Further Studies of the Substitution Reactions of Bis(tetracarbonylcobaltio)mercury with Phosphorus(III) and Arsenic(III) Ligands

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The reactions of $\{Co(CO)_4\}_2Hg$ with various phosphorus(III) ligands in the absence of light give $\{LCo(CO)_3\}_2Hg$ and, under more vigorous conditions, $\{L_2Co(CO)_2\}_2Hg$ derivatives [L = Et_3P, Bu^n_3P, $PhMe_2P$, $Ph(Pr^i)_2P$, Ph_2MeP, $(Et_2N)_3P$, Ph_2POMe, $PhP(OMe)_2$, $(MeO)_3P$, $(2\text{-}ClC_2H_4O)_3P$, $PhOP(OCH_2)_2$ or $(PhO)_3P$]. The bidentate ligand $Ph_2PCH_2CH_2PPh_2$, dp yields $(dp)Co_2(CO)_6Hg$ and $\{(dp)Co(CO)_2\}_2Hg$. Analogous arsenic complexes are also described. Some reactions of these two compounds with mercury(II) halides or tin(IV) chloride have been investigated. The complex $\{(dp)Co(CO)_2\}_2Hg$ yields $(dp)Co(CO)_2X$ (X = HgCl, HgBr, HgI, or $SnCl_3$) and $\{(da)Co(Co)_2\}_2Hg$ reacts similary, but whereas $(Ph_2PCH_2)_2Co_2(CO)_6Hg$ gives a mixture of $(Ph_2PCH_2)_2Co(CO)_2X$ and $Co(CO)_4X$, $(Ph_2AsCH_2)_2Co_2(CO)_6Hg$ gives only $(Ph_2AsCH_2)_2\{Co(CO)_3X\}_2$. The i.r. spectra of all compounds in the 1700—2100 cm^{-1} region are reported, absorption bands due to $\nu(CO)$ vibrations are identified, and structures proposed for the new derivatives.

MERCURY cobalt carbonyl undergoes CO substitution on reaction with secondary and tertiary phosphines,[1,2] and with triphenyl phosphite [2] to give disubstituted derivatives of the type $\{LCo(CO)_3\}_2Hg$ whilst $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$ yields $\{(Ph_2PCH_2)_2Co(CO)_2\}_2Hg$.[3] Other $\{L_2Co(CO)_2\}Hg$ derivatives [L = Ph_3P and $(PhO)_3P$] have been prepared by the reduction of $L_2Co(CO)_2Cl$ with sodium amalgam, and reaction of the reduced species with mercury(II) cyanide.[4] $\{(PF_3)_2Co(CO)_2\}_2Hg$ has been obtained by a similar route.[5]

Unlike the other phosphorus(III) ligands, $(MeO)_3P$ causes $\{Co(CO)_4\}_2Hg$ to precipitate mercury and give $[\{(MeO)_3P\}Co(CO)_3]_2$.[6] The work of Mays *et al.* has shown that many bis(metallo)mercury derivatives are decomposed by u.v. irradiation to mercury and a bismetal compound.[7] Thus it seemed likely that in the absence of light, trimethyl phosphite would react with bis(tetracarbonylcobaltio)mercury in the same way as phosphines. This has been found to be so, and we have prepared new $\{LCo(CO)_3\}_2Hg$ complexes of monodentate phosphites, phosphonites, and phosphinite ligands where L = $(MeO)_3P$, $(2\text{-}ClC_2H_4O)_3P$, $PhOP(OCH_2)_2$, $(PhO)_3P$, $PhP(OMe)_2$, and Ph_2POMe.

Furthermore, when an excess of the ligand is used, and the reactions are carried out at higher temperatures and/or for longer reaction times, the disubstituted compounds are converted into the tetrasubstituted $\{L_2Co(CO)_2\}_2Hg$ derivatives [L = Et_3P, $PhMe_2P$, Ph_2MeP, Ph_2POMe, $PhP(OMe)_2$, $(MeO)_3P$, $(2\text{-}ClC_2H_4O)_3P$, $PhOP(OCH_2)_2$, and $(PhO)_3P$].

