Synthesis of Novel Mercury(I) Complexes containing a Linear Chain Co–Hg–Hg–Co. *X*-Ray Crystal Structure of the Complex $[\{Co[N(CH_2CH_2PPh_2)_3]\}_2(\mu\text{-}Hg_2)]\cdot$thf *

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Reduction of the cobalt(II) complexes $[CoLCl]BPh_4$ [L = $N(CH_2CH_2PPh_2)_3$ (dppea) or $P(CH_2CH_2PPh_2)_3$ (dppep)] with sodium amalgam gives tetrametallic complexes of formula $[(CoL)_2(\mu\text{-}Hg_2)]$. The structure of $[\{Co(dppea)\}_2(\mu\text{-}Hg_2)]\cdot$thf was determined from three-dimensional *X*-ray data collected by the counter method. The crystals are triclinic, space group $P\bar{1}$, with a = 25.691(9), b = 13.387(5), c = 13.471(4) Å, α = 119.56(8), β = 97.51(8), γ = 87.25(7)°, and Z = 2. Full-matrix least-squares refinement converged at the conventional R factor of 0.067 for 2 687 observed reflections. The structure consists of dimeric units of $[\{Co(dppea)\}_2(\mu\text{-}Hg_2)]$ where the Hg_2^{2+} ion linearly bridges two Co(dppea) fragments. The dppea derivative reacts with carbon monoxide or carbon dioxide, at room temperature and atmospheric pressure, with formation of the carbonyl complex $[Co(dppea)(CO)]BPh_4$.

Several of our earlier papers have shown that the tripod-like polytertiary phosphines are ligands suitable for stabilization of low oxidation states of 3*d* metals.[1] In particular, the tetradentate ligands tris(2-diphenylphosphinoethyl)amine, $N(CH_2CH_2PPh_2)_3$ (dppea), and tris(2-diphenylphosphinoethyl)phosphine, $P(CH_2CH_2PPh_2)_3$ (dppep), by enveloping the metal ion, usually permit the further co-ordination of only one group. The latter, shielded by the numerous phenyl rings of the phosphine ligand, generally shows a reduced reactivity. Furthermore, sometimes these tripod ligands can co-ordinate by themselves to the central metal atom producing unusual trigonal pyramidal species such as [Ni(dppea)],[1c] $[Co(dppea)]^+$,[1b] and $[Ni(dppep)]^+$.[1g]

By reaction of the five-co-ordinate complexes $[CoLCl]^+$ (L = dppea or dppep)[2,3] with sodium amalgam we have obtained the novel derivatives $[(CoL)_2(\mu\text{-}Hg_2)]$ which contain the Hg_2^{2+} ion as a linear bridge between the cobalt atoms. As far as we know, although there are several examples containing the Hg^{2+} ion binding two transition-metal atoms, these are the first compounds where the dinuclear Hg_2^{2+} ion is involved in such bonding.

A preliminary report has been previously published.[4]

Experimental

Both $[Co(dppea)Cl]BPh_4$[2] and $[Co(dppep)Cl]BPh_4$[3] were prepared according to procedures described elsewhere. Owing to the air sensitivity of the complexes, the preparations were carried out under a dry oxygen-free nitrogen atmosphere. All solvents were dried and distilled by standard methods.

Preparation of $[\{Co(dppea)\}_2(\mu\text{-}Hg_2)]\cdot$thf.—The compound $[Co(dppea)Cl]BPh_4$ (1 mmol) was added to a suspension of excess of Na–Hg (1.5%) in tetrahydrofuran (thf) (50 cm^3). Continuous magnetic stirring at *ca.* 50 °C caused the mixture to become deep red in *ca.* 30 min. The solution was filtered and dry n-butanol (50 cm^3) added. After cooling at room temperature, deep red crystals precipitated (yield *ca.* 50%). The compound can be recrystallized from thf–n-butanol (1 : 1) (Found: C, 54.95; H, 5.2; Co, 5.95; N, 1.35; P, 9.7. Calc. for $C_{84}H_{84}Co_2Hg_2N_2P_6\cdot C_4H_8O$: C, 55.65; H, 4.9; Co, 6.2; N, 1.5; P, 9.8%).

