GeH ₃ ^e
Ge-H	1.53	1.23	CH ₃ GeH ₃ ^e
Ge-Ge	2.450	1.22	Ge(diamond str) ^e
Ge-Cl	2.26	1.27	Cl ₂ Ge[Fe(C ₅ H ₅)(CO) ₂] ₂ ^f
Sn-C	2.143 (2)	1.37	CH ₃ SnH ₃ ^e
Sn-H	1.70	1.40	CH ₃ SnH ₃ ^e
Sn-Sn	2.810	1.40	Sn(diamond str) ^e
Sn-Cl	2.31 (1.5)	1.32	SnCl ₄ ^g
Sn-Cl	2.43	1.44	ClSn[Mn(CO) ₅] ₃ ^h
Sn-Cl	2.54	1.55	ClSn[Co(CO) ₄] ₃ ⁱ
Sn-Cl	2.50	1.51	ClSn[Fe(C ₅ H ₅)(CO) ₂] ₂ ^j [Mo(C ₅ H ₅)(CO) ₃] ₂ ^k
Pb-C	2.30	1.53	Pb(CH ₃) ₄ ^e
Pb-Pb	2.88 (3)	1.44	Pb ₂ (CH ₃) ₆ ^e
Mn-H	1.60 (2)	1.30	HMn(CO) ₅ ^l
Mn-Cl	2.37	1.38	ClMn(CO) ₅ ^l
Mn-Mn	2.92	1.46	Mn ₂ (CO) ₁₀ ^m
Mo-C	2.40 (2)	1.63	(C ₅ H ₅)Mo(CO) ₃ (C ₂ H ₅) ⁿ
Mo-C	2.29	1.52	(C ₅ H ₅)Mo(CO) ₃ (C ₃ F ₇) ^o
Mo-Cl	2.54	1.55	(C ₅ H ₅)Mo(CO) ₃ Cl ^p
Mo-Mo	3.22	1.61	[(C ₅ H ₅)Mo(CO) ₃] ₂ ^q

^a Unless otherwise indicated, standard deviations are equal to or less than one unit of the least significant figure. ^b Calculated as half the M-M distance or by subtracting 0.77, 0.73, 0.30, or 0.99 Å as the covalent radii²⁶ of C(sp³), C(sp²), H, and Cl, respectively. ^c Reference 48. ^d Reference 40. ^e From ref 51. ^f M. A. Bush and P. Woodward, *J. Chem. Soc. A*, 1833 (1967). ^g Reference 49. ^h J. H. Tsai, J. J. Flynn, and F. P. Boer, *Chem. Commun.*, 702 (1967). ⁱ Reference 50. ^j J. E. O'Connor and E. R. Corey, *J. Amer. Chem. Soc.*, 89, 3930 (1967). ^k S. J. La Placa, W. C. Hamilton, J. A. Ibers, and A. Davison, *Inorg. Chem.*, 8, 1928 (1969). ^l P. T. Greene and R. F. Bryan, *J. Chem. Soc. A*, 1559 (1971). ^m L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, 16, 419 (1963). ⁿ M. J. Bennett and R. Mason, *Proc. Chem. Soc., London*, 273 (1963). ^o M. R. Churchill and J. P. Fennessey, *Inorg. Chem.*, 6, 1213 (1967). ^p S. Chaiwasi and R. H. Fenn, *Acta Crystallogr., Sect. B*, 24, 525 (1968). ^q F. C. Wilson and D. P. Shoemaker, *J. Chem. Phys.*, 27, 809 (1952).

R' = Co(CO)₄⁵⁰). Clearly the covalent radius of these metals is not invariant from compound to compound. It is also noteworthy that the apparent covalent radius varies within a given compound. In the group IV compounds CH₃MH₃⁵¹ (where M = Si, Ge, Sn), the covalent radii of M calculated from the M-C distances are different from those calculated from the M-H distances by 0.03-0.08 Å.