We have also reinvestigated the reaction of $\{Co(CO)_4\}_2Hg$ with $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$ (dp).[3] Both dp and its arsenic analogue, da, yield $\{(dp)Co(CO)_2\}_2Hg$ or $\{(da)Co(CO)_2\}_2Hg$ as the final products, but $(dp)Co_2(CO)_6Hg$ and $(da)Co_2(CO)_6Hg$ are formed as intermediates, and have been isolated. The reactions of these four compounds with mercury(II) halides or tin(IV) chloride show that the last two are best formulated as $(dp)Co(CO)_2HgCo(CO)_4$ and $(da)\{Co(CO)_3\}_2Hg$ respectively.

The i.r. spectra of the compounds have been investigated. Absorption bands due to their $\nu(CO)$ vibrations have been identified, and are reported. The structures of the complexes are discussed.

EXPERIMENTAL

Bis(tetracarbonylcobaltio)mercury was prepared by the method of Hieber *et al.*[8] The ligands were purchased, or obtained by standard techniques.

All reactions were carried out in benzene solution in the dark, and under an atmosphere of nitrogen. The $\{LCo(CO)_3\}_2Hg$ derivatives [L = $PhMe_2P$, $Ph(Pr^i)_2P$, Ph_2MeP, Ph_2POMe, $PhP(OMe)_2$, $(MeO)_3P$, $(2\text{-}ClC_2H_4O)_3P$, $PhOP(OCH_2)_2$, and $(PhO)_3P$] were obtained by the addition of the ligand L to a solution of mercury cobalt carbonyl (0·5 g) using a 2 : 1 mol ratio of reactants. The reactions were complete within 15 min at room temperature. The solutions were filtered, the solvent removed at reduced pressures, and the residues recrystallized from aqueous acetone except for $\{(Ph_2MeAs)Co(CO)_3\}_2Hg$ for which benzene was used. Further substitution to give the tetrasubstituted $\{L_2Co(CO)_2\}_2Hg$ complexes [L = Et_3P, $PhMe_2P$, Ph_2MeP, Ph_2POMe, $PhP(OMe)_2$, $(MeO)_3P$, $(2\text{-}ClC_2H_4O)_3P$, $PhOP(OCH_2)_2$, and $(PhO)_3P$] was effected with L : $Hg\{Co(CO)_4\}_2$ mole ratios of 8 : 1. When L = $(MeO)_3P$ or $(2\text{-}ClC_2H_4O)_3P$, the reactions were complete within 24 h at room temperature. For the other ligands the solutions were refluxed for up to 24 h whilst the reactions were monitored by i.r. spectroscopy. The products were isolated and purified as described above except for $\{(Ph_2MeP)_2Co(CO)_2\}_2Hg$ which was recrystallized from benzene–hexane. Polysubstitution could not be brought about for L = $Ph(Pr^i)_2P$, $(Et_2N)_3P$, and $PhMe_2As$, whilst Pr^n_3P and Bu^n_3P gave products whose i.r. spectra differed from those of the $\{L_2Co(CO)_2\}_2Hg$ complexes. They were unstable and could not be isolated. Reaction yields for the phosphinite, phosphonite, and phosphite derivatives were *ca.* 20—50%, and were >60% for the phosphine compounds.

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[1] A. R. Manning, *J. Chem. Soc.* (*A*), 1968, 1018, and references therein.

[2] L. M. Bower and M. H. B. Stiddard, *J. Organometallic Chem.*, 1968, **13**, 235.

[3] H. Behrens and W. Aquila, *Z. anorg. Chem.*, 1967, **356**, 8.

[4] W. Hieber and H. Duchatsch, *Chem. Ber.*, 1965, **98**, 2933.

[5] S. K. Gondal, A. G. MacDiarmid, F. E. Saalfield, and M. V. McDowell, *Inorg. Nuclear Chem. Letters*, 1969, **5**, 351.

[6] W. Hieber and R. Breu, *Chem. Ber.*, 1957, **90**, 1259.

[7] M. J. Mays and S. M. Pearson, *J. Chem. Soc.* (*A*), 1968, 2291.

[8] R. B. King, 'Organometallic Synthesis,' Academic Press, London, 1965, vol. 1, p. 101.