Preparation of $[\{Co(dppep)\}_2(\mu\text{-}Hg_2)]$.—The complex was prepared by an analogous method, as orange-brown crystals (yield *ca.* 35%) (Found: C, 53.1; H, 4.9; Co, 5.85; Hg, 21.4. Calc. for $C_{84}H_{84}Co_2Hg_2P_8$: C, 54.25; H, 4.55; Co, 6.35; Hg, 21.55%).

Reaction of $[\{Co(dppea)\}_2(\mu\text{-}Hg_2)]$ *with* CO.—Carbon monoxide was bubbled through a solution of $[\{Co(dppea)\}_2(\mu\text{-}Hg_2)]$ (0.5 mmol) in thf (50 cm^3) at room temperature and atmospheric pressure for 30 min. The colour turned red-orange while metallic mercury precipitated. The mercury was separated by decantation, di-n-butyl ether (25 cm^3) was added, and the resulting solution was concentrated by bubbling through a fast stream of nitrogen. A red-orange oil separated; then $NaBPh_4$ (1 mmol) in thf (10 cm^3) was added and immediately red-orange crystals precipitated. Analytical and i.r. spectroscopic data indicate this compound as the previously known carbonyl derivative $[Co(dppea)(CO)]BPh_4$[1c] (yield 75%). All attempts to crystallize the red-orange oil, without reaction with $NaBPh_4$, were unsuccessful.

Reaction of $[\{Co(dppea)\}_2(\mu\text{-}Hg_2)]$ *with* CO_2.—Carbon dioxide was bubbled through a solution of $[\{Co(dppea)\}_2(\mu\text{-}Hg_2)]$ (0.5 mmol) in thf (100 cm^3) at room temperature and atmospheric pressure for 4 h. The colour slowly turned red-orange while very thin drops of mercury together with a greyish powder precipitated. The solid was separated by decantation and the resulting solution was treated as in the previous reaction as long as crystals of $[Co(dppea)(CO)]BPh_4$[1c] (yield 30%) were obtained. The insoluble greyish powder was filtered off, washed with thf, and dried *in vacuo*. This material evolved CO_2 on treatment with HCl and its i.r. spectrum showed a broad, strong band at 1 400—1 450 cm^{-1}. A qualitative analysis of it showed the presence of cobalt.

Crystal Data for $[\{Co(dppea)\}_2(\mu\text{-}Hg_2)]\cdot$thf.—$C_{88}H_{92}Co_2Hg_2N_2OP_6$, M = 1 898.61, Triclinic, space group $P\bar{1}$, a = 25.691(9), b = 13.387(5), c = 13.471(4) Å, α = 119.56(8),

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* Bis{[tris(2-diphenylphosphinoethyl)amine-*NP′P″P‴*]cobaltio}-dimercury (*Hg–Hg*).

