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The structure and reactivity of phenylacetylene-derived metallacycles containing cobalt and mercury

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Abstract

The crystal structure of the product of the reaction of phenylacetylene and $Hg[Co(CO)_4]_2$, viz. $(C_6H_5)_2C_4H_2[Co(CO)_2HgCo(CO)_4]_2$ (**1**) was determined by X-ray diffraction (space group $C2/c$; $Z = 8$; $R = 0.051$; a 22.08, b 11.62, c 28.08 Å; β 114.78°) to be a C_4Co_2-containing dimetallacycle the cobalt–cobalt bond distance of which (2.548(3) Å) is asymmetrically bridged by the mercury atom of an $HgCo(CO)_4$ moiety. The three-coordinate, bridging mercury atom, Hg(2), is 2.553(2) Å from the π-bonded cobalt and 2.641(2) Å from the σ-bonded cobalt of the metallacycle. This bridged Hg is compared to the semi-bridging CO in the iron metallacycles, $Fe_2(CO)_6(C_4R_4)_2$. The two-coordinate mercury, Hg(1), of the second $HgCo(CO)_4$ group is 2.475(2) Å from the σ-bonded cobalt fo the metallacycle. Symmetrization reaction of **1** gave previously known $Hg\{Co_2(CO)_4(C_6H_5C_2H)_2[HgCo(CO)_4]\}_2$ (**2**), the structure of which was also determined by X-ray diffraction (space group $P\bar{1}$; $Z = 1$; $R = 0.065$; a 11.448, b 12.757, c 10.353 Å; α 94.37, β 75.49, γ 66.87°). Compound **2** contains two $[HgCo(CO)_4]$-bridged metallacyclic units symmetrically disposed about a third Hg atom. The metal–metal distances of compound **2** are similar to those in **1**. Sodium amalgam reduction of **1** gave, in addition to $NaCo(CO)_4$, an anion postulated to be $[(CO)_2Co(\eta^5\text{-}C_5H_2(C_6H_5)_2O)]^-$ (**3**) on the basis of its reaction with acetyl chloride to give 1-acetoxy-2,5-diphenylcyclopentadienyldicarbonylcobalt (**4**). Although no reaction was observed with acetic acid, treatment of **3** with trifluoroacetic acid produced a hydroxy-derivative, **5** analogous to the acetoxy compound, **4**.

Introduction

In the course of a study of the reactions between mono-substituted acetylenes with $Hg[Co(CO)_4]_2$, several compounds, having the general formula, $R_2C_4H_2Co_2(CO)_4[HgCo(CO)_4]_2$, were discovered; a cyclobutadiene sandwich structure was proposed [1]. Later, a "fly-over bridge" structure was suggested instead [2].

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In this paper, the results of an X-ray crystal structure determination of the phenyl derivative, $(C_6H_5)_2C_4H_2[Co(CO)_2[HgCo(CO)_4]_2$ (**1**), are presented. Compound **1** had been shown [1] to condense to $Hg\{Co[HgCo(CO)_4](CO)_2C_4H_2Ph_2\}_2$ (**2**), the structure of which is reported here as well. The reduction of **1** with sodium amalgam and the properties and some reactions of the resulting novel anion are described.

Results and discussion

Crystal structure of $Ph_2C_4H_2[Co(CO)_2HgCo(CO)_4]_2$ *(1)*

A perspective view of the molecule is shown in Fig. 1. Selected inter-atomic distances and angles are collected in Tables 1 and 2, respectively. The structure determination revealed that **1** is a dicobalt metallacycle coordinated by four carbonyl ligands and two $HgCo(CO)_4$ groups. It is similar, in some ways, to a 'flyover bridge' structure suggested by Maitlis [2].

An unusual feature of the structure is the asymmetric mercury bridge over the Co–Co bond. A $HgCo(CO)_4$ moiety has been seen to bridge a single metal–metal bond in only one other compound, viz. the salt, $[NEt_4{}^+][\{Co_2(CO)_7Ge\}\{Co_2(CO)_6\text{-}[HgCo(CO)_4]\}]^-$, which has $(CO)_7Co_2Ge$ and $(CO)_4CoHg$ groups bridging the same Co–Co bond [3]. A face bridging $(CO)_4CoHg$ unit has been observed in the cluster $RuCo_3(CO)_6HgCo(CO)_4$ [4]. A few similar derivatives with other one-electron metal donor ligands on mercury are known, e.g. $(PPN)[Fe_4(CO)_{18}HgMo(CO)_3Cp]$ in which Hg bridges an Fe–Fe bond [5].

The Co(1)–Co(2) distance of 2.548(3) Å in **1** is similar to that found in compounds commonly considered to have a cobalt–cobalt bond, e.g. $Co_2(CO)_8$ (2.52 Å) [6], $Cp_2Co_2(\mu\text{-}P(C_6H_5)_2)_2$ (2.56 Å) [7], and $Co_2(CO)_5(C_8H_{12})_2$ (2.46 Å) [8]. The last named complex and **1** share many structural features.