The reactions of the bidentate ligands $Ph_2P{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$, dp, and $Ph_2As{\cdot}CH_2{\cdot}CH_2{\cdot}AsPh_2$, da, to give $(dp)Co_2(CO)_6Hg$ or $\{(dp)Co(CO)_2\}_2Hg$ and the analogous arsenic complexes were carried out using ligand : $\{Co(CO)_4\}_2Hg$ mole ratios of 1 : 1 and 4 : 1 respectively. The hexacarbonyl complexes were quickly formed at room temperature and were purified as above, but the tetracarbonyls could only be obtained after refluxing the reaction mixtures for 15 min with the phosphine and *ca.* 10 h with the arsine. These compounds were insoluble in the reaction mixtures and so the precipitated solids were filtered off and washed with hot benzene; yields were 40—70%.

TABLE 1

Melting points and analyses for $[LCo(CO)_3]_2Hg$ complexes

L	M.p.[a]	Formula	Found (%)			Required (%)		
			C	H	Co	C	H	Co
$(PhO)_3P$	116—117	$C_{42}H_{30}Co_2HgO_{12}P_2$	45·9	2·9		45·6	2·7	10·7
$PhOP(OCH_2)_2$	94—96	$C_{22}H_{18}Co_2HgO_{12}P_2$	30·4	2·0		30·9	2·1	
$(2\text{-}ClC_2H_4O)_3P$	99—100	$C_{18}H_{24}Cl_6Co_2HgO_{12}P_2$	21·1	2·3	11·6	21·1	2·3	11·5
$(MeO)_3P$	dec. 108	$C_{12}H_{18}Co_2HgO_{12}P_2$	20·0	2·5	16·1	19·6	2·5	16·1
$PhP(OMe)_2$	101—102	$C_{22}H_{22}Co_2HgO_{10}P_2$	31·4	2·4	14·2	31·9	2·7	14·7
$Ph_2P(OMe)$	173—175	$C_{32}H_{26}Co_2HgO_8P_2$	41·6	2·5	13·5	41·8	2·8	12·9
$(Et_2N)_3P$	dec. 190	$C_{30}H_{60}Co_2HgN_6O_6P_2$	36·7	6·3	12·3	36·7	6·1	12·1
$Ph(Pr^i)_2P$	165—166	$C_{30}H_{38}Co_2HgO_6P_2$	40·7	4·2	13·7	41·2	4·4	13·5
$\frac{1}{2}(Ph_2PCH_2)_2$	>200	$C_{32}H_{24}Co_2HgO_6P_2$	43·8	2·9	13·1	43·4	2·7	13·3
$\frac{1}{2}(Ph_2AsCH_2)_2$	dec. 156	$C_{32}H_{24}As_2Co_2HgO_6$	39·2	2·8		39·5	2·5	
Ph_2MeAs	152—153(d)	$C_{32}H_{26}As_2Co_2HgO_6$	39·8	3·3		39·4	2·7	

[a] °C; determined in sealed tubes; (d) = decomposes on melting and dec. = decomposes without melting.

TABLE 2

Melting points and analyses for the $[L_2Co(CO)_2]_2Hg$ complexes

L	M.p.[a]	Formula	Found (%)			Required (%)		
			C	H	Co	C	H	Co
$(PhO)_3P$	143—144	$C_{76}H_{60}Co_2HgO_{16}P_4$	54·5	3·4	8·0	54·6	3·6	7·1
$PhOP(OCH_2)_2$	83—84	$C_{36}H_{36}Co_2HgO_{16}P_4$	37·3	3·4	9·7	37·1	3·1	10·1
$(2\text{-}ClC_2H_4O)_3P$	81—82	$C_{28}H_{48}Cl_{12}Co_2HgO_{16}P_4$	22·1	3·3	7·5	22·3	3·2	7·8
$(MeO)_3P$	65—66	$C_{16}H_{36}Co_2HgO_{16}P_4$	20·4	4·2	13·0	20·7	3·9	12·8
$PhP(OMe)_2$	133—135	$C_{36}H_{44}Co_2HgO_{12}P_4$	38·7	4·1		38·9	4·0	10·7
$Ph_2P(OMe)$	155—156	$C_{56}H_{52}Co_2HgO_8P_4$	51·9	4·3		51·9	4·0	11·2
Ph_2MeP [b]	212—214(d)	$C_{62}H_{58}Co_2HgO_4P_4$	56·2	4·4		56·8	4·4	9·0
$PhMe_2P$	139—141	$C_{36}H_{44}Co_2HgO_4P_4$	43·6	4·6	11·5	44·0	4·5	12·0
Et_3P	88—90	$C_{28}H_{60}Co_2HgO_4P_4$	36·8	6·5		37·2	6·7	13·1
$\frac{1}{2}[Ph_2PCH_2]_2$	>200	$C_{56}H_{48}Co_2HgO_4P_4$	54·6	4·0	8·9	54·8	3·9	9·6
$\frac{1}{2}[Ph_2AsCH_2]_2$	>200	$C_{56}H_{48}As_4Co_2HgO_4$	48·0	3·6	8·4	47·9	3·4	8·4