Supplementary data available (No. SUP 23452, 20 pp): structure factors, thermal parameters, bond distances and angles. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Atomic co-ordinates (× 10^4) for [{Co(dppea)}$_2$(μ-Hg$_2$)]·thf with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Hg(1)	2 134(1)	−2 061(2)	607(2)
Hg(2)	3 171(1)	−1 846(2)	1 058(2)
Co(1)	1 184(3)	−2 261(7)	204(7)
Co(2)	4 129(3)	−1 707(6)	1 439(7)
P(1)	1 167(5)	−1 741(11)	−1 058(11)
P(2)	1 212(5)	−4 024(10)	−299(11)
P(3)	1 089(5)	−999(10)	1 937(11)
P(4)	4 104(5)	−51(11)	2 920(12)
P(5)	4 182(5)	−1 827(11)	−203(11)
P(6)	4 168(5)	−3 185(11)	1 626(11)
N(1)	351(15)	−2 439(33)	−150(35)
N(2)	4 945(17)	−1 579(36)	1 725(37)
C(1)	198(20)	−2 625(45)	−1 359(47)
C(2)	451(16)	−1 823(33)	−1 586(34)
C(3)	163(19)	−3 471(43)	−104(42)
C(4)	535(15)	−4 521(33)	−639(35)
C(5)	89(19)	−1 374(42)	682(46)
C(6)	375(17)	−927(35)	1 967(38)
C(7)	1 338(10)	−281(25)	−765(22)
C(8)	1 683(10)	439(25)	200(22)
C(9)	1 823(10)	1 515(25)	381(22)
C(10)	1 620(10)	1 871(25)	−404(22)
C(11)	1 276(10)	1 151(25)	−1 369(22)
C(12)	1 135(10)	75(25)	−1 550(22)
C(13)	1 498(12)	−2 538(22)	−2 402(23)
C(14)	2 023(12)	−2 252(22)	−2 315(23)
C(15)	2 303(12)	−2 852(22)	−3 256(23)
C(16)	2 057(12)	−3 737(22)	−4 285(23)
C(17)	1 531(12)	−4 023(22)	−4 372(23)
C(18)	1 252(12)	−3 423(22)	−3 431(23)
C(19)	1 477(8)	−4 570(21)	706(26)
C(20)	1 173(8)	−4 700(21)	1 423(26)
C(21)	1 407(8)	−5 032(21)	2 207(26)
C(22)	1 945(8)	−5 234(21)	2 275(26)
C(23)	2 249(8)	−5 104(21)	1 559(26)
C(24)	2 015(8)	−4 772(21)	774(26)
C(25)	1 480(11)	−5 206(19)	−1 584(26)
C(26)	1 827(11)	−4 922(19)	−2 125(26)
C(27)	2 048(11)	−5 787(19)	−3 066(26)
C(28)	1 921(11)	−6 936(19)	−3 466(26)
C(29)	1 574(11)	−7 220(19)	−2 925(26)
C(30)	1 354(11)	−6 355(19)	−1 984(26)
C(31)	1 326(11)	521(24)	2 620(25)
C(32)	1 845(11)	778(24)	3 140(25)
C(33)	2 050(11)	1 886(24)	3 597(25)
C(34)	1 736(11)	2 737(24)	3 533(25)
C(35)	1 217(11)	2 480(24)	3 013(25)
C(36)	1 012(11)	1 372(24)	2 557(25)
C(37)	1 284(11)	−1 185(22)	3 217(23)
C(38)	1 685(11)	−1 913(22)	3 248(23)
C(39)	1 841(11)	−1 955(22)	4 259(23)
C(40)	1 596(11)	−1 268(22)	5 238(23)
C(41)	1 195(11)	−539(22)	5 207(23)
C(42)	1 039(11)	−498(22)	4 196(23)
C(43)	5 183(16)	−1 918(35)	600(38)
C(44)	4 868(17)	−1 397(35)	−14(37)
C(45)	5 203(19)	−2 404(44)	2 148(42)
C(46)	4 865(17)	−3 513(36)	1 584(37)
C(47)	5 137(16)	−372(36)	2 636(39)
C(48)	4 791(18)	170(36)	3 578(38)
C(49)	3 959(11)	1 308(24)	2 847(25)
C(50)	3 432(11)	1 585(24)	2 732(25)
C(51)	3 300(11)	2 602(24)	2 719(25)
C(52)	3 694(11)	3 342(24)	2 822(25)
C(53)	4 220(11)	3 064(24)	2 938(25)
C(54)	4 353(11)	2 047(24)	2 951(25)
C(55)	3 749(10)	351(24)	4 210(27)
C(56)	3 835(10)	1 457(24)	5 145(27)
C(57)	3 518(10)	1 870(24)	6 029(27)
C(58)	3 116(10)	1 178(24)	5 978(27)
C(59)	3 029(10)	72(24)	5 043(27)
C(60)	3 346(10)	−341(24)	4 159(27)
C(61)	4 082(12)	−3 246(29)	−1 615(31)
C(62)	3 573(12)	−3 652(29)	−2 140(31)
C(63)	3 497(12)	−4 671(29)	−3 188(31)
C(64)	3 929(12)	−5 284(29)	−3 712(31)
C(65)	4 437(12)	−4 878(29)	−3 187(31)
C(66)	4 513(12)	−3 859(29)	−2 138(31)
C(67)	3 826(12)	−931(26)	−756(21)
C(68)	3 419(12)	−229(26)	−207(21)
C(69)	3 102(12)	300(26)	−729(21)
C(70)	3 192(12)	126(26)	−1 802(21)
C(71)	3 599(12)	−577(26)	−2 352(21)
C(72)	3 916(12)	−1 105(26)	−1 829(21)
C(73)	3 860(10)	−4 620(28)	604(21)
C(74)	3 929(10)	−5 524(28)	841(21)
C(75)	3 638(10)	−6 544(28)	155(21)
C(76)	3 279(10)	−6 658(28)	−768(21)
C(77)	3 211(10)	−5 754(28)	−1 005(21)
C(78)	3 501(10)	−4 734(28)	−319(21)
C(79)	4 020(10)	−3 148(24)	3 000(23)
C(80)	3 492(10)	−3 268(24)	3 068(23)
C(81)	3 345(10)	−3 299(24)	4 014(23)
C(82)	3 728(10)	−3 211(24)	4 892(23)
C(83)	4 256(10)	−3 091(24)	4 824(23)
C(84)	4 402(10)	−3 060(24)	3 878(23)
O *	−266(33)	−6 636(86)	−3 720(71)
C(85) *	25(45)	−7 723(90)	−4 655(93)
C(86) *	368(38)	−7 202(100)	−4 896(81)
C(87) *	276(40)	−5 992(87)	−4 388(82)
C(88) *	−157(38)	−5 748(77)	−3 812(73)