The coordination sphere of Co(1) in **1** can be described as a face-capped pseudo-octahedron; occupying approximately octahedral sites are C(1), C(4), Hg(1),

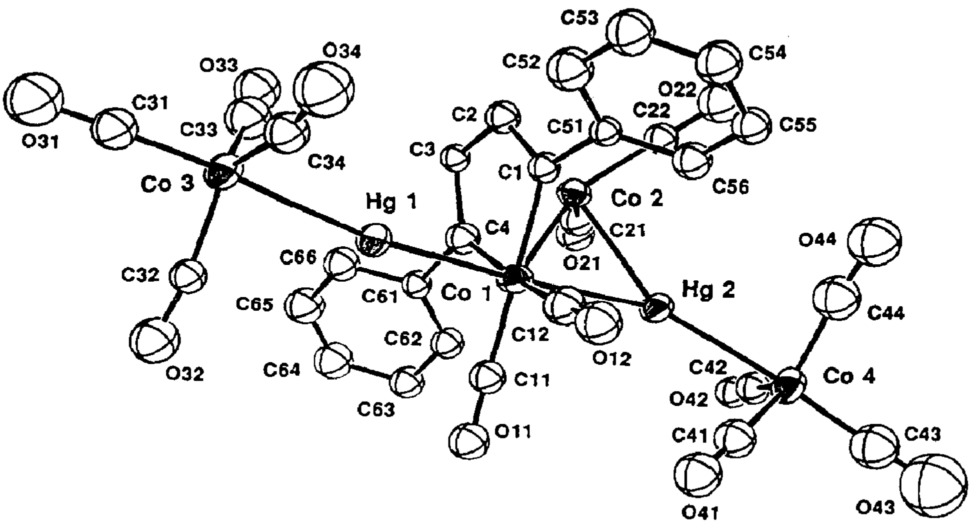

Fig. 1. An ORTEP drawing of **1**, with thermal ellipsoids at 30% probability.

Table 1

Selected interatomic distances for compound 1 in Å. [a]

Hg(1)-Co(1)	2.475(2)	C(1)-C(2)	1.43(2)
Hg(1)-Co(3)	2.552(2)	C(2)-C(3)	1.42(2)
Hg(2)-Co(2)	2.553(2)	C(3)-C(4)	1.44(2)
Hg(2)-Co(1)	2.641(2)	C(51)-C(52)	1.43(2)
Hg(2)-Co(4)	2.536(2)	C(52)-C(53)	1.41(2)
		C(53)-C(54)	1.35(2)
Co(1)-Co(2)	2.548(3)	C(54)-C(55)	1.35(2)
Co(1)-C(1)	1.94(2)	C(55)-C(56)	1.42(2)
Co(1)-C(4)	1.96(1)	C(56)-C(51)	1.40(2)
Co(1)-C(11)	1.78(2)	C(61)-C(62)	1.38(2)
Co(1)-C(12)	1.75(2)	C(62)-C(63)	1.38(2)
		C(63)-C(64)	1.40(2)
Co(2)-C(1)	2.04(1)	C(64)-C(65)	1.27(3)
Co(2)-C(2)	2.07(2)	C(65)-C(66)	1.41(3)
Co(2)-C(3)	2.08(1)	C(66)-C(61)	1.38(2)
Co(2)-C(4)	2.03(1)		
Co(2)-C(21)	1.78(1)	C(11)-O(11)	1.16(2)
Co(2)-C(22)	1.75(1)	C(12)-O(12)	1.19(2)
		C(21)-O(21)	1.13(2)
Co(3)-C(31)	1.75(2)	C(22)-O(22)	1.16(2)
Co(3)-C(32)	1.76(2)	C(31)-O(31)	1.21(2)
Co(3)-C(33)	1.80(2)	C(32)-O(32)	1.16(2)
Co(3)-C(34)	1.80(2)	C(33)-O(33)	1.16(2)
		C(34)-O)34)	1.13(2)
Co(4)-O(41)	1.75(1)	C(41)-O(41)	1.17(2)
Co(4)-O(42)	1.74(1)	C(42)-O(42)	1.13(2)
Co(4)-O(43)	1.76(2)	C(43)-O(43)	1.16(3)
Co(4)-O(44)	1.76(2)	C(44)-O(44)	1.16(3)
C(1)-C(51)	1.52(2)		
C(4)-C(61)	1.50(2)		

[a] The standard deviation of the last significant figure is given in parentheses.

Hg(2), C(11) and C(12), while Co(2) caps a face. The coordination sphere of Co(2) can also be described as a face-capped pseudo-octahedron; C(1), C(4), C(21), C(22) and Hg(2) are close to octahedral coordination sites, and the C(2)-C(3) bond is tangential to the sixth site, *trans* to Hg(2).

There are several noteworthy aspects to the distribution of mercury-cobalt distances and angles. Three Hg-Co distances, (Hg(1)-Co(3), 2.551(2) Å; Hg(2)-Co(2), 2.553(2) Å; and Hg(2)-Co(4), 2.536(2) Å), are typical of such distances in two-coordinate mercury compounds [9 *]. The displacement of the equatorial carbonyls on the tetracarbonylcobaltate groups towards the mercury atoms is typical of this group and was seen in $Zn[Co(CO)_4]_2$ [10], $Hg[Co(CO)_4]_2$ [11], and in $\{Hg[Fe(CO)_4]_2{}^{2-}\}$ [12].

Of the other two mercury-cobalt distances, one, Hg(1)-Co(1), 2.475(2) Å, is somewhat shorter than these three and is the shortest mercury-cobalt distance yet determined, whereas the other, Hg(2)-Co(1), 2.641(2) Å, is noticeably longer. A

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* Reference numbers with asterisks indicate notes in the list of references.