[a] See Table 1. [b] Crystallized from C_6H_6–Hexane as $[(Ph_2MeP)_2Co(CO)_2]_2Hg,C_6H_6$ % P found = 8·8, required 9·4.

TABLE 3

Melting points and analyses for some halogenomercury and trichlorotin–cobalt compounds

Compound	M.p.[a]	Formula	Found (%)			Required (%)		
			C	H	Cl	C	H	Cl
$(Ph_2MeAs)Co(CO)_3HgBr,Me_2CO$	dec. 106	$C_{19}H_{19}AsBrCoHgO_4$	31·1	2·4		31·5	2·6	
$(Ph_2AsCH_2)_2\{Co(CO)_3HgBr\}_2$	dec. 96	$C_{32}H_{24}As_2Br_2Co_2Hg_2O_6$	29·3	1·9		28·8	1·8	
$(Ph_2PCH_2)_2Co(CO)_2HgCl,\frac{1}{2}C_6H_6$	dec. 115	$C_{31}H_{27}ClCoHgO_2P_2$	47·2	3·9		47·2	3·4	
$(Ph_2MeAs)Co(CO)_3SnCl_3$	199—200	$C_{16}H_{13}AsCl_3CoO_3Sn$	31·3	2·4	17·6	31·4	2·1	17·4
$Co(CO)_4SnCl_3$	73—75	$C_4Cl_3CoO_4Sn$	11·6		27·1	12·1		26·9
$(Ph_2PCH_2)_2Co(CO)_2SnCl_3$	dec. 145	$C_{28}H_{24}Cl_3CoO_2P_2Sn$	45·2	3·3	14·2	45·5	3·3	14·4

[a] See Table 1.

The reactions of (*a*) $\{(Ph_2MeAs)Co(CO)_3\}_2Hg$ with $HgBr_2$, (*b*) $(dp)Co_2(CO)_6Hg$ with HgI_2, (*c*) $(da)Co_2(CO)_6Hg$ with $HgBr_2$, and (*d*) $\{(dp)Co(CO)_2\}_2Hg$ with $HgCl_2$ were carried out in acetone solution using *ca.* 0·3 g of the cobalt complex and a 1 : 1 mole ratio of reactants. No attempts were made to isolate the products from (*b*), but the i.r. spectrum of the reaction mixture showed that $(dp)Co(CO)_2HgI$, $Co(CO)_4HgI$, and $\{Co(CO)_4\}_2Hg$ were present. For the other reaction mixtures, the solvents were removed at reduced pressures, and the following products purified by crystallization (*a*) $(Ph_2MeAs)Co(CO)_3HgBr,Me_2CO$ from acetone–water, (*c*) $(da)\{Co(CO)_3HgBr\}_2$ from acetone–water, and (*d*) $(dp)Co(CO)_2HgCl,\frac{1}{2}C_6H_6$ from benzene–hexane.

The reactions of tin(IV) chloride with (*a*) $[(Ph_2MeAs)Co(CO)_3]_2Hg$, (*b*) $(dp)Co_2(CO)_6Hg$, and (*c*) $[(dp)Co(CO)_2]_2Hg$ were carried out as described in ref. 9 using reactant mole ratios of 2 : 1. The products were isolated by removal of the solvent at reduced pressure, and purified by crystallization from the following solvents (*a*) $(Ph_2MeAs)Co(CO)_3SnCl_3$ from benzene, (*b*) $(dp)Co(CO)_2SnCl_3$, and $Co(CO)_4SnCl_3$ by fractional crystallization from benzene–hexane, and (*c*) $(dp)Co(CO)_2SnCl_3$ from benzene–hexane.