Atoms labelled (*) belong to the solvent molecule.

$\beta = 97.51(8)$, $\gamma = 87.25(7)°$, $U = 3\,994.48$ Å^3, $Z = 2$, $D_c = 1.78$ g cm^{-3}, λ(Mo-K_α) = 0.7107 Å, μ(Mo-K_α) = 44.0 cm^{-1}.

Data Collection.—Data collection was carried out on a Philips PW 1 100 four-circle diffractometer with Mo-K_α radiation monochromatized with a graphite crystal. A crystal of dimensions *ca.* 0.22 × 0.15 × 0.10 mm was coated in paraffin to prevent air decomposition. The cell dimensions were determined by least-squares refinements of the setting angles of 22 carefully centred reflections. Reflections within $2\theta \leqslant 40°$ were collected at a scan rate of 0.08° s^{-1} using the ω—2θ scan technique with a scan width calculated according to the formula of Alexander and Smith,[5] scan range = $A + B\tan\theta$ with $A = 0.70°$ and $B = 0.69$. Stationary background measurements were taken before and after each scan for a time equal to half the scan time. The intensities of three reflections measured every 2 h were used to establish on a common scale the observed intensities which showed at the end of the data collection a decay of *ca.* 25%. After correction for background the intensities were assigned standard deviations calculated as described elsewhere [6] using a value of 0.03 for the instability factor *K*. 2 687 Reflections having $I \geqslant 3\sigma(I)$ were considered observed.

Structure Solution and Refinement.—All the calculations were carried out on a SEL 32/70 computer using the SHELX 76 programs.[7] Atomic scattering factors of the appropriate neutral atoms were taken from ref. 8. Both the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms.[9] The structure was solved by the heavy-