Table 2

Interatomic angles for compound **1** (degrees) [a]

Co(1)–Hg(1)–Co(3)	168.88(7)	Hg(2)–Co(4)–C(41)	77.7(6)
		Hg(2)–Co(4)–C(42)	80.4(5)
Co(1)–Hg(2)–Co(2)	58.73(6)	Hg(2)–Co(4)–C(43)	174.8(7)
Co(1)–Hg(2)–Co(4)	146.61(7)	Hg(2)–Co(4)–C(44)	83.6(7)
Co(2)–Hg(2)–Co(4)	152.69(7)	C(41)–Co(4)–C(42)	119.8(7)
		C(41)–Co(4)–C(43)	98.7(8)
Hg(1)–Co(1)–Hg(2)	176.52(9)	C(41)–Co(4)–C(44)	116.1(8)
Hg(1)–Co(1)–Co(2)	118.1(1)	C(42)–Co(4)–C(43)	98.4(8)
Hg(1)–Co(1)–C(1)	85.0(4)	C(42)–Co(4)–C(44)	116.1(8)
Hg(1)–Co(1)–C(4)	82.1(4)	C(43)–Co(4)–C(44)	101(1)
Hg(1)–Co(1)–C(11)	97.0(4)		
Hg(1)–Co(1)–C(12)	94.0(5)	Co(1)–C(1)–Co(2)	79.6(6)
Hg(2)–Co(1)–C(1)	91.6(4)	Co(1)–C(1)–C(2)	118(1)
Hg(2)–Co(1)–C(4)	96.6(4)	Co(1)–C(1)–C(51)	122(1)
Hg(2)–Co(1)–C(11)	86.3(4)	C(1)–C(2)–C(3)	111(1)
Hg(2)–Co(1)–C(12)	87.0(5)	C(2)–C(1)–C(51)	119(1)
Hg(2)–Co(1)–Co(2)	58.90(6)	C(2)–C(3)–C(4)	113(1)
		Co(1)–C(4)–C(61)	125(1)
Hg(2)–Co(2)–Co(1)	62.37(7)	C(3)–C(4)–Co(1)	116(1)
Hg(2)–Co(2)–C(1)	91.7(4)	C(3)–C(4)–C(61)	118(1)
Hg(2)–Co(2)–C(4)	97.4(5)	Co(1)–C(4)–Co(2)	79.4(5)
Hg(2)–Co(2)–C(21)	91.0(6)	Co(1)–C(11)–O(11)	178(1)
Hg(2)–Co(2)–C(22)	90.9(6)	Co(1)–C(12)–O(12)	177(1)
Co(1)–Co(2)–C(21)	123.8(5)	Co(2)–C(21)–O(21)	176(1)
Co(1)–Co(2)–C(22)	130.7(5)	Co(2)–C(22)–O(22)	176(1)
C(1)–Co(2)–C(4)	75.3(5)	Co(3)–C(31)–O(31)	178(2)
C(1)–Co(2)–C(21)	168.0(6)	Co(3)–C(32)–O(32)	171(1)
C(1)–Co(2)–C(22)	96.7(6)	Co(3)–C(33)–O(33)	175(2)
C(4)–Co(2)–C(21)	92.7(6)	Co(3)–C(34)–O(34)	166(2)
C(4)–Co(2)–C(22)	168.6(7)	Co(4)–C(41)–O(41)	177(2)
C(21)–Co(2)–C(22)	95.0(6)	Co(4)–C(42)–O(42)	177(2)
		Co(4)–C(43)–O(43)	177(2)
C(1)–Co(1)–C(4)	79.5(6)	Co(4)–C(44)–O(44)	176(2)
C(1)–Co(1)–C(12)	93.9(7)		
C(4)–Co(1)–C(11)	95.8(7)	C(51)–C(52)–C(53)	117(1)
C(11)–Co(1)–C(12)	90.9(8)	C(52)–C(53)–C(54)	122(2)
		C(53)–C(54)–C(55)	123(2)
Hg(1)–Co(3)–C(31)	175.5(6)	C(54)–C(55)–C(56)	119(1)
Hg(1)–Co(3)–C(32)	80.1(4)	C(55)–C(56)–C(51)	120(1)
Hg(1)–Co(3)–C(33)	84.9(6)	C(56)–C(51)–C(52)	120(1)
Hg(1)–Co(3)–C(34)	81.3(5)		
C(31)–Co(3)–C(32)	97.3(8)	C(61)–C(62)–C(63)	123(1)
C(31)–Co(3)–C(33)	99.6(8)	C(62)–C(63)–C(64)	116(2)
C(31)–Co(3)–C(34)	97.0(8)	C(63)–C(64)–C(65)	122(2)
C(32)–Co(3)–C(33)	119.8(8)	C(64)–C(65)–C(66)	123(2)
C(32)–Co(3)–C(34)	120.3(7)	C(65)–C(66)–C(61)	117(2)
C(33)–Co(3)–C(34)	114.2(8)	C(66)–C(61)–C(62)	118(1)

[a] The standard deviation of the last significant figure is given in parentheses.

count of electrons around both cobalt atoms, to satisfy the EAN rule, leads to the expectation that no Hg(2)–Co(2) interaction is needed. Yet, this distance is shorter than the Hg(2)–Co(1) bond! It is instructive to compare **1** with the iron containing dimetallacycles, which have the general formula $Fe_2(CO)_6(C_4R_4)$ [13]. Structures of the iron metallacycles usually have a distinctly asymmetric bridging carbonyl, terminally bonded to the iron atom which is π-bonded to the C_4R_4 hydrocarbon group. This so-called semi-bridging CO, weakly coordinated, at a distance of 2.4 to 2.5 Å, to the iron atom that is σ-bonded to the C_4R_4 group [13], is analogous to the asymmetric bridging mercury Hg(2) of **1**. On the σ-bonded iron there is an apical CO that is approximately *trans* to the semi-bridging CO. The iron–carbon distance to this *trans* CO is often short, as is the corresponding distance, Co(1)–Hg(1) of **1**.