The melting points and analyses for the new complexes are given in Tables 1—3. Carbon, hydrogen, and halogen

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[9] M. Casey and A. R. Manning, *Chem. Comm.*, 1970, 674; *J. Chem. Soc.* (*A*), 1971, 256.

analyses were carried out in the analytical laboratory of this department, and cobalt was determined colorimetrically.[10]

I.r. spectra were obtained as described previously.[1] The frequencies and relative intensities of absorption bands lying between 1700—2100 cm^{-1}, which are due to the C–O stretching vibrations of the compounds, are summarised in Tables 4—6.

TABLE 4

The i.r. spectra of $\{LCo(CO)_3\}_2Hg$ complexes between 1700—2100 cm^{-1} for carbon disulphide solutions {peak positions (cm^{-1}) with relative intensities in parentheses}

$(PhO)_3P$	1957(sh), 1963(sh), 1969(10), 1980(sh), 2011 (1·25)a, 2022(0·9), 2049(1)a
$PhOP(OCH_2)_2$	1956(sh), 1963(sh), 1969(10), 1982(sh), 2012 (1·0), 2021(1·6), 2046(1·6)
$(2\text{-}ClC_2H_4O)_3P$	1966(10), 2007(4·4)
$(MeO)_3P$	1956(10), 2000(1·25)
$PhP(OMe)_2$	1953(10), 1996(1·4)
$Ph_2P(OMe)$	1949(10), 1991(1·0)
$(Et_2N)_3P$	1930(10), 1976(1·1)
$Ph(Pr^i)P_2$	1941(10), 1986(2·0)
$\frac{1}{2}(Ph_2PCH_2)_2$	1915(5·25), 1968(10), 1994(3·2), 2059(9·0)
$\frac{1}{2}(Ph_2AsCH_2)_2$	1949(10), 1988(5·5), 1999(sh), 2016(1·9), 2073 (2·25)
Ph_2MeAs	1947(10), 1987(1·25)

TABLE 5

The i.r. spectra of $\{L_2Co(CO)_2\}_2Hg$ complexes between 1700—2100 cm^{-1} for carbon disulphide solutions unless otherwise stated. {Peak positions (cm^{-1}) with relative peak heights in parentheses}

L	Absorption bands
$(PhO)_3P$	1937(10), 1959(sh), 1971(4·75), 1990(1·2)
$PhOP(OCH_2)_2$	1936(10), 1972(4), 1991(1·8), 2006(1·9)
$(2\text{-}ClC_2H_4O)_3P$	1917(10), 1952(3·6), 1975(2·6)
$(MeO)_3P$	1908(10), 1943(4), 1966(2·1)
$PhP(OMe)_2$	1903(10), 1937(4·3), 1956(2·1)
Ph_2POMe	1895(10), 1931(4·5), 1948(0·6)
Ph_2MeP	1882(10), 1920(4·1), 1938(2·0)
$PhMe_2P$	1874(10), 1911(4·0), 1932(2·0)
Et_3P	1866(10), 1902(5·0), 1923(2·5)
$\frac{1}{2}\{Ph_2PCH_2\}_2$ [a]	1888(10), 1926(8·6)
$\frac{1}{2}\{Ph_2AsCH_2\}_2$ [a]	1887(10), 1927(8·7)

[a] Chloroform solution.

TABLE 6

The i.r. spectra of some halogenomercury and trichlorotin–cobalt compounds between 1700—2100 cm^{-1}. {Peak positions (cm^{-1}) with peak heights in parentheses}

Compound	Absorption bands
$(Ph_2MeAs)Co(CO)_3HgBr$ [a]	1962(10), 2029(0·6)
$(Ph_2AsCH_2)_2\{Co(CO)_3HgBr\}_2$ [b]	1970(10), 2033(0·5)
$(Ph_2PCH_2)_2Co(CO)_2HgCl$ [a]	1930(10), 1977(5)
$(Ph_2MeAs)Co(CO)_3SnCl_3$ [b]	2000(10), 2061(0·3)
$Co(CO)_4SnCl_3$ [c]	2046(10), 2067(2·6), 2118(5)
$(Ph_2PCH_2)_2Co(CO)_2SnCl_3$ [c]	1963(10), 1895(sh), 2011(5·5), 2032(2·25)

[a] Carbon disulphide solution. [b] Chloroform solution. [c] n-Hexane solution.