With metal carbonyl derivatives large variations in covalent radii are also observed. These range from 1.22 to 1.46 Å in the manganese systems and from 1.52 to 1.63 Å in the molybdenum systems. The assumption that Cl and C₃F₇ are not π-bonding substituents and thus may be used in determinations of single-bond covalent radii is based on the work of Fensky, whose calculations have shown that there is no π bonding in the Cl-Mn⁵² bond in ClMn(CO)₅ and that a reduction of the Mn-CR₃ distance upon going from H₃CMn(CO)₅ to F₃CMn(CO)₅ would result from the change in electronegativity of R and not from Mn-CF₃ π bonding.⁵³

In view of the variations in both posttransition metal and transition metal single-bond radii it is not necessary to postu-

late any type of π bonding to explain the observed metal-metal distances since it has not been shown that these distances do not correspond to single-bond distances. Indeed the structure of In[Co(CO)₄]₃ when compared with those of Br₃In₃Co₄(CO)₁₅ and Br₂In[Co(CO)₄]₂⁻ suggests that dπ-pπ bonding is not significant in the trigonal-planar indium compound although there are indications of an intramolecular interaction between the indium and equatorial carbonyl groups. No information concerning the presence or absence of dπ-dπ bonding in the indium-cobalt bonds is available from this structure.

Both Br₃In₃Co₄(CO)₁₅³² and Br₂In[Co(CO)₄]₂⁻³³ contain four-coordinate indium in an approximately tetrahedral geometry. Upon going from the trigonal-planar three-coordinate indium of In[Co(CO)₄]₃ to the four-coordinate indium of the other compounds, the vacant p_z orbital which was not required for σ bonding in In[Co(CO)₄]₃ is required for σ bonding in the four-coordinate systems and is consequently no longer available for dπ-pπ overlap with the cobalt. If dπ-pπ overlap were significant in the three-coordinate species, the loss of the p_z orbital from the π system should result in a marked increase in the In-Co bond length. Such increases are observed⁵¹ upon going from BF₃ (B-F = 1.30 Å) to BF₄⁻ (B-F = 1.43 Å) and from the trigonal-planar BO₃ group in B(OH)₃ (B-O = 1.36 Å) to the tetrahedral group in BaBF₃O (B-O = 1.43 Å). No such variations were found in the In-Co distances. The In-Co distances in the trigonal-planar and tetrahedral compounds are equal within the errors of the determinations as is found in the In-CH₃ distances in In-(CH₃)₃^{22,23} and In(CH₃)₄⁻⁵⁴.

The displacement of the equatorial carbonyl groups of Co(CO)₄ and Mn(CO)₅ moieties in posttransition metal, M, derivatives giving M-Co-C and M-Mn-C angles of less than 90° is a well established phenomenon.^{2-6,45} In derivatives of R₃MMn(CO)₅, R₃MCo(CO)₄, and R₃MCo(CO)₃P(C₆H₅)₃ (where M is a group IV derivative), all of the equatorial carbonyls are bent toward the substituent with the M-M'-C (M' = Co, Mn) angles in these derivatives ranging from 81.7° for F₃SiCo(CO)₄⁵⁵ to 86.7° for (C₆H₅)₃SnMn(CO)₅.⁵⁵ Zinc(II)³⁰ and mercury(II)²⁹ derivatives show similar variations with the M-M'-C angles ranging from 81.1 (5) to 84.3 (2)°. Four-coordinate indium tetracarbonylcobaltate derivatives show geometries similar to those of the group II and IV derivatives. The In-Co-C angles observed in Br₃In₃Co₄(CO)₁₅³² for the terminal Co(CO)₄ groups vary from 83 (2) to 85 (1)° with an average of 84°. The average In-C and In-O distances are 2.93 and 3.68 Å, respectively. Also Br₂In[Co(CO)₄]₂⁻³³ has In-Co-C angles from 75 (3) to 89 (5)° (average 85°) with average In-C and In-O distances of 2.94 and 3.60 Å, respectively.

The In-Co-C angles in In[Co(CO)₄]₃ are unusual in that only two of the CO groups are bent toward the indium giving two shorter and one longer In-C distances. The In-Co-C(op) angles average 80.1° while the In-Co-C(ip) angles average 90.0°. The In-C(op) and In-C(ip) distances average 2.86 (7) and 3.13 (5) Å, respectively. In the Co(CO)₄ derivatives of four-coordinate indium(III) noted above all equatorial carbonyl groups are displaced toward the posttransition metal by an equivalent amount with equivalent M-C distances.