Cotton proposed a qualitative theoretical explanation for the semi-bridging CO in the iron metallacycles and other compounds [14]. The σ-bonded iron atom would have only seventeen electrons unless the iron–iron bond is of the donor–acceptor type in which an electron pair is donated from the π-bonded iron atom to the σ-bonded iron atom. In Cotton's model, the donor–acceptor bond makes the σ-bonded iron atom electron rich. The coordination of the carbon atom of the semi-bridging CO to the σ-bonded iron atom contributes to the stability of the molecule by relieving the build-up of negative charge on the σ-bonded iron atom. The interaction between the σ-bonded Fe and the semi-bridging CO probably involves donation from a metal d orbital to the π^* orbital of the CO. In **1**, the interaction between the σ-bonded cobalt and Hg(2) may involve donation of electron density from a Co(1) *d*-orbital to the σ^* orbital of $Hg(2)-Co(CO)_4$ fragment.

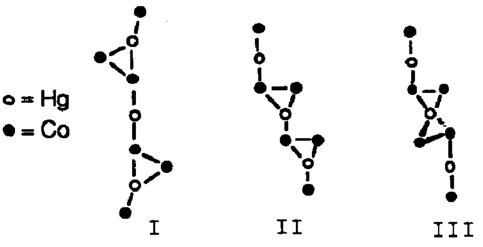
The crystal structure of $Hg\{Co[HgCo(CO)_4](CO)_2C_4H_2Ph_2\}_2$ *(2)*

In a hydrocarbon solution, **1** slowly undergoes a symmetrization reaction, which results in deposition of a red powder and accumulation, in solution, of $Hg[Co(CO)_4]_2$. Symmetrization reactions, described by equation 1 are known for

$$2\ R{-}Hg{-}ML_n \rightarrow HgR_2 + Hg(ML_n)_2 \qquad (1)$$

unsymmetrical derivatives in which one of the groups is an organic moiety, but there are very few examples in which both substituents on mercury are metals [15].

There are three ways in which the symmetrization of **1** could occur; the metal frameworks, labelled I-III, are shown below.



None of these three would seem to be strongly favored. To our knowledge, there are no examples of mercury simultaneously bridging two transition metal single bonds, as in III. The crystal structure of compound **2** is shown in Fig. 2. Selected interatomic distances and angles are listed in Tables 3 and 4, respectively.

The analysis showed **2** to have the metal framework of I above. Hg(1) is located on a crystallographic inversion center in the space group $P\bar{1}$. The primed numbered atoms in Fig. 2 are related to the unprimed numbered atoms by inversion through the position of Hg(1). The angle Co(1)–Hg(1)–Co(1)′ is necessarily 180°. This

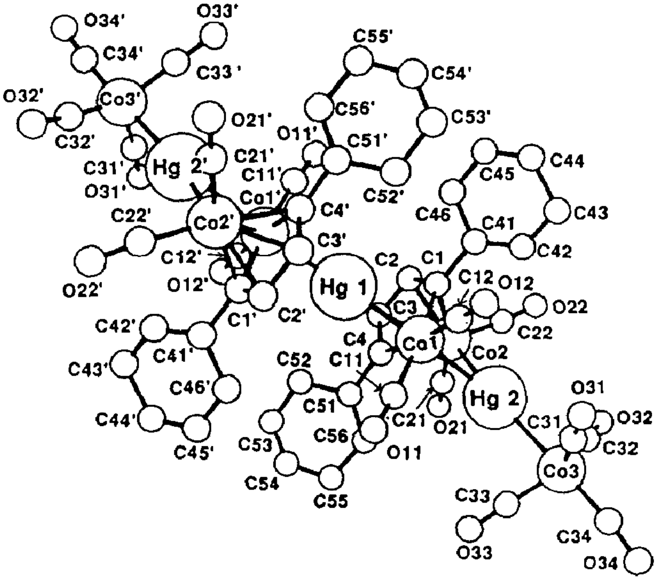


Fig. 2. A PLUTO drawing of **2**.

Table 3

Selected interatomic distances for compound **2** (Å) [a]

Hg(1)-Co(1)	2.480(4)	C(4)-C(51)	1.45(4)
		C(11)-O(11)	1.13(4)
Hg(2)-Co(1)	2.640(4)	C(12)-O(12)	1.14(4)
Hg(2)-Co(2)	2.578(4)	C(21)-O(21)	1.12(5)
Hg(2)-Co(3)	2.551(4)	C(22)-O(22)	1.15(5)
		C(31)-O(31)	1.15(4)
		C(32)-O(32)	1.15(4)
Co(1)-Co(2)	2.553(6)	C(33)-O(33)	1.17(5)
Co(1)-C(1)	1.93(2)	C(34)-O(34)	1.18(5)
Co(1)-C(4)	1.96(4)	C(41)-C(42)	1.31(4)
Co(1)-C(11)	1.78(4)	C(42)-C(43)	1.34(5)
Co(1)-C(12)	1.76(4)	C(43)-C(44)	1.58(6)
		C(44)-C(45)	1.27(5)
Co(2)-C(1)	2.04(3)	C(45)-C(46)	1.41(5)
Co(2)-C(2)	2.05(3)	C(51)-C(52)	1.45(5)
Co(2)-C(3)	2.08(3)	C(52)-C(53)	1.42(5)
Co(2)-C(4)	2.11(3)	C(53)-C(54)	1.29(6)
Co(2)-C(21)	1.79(5)	C(54)-C(55)	1.32(6)
Co(2)-C(22)	1.76(5)	C(55)-C(56)	1.44(5)
Co(3)-C(31)	1.75(5)		
Co(3)-C(32)	1.77(5)		
Co(3)-C(33)	1.72(5)		
Co(3)-C(34)	1.72(5)		
C(1)-C(2)	1.39(4)		
C(1)-C(41)	1.51(5)		
C(2)-C(3)	1.38(4)		
C(3)-C(4)	1.45(4)		

[a] The standard deviation of the last significant figure is given in parentheses.