RESULTS AND DISCUSSION

The two series of complexes, $[LCo(CO)_3]_2Hg$ and $[L_2Co(CO)_2]_2Hg$ [L = Et_3P, $PhMe_2P$, $Ph(Pr^i{}_2)P$, Ph_2MeP, $(Et_2N)_3P$, Ph_2POMe, $PhP(OMe)_2$, $(MeO)_3P$, $(2\text{-}ClC_2H_4O)_3P$, $PhOP(OCH_2)_2$, $(PhO)_3P$, or Ph_2MeAs; see Tables 1 and 2] are yellow to orange crystalline solids. With the exception of the insoluble $\{(dp)Co(CO)_2\}_2Hg$ and $[(da)Co(CO)_2]_2Hg$ derivatives, they are soluble in organic solvents. Although stable towards oxidation in the solid state, the compounds are darkened by light, and they decompose slowly in solution. The tetrasubstituted derivatives are more readily attacked than their bis-substituted counterparts.

The initial reactions of the ligands with $[Co(CO)_4]_2Hg$ to give $L_2Co_2(CO)_6Hg$ complexes are rapid in the dark, but further substitution requires more drastic conditions or longer reaction times. It proceeds most readily for L = $(MeO)_3P$, $(2\text{-}ClC_2H_4O)_3P$, and $PhP(OMe)_2$, but does not occur at all for L = $Ph(Pr^i)_2P$, or $(Et_2N)_3P$, where there may be a steric limitation upon tetrasubstitution imposed by their greater bulk, or for Ph_2MeAs.

The i.r. spectra of all $\{LCo(CO)_3\}_2Hg$ derivatives, except for L = $(PhO)_3P$ or $PhOP(OCH_2)_2$, show only two absorption bands which may be attributed to C–O stretching vibrations (Table 4). Their relative intensities indicate that these complexes have D_{3d} symmetry and molecular structures similar to that found for $\{(Et_3P)Co(CO)_3\}_2Hg$.[11] The i.r. spectra of this class of compounds have been discussed and assigned elsewhere.[1,2]

It is clear that $[\{(PhO)_3P\}Co(CO)_3]_2Hg$ and $[\{PhOP(OCH_2)_2\}Co(CO)_3]_2Hg$ cannot have symmetrical structures. Their i.r. spectra (Table 4) show four well-resolved absorption bands due to their ν(CO) vibrations together with a number of shoulders. It is possible that a number of isomers of these compounds are present in solution, but the spectra are independent of solvent, and that of the triphenyl phosphite derivative is the same in the solid as in its solutions. Therefore it is more likely that either the Co–Hg–Co system is non-linear, or that one or more of the phosphite ligands occupies an equatorial co-ordination position of mercury cobalt carbonyl.[12,13]

On the basis of its i.r. spectrum, it has been suggested that $\{(dp)Co(CO)_2\}_2Hg$ has a centrosymmetric structure based on that of $\{Co(CO)_4\}_2Hg$ with the bidentate ligand occupying an axial and an equatorial co-ordination position about each cobalt atom.[3] It is clear that $\{(da)Co(CO)_2\}_2Hg$ has a similar structure, but that the $\{L_2Co(CO)_2\}_2Hg$ derivatives of monodentate ligands do not. Their spectra show three absorption bands which may be assigned to their ν(CO) vibrations. It is difficult to reconcile the observed intensity patterns (Table 5) with any molecular structure involving trigonal bipyramidal co-ordination about the cobalt atoms, a linear Co–Hg–Co system, and a staggered arrangement of the two sets of equatorial ligands. It is possible that either these complexes exist as isomers in solution or that Co–Hg–Co is non-linear. However, in view of the centrosymmetric nature of $\{(dp)Co(CO)_2\}_2Hg$, it is more probable that a relatively small rotation of one $L_2Co(CO)_2$

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[10] 'Organic Reagents for Metals,' ed. W. C. Johnson, Hopkins and Williams Ltd., vol. 2, p. 139.