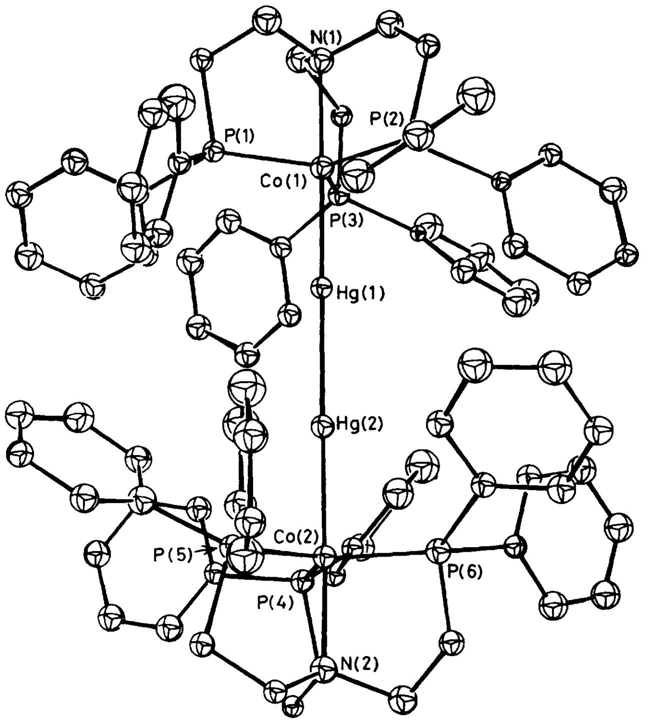

Figure. Perspective view of the $[\{Co(dppea)\}_2(\mu\text{-}Hg_2)]$ molecule

atom technique. Several Fourier maps revealed all the non-hydrogen atoms. Full-matrix least-squares refinements were carried out, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ with the weights $w = 1/\sigma^2(F_o)$. The 12 phenyl rings were treated as rigid groups with d(C–C) = 1.395 Å, each carbon atom being assigned an individual thermal parameter. Owing to the large number of variables exceeding the capacity of the programs, even the heavy atoms were assigned isotropic thermal parameters. Refinements converged at values of 0.067 and 0.064 for the R and R' factors respectively. The agreement factors are defined as $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R' = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. Final positional parameters are given in Table 1.

Results and Discussion

As reported in previous papers,[1c,10] by reacting the five-co-ordinate cobalt(II) complexes [CoLCl]BPh$_4$ (L = dppea or dppep) in thf solution with sodium tetrahydroborate as a reducing agent, cobalt(I) hydride derivatives have been obtained.

When sodium amalgam is used in place of sodium tetrahydroborate as reducing agent, the tetranuclear cobalt(−I) compounds $[(CoL)_2(\mu\text{-}Hg_2)]$ are formed [equation (1)]. The

$$2[CoLCl]^+ + 4Na + 2Hg \longrightarrow [(CoL)_2(\mu\text{-}Hg_2)] + 2NaCl + 2Na^+ \quad (1)$$

crystalline compounds are diamagnetic and scarcely soluble without decomposition in organic solvents such as thf and benzene. Both the complexes decompose in air: the dppea derivative immediately, the dppep in some minutes.

The structure of the complex $[\{Co(dppea)\}_2(\mu\text{-}Hg_2)]$·thf consists of discrete molecules of $[(dppea)Co(\mu\text{-}Hg_2)Co(dppea)]$ with interspersed tetrahydrofuran solvent. The Figure shows a perspective view of the molecule and Table 2 reports selected bond distances and angles (for other bond distances and angles see SUP 23452).

Table 2. Selected bond distances (Å) and angles (°) for $[\{Co(dppea)\}_2(\mu\text{-}Hg_2)]$·thf, with estimated standard deviations in parentheses

Hg(1)-Hg(2)	2.651(4)	Co(2)-Hg(2)	2.444(9)
Co(1)-Hg(1)	2.429(9)	Co(2)-P(4)	2.13(1)
Co(1)-P(1)	2.13(2)	Co(2)-P(5)	2.16(2)
Co(1)-P(2)	2.11(1)	Co(2)-P(6)	2.11(2)
Co(1)-P(3)	2.14(1)	Co(2)-N(2)	2.08(4)
Co(1)-N(1)	2.13(4)		
Hg(2)-Hg(1)-Co(1)	179.7(2)	N(1)-Co(1)-P(3)	88.2(1.2)
Hg(1)-Hg(2)-Co(2)	178.4(3)	Hg(2)-Co(2)-N(2)	178.4(1.5)
Hg(1)-Co(1)-N(1)	179.9(1.2)	Hg(2)-Co(2)-P(4)	91.8(4)
Hg(1)-Co(1)-P(1)	92.0(5)	Hg(2)-Co(2)-P(5)	91.1(5)
Hg(1)-Co(1)-P(2)	91.8(5)	Hg(2)-Co(2)-P(6)	91.8(5)
Hg(1)-Co(1)-P(3)	91.9(5)	P(4)-Co(2)-P(5)	119.1(6)
P(1)-Co(1)-P(2)	119.6(6)	P(4)-Co(2)-P(6)	119.6(7)
P(1)-Co(1)-P(3)	119.2(6)	P(5)-Co(2)-P(6)	121.1(6)
P(2)-Co(1)-P(3)	120.9(7)	N(2)-Co(2)-P(4)	88.7(1.2)
N(1)-Co(1)-P(1)	88.1(1.3)	N(2)-Co(2)-P(5)	87.4(1.4)
N(1)-Co(1)-P(2)	88.1(1.2)	N(2)-Co(2)-P(6)	89.3(1.4)