Table 4

Selected interatomic angles for compound **2** (deg.) [a]

Co(1)–Hg(1)–Co(1)′	180.0(0)	Hg(2)–Co(3)–C(31)	82(1)
		Hg(2)–Co(3)–C(32)	82(1)
Co(1)–Hg(2)–Co(2)	58.6(1)	Hg(2)–Co(3)–C(33)	81(1)
Co(1)–Hg(2)–Co(3)	147.6(2)	Hg(2)–Co(3)–C(34)	179(2)
Co(2)–Hg(2)–Co(3)	153.7(2)	C(31)–Co(3)–C(32)	117(2)
		C(31)–Co(3)–C(33)	116(2)
Hg(1)–Co(1)–Co(2)	120.5(2)	C(31)–Co(3)–C(34)	98(2)
Hg(1)–Co(1)–C(1)	85(1)	C(32)–Co(3)–C(33)	121(2)
Hg(1)–Co(1)–C(4)	84(1)	C(32)–Co(3)–C(34)	99(2)
Hg(1)–Co(1)–C(11)	91(1)	C(33)–Co(3)–C(34)	99(2)
Hg(1)–Co(1)–C(12)	93(1)		
Hg(2)–Co(1)–Co(2)	59.5(1)		
C(1)–Co(1)–C(4)	80(1)	Co(1)–C(1)–C(2)	116(3)
C(1)–Co(1)–C(11)	171(2)	Co(1)–C(1)–C(41)	123(2)
C(1)–Co(1)–C(12)	95(2)	Co(1)–C(1)–Co(2)	80(1)
C(4)–Co(1)–C(11)	91(1)	Co(1)–C(4)–Co(2)	78(1)
C(4)–Co(1)–C(12)	174(1)	Co(1)–C(4)–C(51)	128(3)
C(11)–Co(1)–C(12)	94(2)	C(3)–C(4)–C(51)	117(3)
Co(2)–Co(1)–C(11)	124(1)	C(2)–C(3)–C(4)	112(3)
Co(2)–Co(1)–C(12)	125(1)	C(2)–C(1)–C(41)	119(3)
		C(1)–C(2)–C(3)	115(3)
Co(1)–Co(2)–Hg(2)	61.9(1)	Co(1)–C(4)–C(3)	115(2)
Co(1)–Co(2)–C(21)	130(1)		
Co(1)–Co(2)–C(22)	130(2)	Co(1)–C(11)–O(11)	174(3)
C(1)–Co(2)–C(4)	75(1)	Co(1)–C(12)–O(12)	178(3)
C(1)–Co(2)–C(21)	165(2)	Co(2)–C(21)–O(21)	178(4)
C(1)–Co(2)–C(22)	100(2)	Co(2)–C(22)–O(22)	171(5)
C(4)–Co(2)–C(21)	94(2)	Co(3)–C(31)–O(31)	177(4)
C(4)–Co(2)–C(22)	174(2)	Co(3)–C(32)–O(32)	176(4)
C(21)–Co(2)–C(22)	91(2)	Co(3)–C(33)–O(33)	176(4)
		Co(3)–C(34)–O(34)	173(4)

[a] The standard deviation of the last significant figure is given in parentheses.

contrasts with the situation at Hg(1) in **1** in which the angle was found to be 168.88(7)°. The bending at Hg(2) in **2** is nearly the same as in **1**. The angle Co(2)–Hg(2)–Co(3) was found to be 153.7(2)° in **2**, compared with 152.69(7)° in **1**.

With the exception of the Hg(2)–Co(2) distance, the metal–metal distances in **2** are remarkably close to those in **1**. With such similarity, the previous discussion of the metal–metal bonds in **1**, applies equally well to those in **2**. A further observation about **2** is that Hg(1) is involved in two quite short bonds: to Co(1) and to Co(1)′. There is evidently little competition between Co(1) and Co(1)′ for the orbitals or the electrons of Hg(1), since both bonds are nearly as short as the Hg(1)–Co(1) bond in **1** [16*].

Reduction of 1 and reactions of the resulting anion 3

Mercury derivatives of organo-transition metal anions are a convenient form of storage of these species, because they are not air sensitive and the anion can be easily regenerated without by-products as its sodium salt by sodium amalgam reduction [17]. Compound **1** can be regarded as a mercury(II) derivative of $Co(CO)_4^-$

and an as yet unknown metallacyclic dianion, $[Co_2(CO)_4C_4H_2Ph_2]^{2-}$ that is isoelectronic with the analogous neutral di-iron metallacyclic compound, $Fe_2(CO)_4C_4H_2Ph_2$ [13]. Our many efforts to prepare this di-anion by reduction of **1** using sodium amalgam inevitably produced a mono-cobalt anion, **3**, the identity of which was inferred from analysis of two derivatives, discussed below.

When **1** was treated with sodium amalgam in THF, a solution containing anionic metal carbonyl species resulted, as indicated by the presence of several bands near 1900 cm^{-1} in the IR spectrum. Removal of the expected side product, $NaCo(CO)_4$, was achieved by a fortuitous difference in solubility; addition of diethyl ether caused the sodium salt of **3** to precipitate as a brown solid, while $NaCo(CO)_4$ remained in solution. Washing the precipitate with ether removed nearly all of the $NaCo(Co)_4$.