[11] R. F. Bryan and A. R. Manning, *Chem. Comm.*, 1968, 1316.

[12] G. Bor and L. Marko, *Spectrochim. Acta*, 1960, **16**, 1105.

[13] G. M. Sheldrick and R. N. F. Simpson, *Chem. Comm.*, 1967, 1015; *J. Chem. Soc.* (*A*), 1968, 1005.

moiety relative to the other produces a molecule which is not perfectly centrosymmetric. This, or any other small distortion, would allow the totally symmetric ν(CO) mode of these complexes, which has the highest frequency, to become i.r. allowed and to give rise to a weak absorption band.

The spectra of (dp)$Co_2(CO)_6Hg$ and (da)$Co_2(CO)_6Hg$ show marked differences, and it is unlikely that these compounds have similar structures. On the basis of their reactions with mercuric halides and stannic chloride (see later), it is suggested that they are best formulated as (dp)$Co(CO)_2HgCo(CO)_4$ and (da)$\{Co(CO)_3\}_2Hg$. In the first, the diphosphine is probably co-ordinated to an equatorial and the axial co-ordination position of a single cobalt atom of mercury cobalt carbonyl. The i.r. spectrum of the compound is consistent with this suggestion. In the second complex, the bidentate arsine bridges two cobalt atoms; the solubility of this complex tends to rule out a dimeric structure.

The reactions of M_2Hg complexes [*M* is a transition-metal group, *e.g.* $Fe(CO)_3NO$] with either mercury(II) halides [14] or tin(IV) chloride [9] under mild conditions yield MHgX or $MSnCl_3$ derivatives which contain one transition-metal group only. The spectra of these are often simpler than those of the parent compounds. The symmetrical complexes $[(Ph_2MeAs)Co(CO)_3]_2Hg$, $[(dp)Co(CO)_2]_2Hg$, and $[(da)Co(CO)_2]Hg$ react to give $(Ph_2MeAs)Co(CO)_3X$, (dp)$Co(CO)_2Y$, and (da)$Co(CO)_2X$ (X = HgBr or $SnCl_3$; Y = HgCl or $SnCl_3$). The i.r. spectra of all six compounds (Table 6) are consistent with molecular structures in which there is trigonal bipyramidal co-ordination about the cobalt atoms with either two or three of the equatorial co-ordination positions occupied by the carbonyl groups. The spectrum of (dp)$Co(CO)_2SnX_3$ indicates that this probably exists as a mixture of isomers in solution.

The reaction of (dp)$Co_2(CO)_6Hg$ with mercuric iodide gives a complex mixture of products. They may be identified as (dp)$Co(CO)_2HgI$, $Co(CO)_4HgI$, and $\{Co(CO)_4\}_2Hg$ by means of i.r. spectroscopy. The third compound arises from disproportionation of the second [*cf.* $Fe(CO)_3(NO)HgI$ [14]]. No attempt was made to separate these products, but if $SnCl_4$ is used in place of HgI_2, (dp)$Co(CO)_2SnCl_3$, and $Co(CO)_4SnCl_3$ are the only compounds formed, and both have been isolated (Tables 3 and 6).

Mercury(II) bromide converts (da)$Co_2(CO)_6Hg$ into a single product, (da)$[Co(CO)_3HgBr]_2$. It has an i.r. spectrum which is very similar to that of *trans*-$(Ph_2MeAs)Co(CO)_3HgBr$ (Table 6). Consequently it is formulated as the all-*trans* $BrHgCo(CO)_3As(Ph)_2CH_2CH_2(Ph)_2AsCo(CO)_3HgBr$ with trigonal bipyramidal co-ordination about the cobalt atoms and a bridging bidentate ditertiary arsine ligand.

These observations are consistent with the structures proposed for the hexacarbonyl complexes *viz.* (dp)$Co(CO)_2HgCo(CO)_4$ and (da)$\{Co(CO)_3\}_2Hg$.

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[14] M. Casey and A. R. Manning, *J. Chem. Soc.* (*A*), 1970, 2258, and references therein.