The Hg_2^{2+} ion linearly bridges two Co(dppea) moieties so that the four metal atoms of the Co–Hg–Hg–Co fragment are collinear, with Co(1)–Hg(1)–Hg(2) and Hg(1)–Hg(2)–Co(2) angles of 179.7(2) and 178.4(3)° respectively. The mercury atoms are two-co-ordinate being shielded by the 12 phenyl rings of the dppea ligands. The shortest contact distance between the carbon atoms of the phenyl rings and the mercury atoms is 3.48 Å. The Hg–Hg bond distance of 2.651(4) Å may be compared with those reported for mercury(I) compounds and ranging from 2.50 to 2.69 Å.[11]

Each cobalt atom is five-co-ordinate by the four donor atoms of the dppea ligand and by one mercury atom in a trigonal bipyramidal geometry. Although the molecule has no imposed crystallographic symmetry, corresponding bond distances and angles in the two co-ordination polyhedra do not show significant differences. Deviations from the idealized trigonal bipyramidal geometry are particularly small, the only significant distortion being the displacements, 0.07 and 0.06 Å, of the cobalt atoms from the equatorial planes towards the mercury atoms occupying the axial positions.

The values of the two Hg–Co bond distances, which are equal within experimental errors [2.429(9) and 2.444(9) Å], are slightly shorter than those of 2.498(7) and 2.500(7) Å reported for $[\{Co(CO)_4\}_2(\mu\text{-}Hg)]$.[12] The replacement of the carbonyl group *trans* to the mercury by a nitrogen can probably account for the shorter Hg–Co bond distance in the title compound.

An analogous structure can be attributed to the dppep derivative, whose reduced reactivity with respect to the dppea compound can be attributed to the different set of donor atoms (P_4 *vs.* NP_3) which seems to be more suitable to stabilize the very low oxidation state of the cobalt atom.

It is well known that reaction of sodium amalgam with cobalt carbonyl complexes under particular conditions produces the stable mercury(II) derivative of formula $[\{Co(CO)_4\}_2(\mu\text{-}Hg)]$.[13] In the present case the unexpected stabilization of mercury(I) derivatives may be attributed to the particular conformation of the tetradentate tripod-like ligands dppea and dppep. In fact a closer approach of CoL moieties such as in the hypothetical species $(CoL)_2(\mu\text{-}Hg)$ (L = dppea or dppep) is probably prevented by the steric requirements of these bulky ligands. This is in agreement with the finding of some contact distances of *ca.* 3.7—3.8 Å between the phenyl groups of the two Co(dppea) moieties in the structure of the dppea complex. On the other hand it is reasonable to admit that in the present complexes the numerous phenyl groups of the ligands, by shielding the Hg_2^{2+} ion, prevent the possible disproportionation process ($Hg_2^{2+} \longrightarrow Hg^{2+} + Hg$) towards the more stable Hg^{2+} species.

The compound [{Co(dppea)}$_2$(μ-Hg_2)] rapidly reacts in thf solution with carbon monoxide at room temperature and atmospheric pressure to form metallic mercury and a red-orange solution. From this solution an orange oil, which we were unable to crystallize, can be isolated. This oil, by addition of $NaBPh_4$, forms the previously reported, red-orange carbonyl derivative [Co(dppea)(CO)]BPh_4[1c] in high yield (75%). Unfortunately the mechanism of this reaction remains unknown: clearly there are some unidentified species (from the system or outside) which oxidize the cobalt to the formal oxidation state of +1. Interestingly, the same final product, [Co(dppea)-(CO)]BPh_4, can be obtained by reaction of [{Co(dppea)}$_2$-(μ-Hg_2)] with carbon dioxide, in similar conditions. In this case the reaction is slower, the yield is smaller (30%), and some other insoluble material in addition to the metallic mercury is obtained. There is evidence for CO_3^{2-} in this material: indeed it evolves CO_2 by treatment with HCl and its i.r. spectrum shows a broad, strong band at 1 400—1 450 cm^{-1}. The formation of [Co(dppea)(CO)]$^+$ in this latter reaction can be attributed probably to the reductive disproportionation process of CO_2 to CO and CO_3^{2-} which has been observed previously in some reactions of CO_2 with organometallic systems.[14] However, other redox processes, involving displaced dppea or external moisture, cannot be ruled out.

A systematic investigation on the reactivity of these mercury(I) complexes is in progress.

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