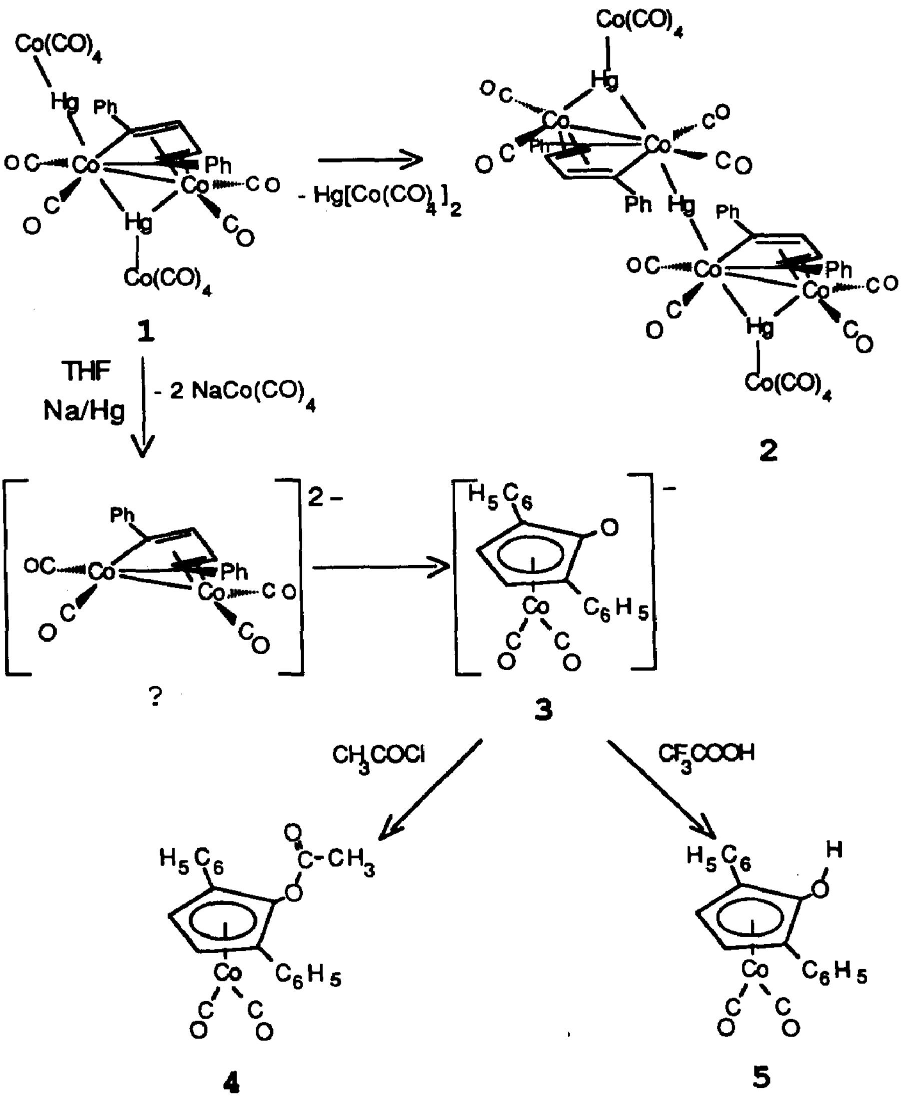
When the resulting, brown, sodium salt of anion **3** was treated with acetyl chloride in THF, a reaction occurred that produced, after workup, an orange-red crystalline product, **4**. In the ^1H NMR spectrum of **4**, the 10/2 ratio of the phenyl resonances at δ 7–8 ppm to that at 5.73 ppm, suggests that the latter is due to the metallacycle ring protons. Resonances of the methyl protons of the acetyl group appeared at δ 2.23 ppm, somewhat downfield from their position in acetone, 2.05 ppm. From the 3/10 ratio of the methyl to the phenyl resonances, it is apparent that only one acetyl group has been added to the anion, **3**, which must, then, have a charge of -1.

The IR spectrum of **4** in the terminal CO region has strong absorptions at 2005 and 1943 cm^{-1}, resembling that of η^5-$C_5H_5Co(CO)_2$, (ν(CO) 2017 and 1949 cm^{-1}), [18] and is consistent with the presence of two terminal carbonyl groups bonded to the cobalt. The band at 1773 cm^{-1} occurs at a much higher frequency than is found for ν(C=O) in the cobalt acyl complexes (ca. 1680 cm^{-1}) [18]. Rather, it is in the range expected for the ν(C=O) of an ester of the type aryl–O–CO–alkyl, viz. 1800 to 1750 cm^{-1} [20]. Esters have at least two strong bands in the C–O stretching region, 1300 to 1050 cm^{-1}, corresponding to the symmetric and antisymmetric modes of the C–O–C linkage [20]. Indeed, two strong bands are found in this region for **4** at 1196 and 1175 cm^{-1}. The mass spectrum of **4** shows the molecular ion at m/z 390 and an $M+1$ peak about 20 percent as intense.

On the basis of the foregoing spectroscopic evidence and on the elemental analysis, **4** is identified as 1-acetoxy-2,5-diphenylcyclopentadienylcobalt dicarbonyl; the proposed structure of **4** and of the ion whence it came are shown in Scheme 1.

Assignment of the peaks of the ^{13}C NMR spectrum of **4**, on the basis of the proposed structure, is straightforward; details are given in the experimental section. The acyl oxygen of the acetate group presumably comes from acetyl chloride, but the ether oxygen probably derives from carbon monoxide. If that is the case, there must be a total of three carbon monoxide equivalents in **4**. Insertions of CO into the metal–carbon bond of di-metal metallacyclopentadienes, causing conversion to mono-metal metallacycles, have been observed [21,22]. A similar process may be responsible for the formation of **3** from an initially formed dianion.