Two equally consistent explanations may be offered for the geometry about the cobalt atoms in In[Co(CO)₄]₃. The out-of-plane equatorial groups (Table IV) are of proper symmetry

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to allow overlap between the empty indium p_z orbital and the filled carbon p orbitals while the p orbitals of the in-plane equatorial carbonyls are not capable of such overlap. Thus an intramolecular In-C interaction between the p_z orbital and the out-of-plane carbonyl is possible while no such interaction involving the in-plane carbonyl group can occur. Molecular orbital calculations⁴⁵ for group IV derivatives of $\text{Co}(\text{CO})_4$ show positive overlap between silicon d or p orbitals and carbon p orbitals in $\text{F}_3\text{SiCo}(\text{CO})_4$ and lead one to expect a similar overlap in $\text{In}[\text{Co}(\text{CO})_4]_3$. An In-C interaction limited to the out-of-plane carbonyl groups is consistent with the observation that only the two out-of-plane carbonyl groups are displaced toward the indium. It may also be argued that the larger displacement of the carbonyls toward the indium in $\text{In}[\text{Co}(\text{CO})_4]_3$ as compared to the heavier group IV derivatives of $\text{Co}(\text{CO})_4$ is due to the $\text{In}(p)\text{-C}(p)$ overlap which is not possible with the group IV derivatives where the lower lying valence orbitals are not available.

Alternatively, the geometry about the cobalt atoms may be due to steric repulsions between carbonyl groups of different $\text{Co}(\text{CO})_4$ groups on the same molecule. The closest approach of groups 1 and 2 (Figure 1), for example, is between O1c (in-plane) of group 1 and C2a and C2b (out-of-plane) of group 2 where the distances are 3.35 (2) and 3.52 (2) Å, respectively. Since the oxygen atom is on the end of a carbonyl group, its position will change more rapidly with changes in the In-Co-C angle than will the positions of the carbon atom of the group. Thus, since the O1c-C2a and O1c-C2b distances are relatively insensitive to the In-Co-C2a and In-Co-C2b angles, the out-of-plane groups are free to move closer to the indium atom and minimize repulsions with the axial carbonyl group. The in-plane group, on the other hand, is restricted to larger In-Co-C angles due to the oxygen-carbon repulsions. It is noteworthy that the closest approach of two $\text{In}[\text{Co}(\text{CO})_4]_3$ molecules (2.98 (2) Å between two oxygen atoms) is much smaller than the closest approach of two carbonyl groups in the same molecule (3.35 (2) Å). However, it must be kept in mind that in the former case two oxygens are approaching from the top of the carbonyl group and in the latter case an oxygen approaches the side of a carbonyl. If the carbonyl group may be regarded as a cylinder with a radius similar to that of cyanoacetylene, its radius can be estimated to be 1.85 Å from the closest approach of two parallel cyanoeth-

ylene molecules (3.70 Å).⁵⁶ The effective van der Waals radius of a carbonyl oxygen along the C-O internuclear axis can be estimated from the closest O-O approach of two molecules of $\text{In}[\text{Co}(\text{CO})_4]_3$ as 1.49 Å. Thus, the expected van der Waals distance for the intramolecular approach of O1c to C2a is about 3.35 Å, identical with that observed.

Although the choice between these two alternative explanations for the variation in the In-Co-C angles is not obvious and both may be important, we favor the explanation based on In-C bonding interactions for the following reasons. The peculiar arrangement of the equatorial carbonyls of $\text{In}[\text{Co}(\text{CO})_4]_3$ with two shorter and one longer In-C distances is not preserved in related cobalt tetracarbonyl derivatives. For example, the equatorial carbonyl carbon atoms of the two $\text{Co}(\text{CO})_4$ groups of $\text{Br}_2\text{In}[\text{Co}(\text{CO})_4]_2^-$ ³³ are equidistant from the indium although the CO groups are staggered as observed in $\text{In}[\text{Co}(\text{CO})_4]_3$. Moreover, since three-coordination is very rare for indium (even $\text{In}(\text{CH}_3)_3$ has bridging methyl groups²²) and carbonyl groups are known to act as Lewis bases using the lone pair of electrons on the oxygen,^{27,57} it is difficult to explain the absence of an intermolecular In-O bond unless the empty p orbital is getting electron density from another source.⁵⁸⁻⁶⁰ Since the cobalt d orbitals have already been eliminated as potential donors to the p orbital, the most likely alternative is an In-C bonding interaction.

Registry No. Indium amalgam, 11146-92-2; $\text{Hg}[\text{Co}(\text{CO})_4]_2$, 38188-06-6; $\text{In}[\text{Co}(\text{CO})_4]_3$, 38188-07-7.

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(58) $\text{In}[\text{Co}(\text{CO})_4]_3$ readily forms adducts with other groups such as tetrahydrofuran,⁵⁹ Cl^- ,⁶⁰ $\text{OP}(\text{C}_6\text{H}_5)_3$,⁶⁰ and $\text{Co}(\text{CO})_4^-$.⁶⁰

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