Anion **3** did not react with acetic acid in acetone solution, but did react with trifluoroacetic acid in diethyl ether. The spectroscopic properties of the product, **5**, a fine red powder, are consistent with a hydroxyl analogue of the more fully characterized acetyl derivative, **4**. Though much effort was expended, we were unable to obtain **5** in crystalline form. The IR spectrum of **5** shows a weak, sharp



Scheme 1.

peak at 3453 cm^{-1}. The IR spectrum of free, i.e., not hydrogen bonded, O–H groups typically exhibits a sharp stretching absorption at about 3600 cm^{-1} of weak to medium intensity. In the deuterated analogue of **5**, prepared in the same manner from CF_3COOD, there is a similarly shaped peak at 2569 cm^{-1}. The ratio of these two frequencies is 1.35, which is quite close to the square root of the ratio of the reduced masses: $(\mu_{O-D}/\mu_{O-H})^{1/2} = 1.37$ and confirms that the 3453 cm^{-1} absorbtion is due to ν(OH). The terminal CO stretching modes at 1997 and 1942 cm^{-1} occur at the same positions as in the acetyl compound **4**.

The mass spectrum of **5** shows the molecular ion as the highest mass peak and peaks at 28 and 56 mass units lower, corresponding to the sequential loss of two CO's. The hydroxyl resonance in the ^1H NMR spectrum occurs at δ 4.08 ppm in benzene-d_6. Contrary to expectation, there are two peaks separated by 4 Hz (0.02 ppm) for the two cyclopentadienyl protons at δ 4.48 and 4.50 ppm. Only one resonance at δ 5.73 ppm is observed in the spectrum of **4**. There are two types of interaction which could produce non-equivalence of the protons: (a) partial double bond character of the hydroxyl oxygen–cyclopentadienyl carbon bond [23*], or (b) intramolecular hydrogen bonding between the hydroxyl proton and the phenyl ring [24*].

Exposure of **5** to air produced small amounts of a deep red crystalline product which had ν(CO) in the bridging and ketonic regions of the spectrum. This was not characterized fully [29].

Summary and conclusions

Extension of the chemistry of mixed metal organometallic complexes of cobalt and mercury, started years ago [1], has produced some structural and chemical surprises. The crystal structure of $(C_6H_5)_2C_4H_2[Co(CO)_2HgCo(CO)_4]_2$ (**1**), was found to be a metallacycle which is asymmetrically bridged by $HgCo(CO)_4$. The structure of the product, $Hg\{Co_2(CO)_4(C_6H_5C_2H)_2[HgCo(CO)_4]\}_2$ (**2**), from the symmetrization reaction of **1**, was found to contain two $HgCo(CO)_4$-bridged metallacyclic units symmetrically disposed about a third Hg atom. Reduction of **1** with sodium amalgam gave an anion **3** characterized as $[(CO)_2Co(\eta^5\text{-}C_5H_2(C_6H_5)_2O)]^-$ by its reaction with acetyl chloride in which 1-acetoxy-2,5-diphenylcyclopentadienyldicarbonylcobalt (**4**) was formed; no evidence for the expected dianion, $[Ph_2C_4H_2Co_2(CO)_4]^{2-}$ was obtained. A hydroxy derivative, **5**, was isolated from the reaction of **3** with trifluoroacetic acid. The various chemical transformations, are summarized in Scheme 1.

Experimental

General conditions. The inert atmosphere (argon) techniques that were employed for all manipulations have been described previously [30]. Microanalyses were performed by Galbraith Laboratories or by MicAnal.

Starting materials. Acetyl chloride (Baker) was distilled immediately prior to use. Trifluoroacetic acid (Aldrich) was distilled and used without subsequent purification over a period of several months. Methyl trifluoromethylsulfonate (Aldrich) was degassed and stored under argon. Tetrahydrofuran, toluene, hexanes, isooctane (Fisher) and diethyl ether were distilled twice from sodium/benzophenone.

Instruments. All IR spectra were recorded on a Perkin–Elmer 337 grating spectrometer; a modified commercial cell, with CaF_2 windows, was used for liquids [31]. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer. The ^{13}C NMR spectrum of **1** was recorded on a Bruker WM-300 instrument. Mass spectra were obtained with an AEI MS902/CI instrument equipped with a Visicorder and a V6 datasystem.

Preparation of 1. The literature method [1] gave variable yields unless considerable attention was paid to reaction time and temperature; a somewhat more detailed description of the synthesis is given here. Into a 250 ml 3-neck round bottom flask, fitted with a stirring bar, two gas adapters and a thermometer, were placed isooctane (88 ml), 14.6 g (26.9 mmol) of $Hg[Co(CO)_4]_2$ [32] and 5.5 ml (50.1 mmol) of phenylacetylene (Aldrich). The flask was immersed in an oil bath at 91° C. The solution was stirred under a flow of argon through the gas adapters to a mineral oil bubbler. After 12 min, the solution temperature was 81.5 ° C, and gas evolution was observed in the solution. After 30 min, the solution was filtered under argon through a layer of Celite filter aid covering a "medium" porosity fritted filter. After standing for 18 h, the supernatant solution was decanted from the crystals which formed. The dark violet crystals which remained were rinsed with hexanes and dried under vacuum. The yield of **1** was 5.2 g (29.7%). ^{1}H NMR (acetone-d_6): δ 7.31 (s, C_6H_5, 10H); 6.69 (s, CHCH, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 200 (Co–CO); 148.41 (C–C_6H_5); 128.38 (*o*- or *m*-C_6H_5); 128.22 (*i*-C_6H_5); 128.05 (*p*-C_6H_5); 127.74 (*o*- or *m*-C_6H_5); 109.58 (CHCH) ppm. IR (KBr): 2062vs, 2050w, 2035w, 2012m, 2003(sh), 1980(sh), 1972(sh), 1960s, 1490vw, 1455w, 1390w, 765w, 707m, 642vw, 629w, 608s, 593vw, 571w, 550(sh), 539vs, 531vs, 505w, 488w cm^{-1}; lit. [1]. (KBr): 2066, 2037, 2008, and 1961 cm^{-1}.

Crystal structure determination of 1. A rhomboid shaped crystal of **1** was mounted in a sealed, argon-filled capillary. An X-ray reflection data set was collected on a Syntex $P2_1$ diffractometer utilizing a low temperature apparatus which directed a flow of nitrogen at − 84 ° C onto the sample. An ω scan technique was employed, with the scan rate varying with the reflection intensity.

Reflection intensities were corrected for the Lorentz and polarization effects. Intensities were also corrected for X-ray absorption by an analytical method [33]. Mercury and cobalt atomic scattering factors were corrected for the real and imaginary contributions of anomalous dispersion.

The positions of the mercury and cobalt atoms were determined by direct methods [34]. Phasing of the data set based on the heavy atom positions gave a residual index of 0.18. The remaining non-hydrogen atoms were located in a series of Fourier difference maps. Hydrogen atoms were assigned positions 1.08 Å from the carbon atoms to which they are bonded and the positions were recalculated prior to each of the last three cycles of full matrix least squares refinement, calculated with the XRAY76 programs [35]. The final difference map had peaks of electron density corresponding to 2 electrons per Å^3 on either side of the mercury atoms, but was otherwise featureless. Experimental details are given in Table 5 Positional parameters and temperature factors are listed in Table 6.

The crystal structure of dimer 2. A small quantity of compound **2** was prepared by the literature method [1]. Several small crystals were grown by slow evaporation of a tetrahydrofuran solution. One of these crystals was mounted externally on the tip of a broken capillary and an X-ray data set was collected at room temperature. Experimental details are collected in Table 5.

The metal atoms were located by the use of Patterson maps and the remaining atoms were locate by Fourier difference maps. The CRYSTALS package of computer programs [36] was employed in the preparation of maps, the least squares refinement of parameters, and the calculation of derived results. Positional and thermal parameters are listed in Table 7. Copies of observed and calculated structure factors for both structures are available from the authors.

Sodium amalgam reduction of 1. Preparation of sodium salt of 3. Sodium amalgam was prepared in a 100 ml Schlenk reaction vessel (SRV, Ace Glass Co.) from 1.0 g of sodium and 7.2 ml of mercury. Tetrahydrofuran (65 ml) was collected in a separate SRV. To this SRV was also added 6.07 g (5.16 mmol) of **1**. The resulting solution was transferred by cannula into the amalgam containing vessel. After stirring for 4.5 h, the solution was filtered through a Celite-covered "medium"

Table 5

Crystal data and experimental details for X-ray diffraction analysis of compounds **1** and **2**

	1	**2**
formula	$C_{28}H_{12}Co_4Hg_2O_{12}$	$C_{32}Hg_{24}Co_6Hg_3O_{16}$
*f*w	1177	1619.9
space group	$C2/c$	$P\bar{1}$
a, Å	22.08(1)	11.448(8)
b, Å	11.624(4)	12.757(6)
c, Å	28.08(1)	10.353(5)
α, deg.	90	94.37(4)
β, deg.	114.78(3)	75.49(5)
γ, deg.	90	66.87(4)
V, Å^3	6545	1320(1)
Z	8	1
cryst. dim., mm	0.3×0.2×0.4	0.1×0.1×0.1
radiation, Å	Mo, K_α, 0.71069	Mo, K_α, 0.71069
diffractometer	Syntex $P2_1$	Syntex $P2_1$
2θ limits, deg.	$0 < 2\theta < 47$	0–47.45
temperature	−84°C	ambient
abs. coeff., cm^{-1}	113.8	107.0
abs. correction	analytical *	none
* min T	0.145	–
* max T	0.253	–
D_m, D_c, g/cm^3	2.50, 2.39	–, 2.04
scan technique	ω	ω
scan speed, deg./min.	1.5–11.72	3.0–29.3
check reflections	3/97	3/97
unique refl.	5260	3000
unique ref., $I > 3\sigma(I)$	4164	1777
R_F, R_{wF}	0.051, 0.111	0.065, 0.068
No. of param refined	353	173
Highest resid. peak, eÅ^{-3}	2	–

porosity frit, and was collected in another SRV. Diethyl ether was collected in two large SRV's, 350 ml in one and 225 ml in the other. The filtered solution was transferred by cannula into the ether containing vessels, 35 ml into the first and 25 ml into the second, producing a dark brown precipitate immediately. The resulting suspension was allowed to settle for 12 h.

The amber supernatant solution was transferred by cannula into a 3-necked 2 l flask fitted with a glass stopper, a gas adapter and a rubber septum. The precipitate was washed with two 120 ml aliquots of diethyl ether for each of the two large SRV's. The contents of the SRV's were stirred briefly and allowed to settle, and the washing solvent was transferred by cannula into the 2 l flask. The remaining ether was removed under reduced pressure. After 12 h, in vacuo, the sodium salt of **3** (2.21 g) was obtained as a brown, finely divided solid. IR (THF): 1933vw, 1905s, 1892s, and 1858m cm^{-1}.

Reaction of the sodium salt of 3 with acetyl chloride. THF (90 ml) was distilled onto 1.0 g (ca. 2.8 mmol) of the sodium salt of **3** in a 100 ml SRV and 0.37 ml (5.2 mmol) of acetyl chloride was added by syringe. After stirring magnetically for 40 min, an IR spectrum of the reaction mixture showed the absence of absorption due

Table 6. Fractional coordinates and temperature factors, Å^2, for the non-hydrogen atoms of **1**

Atom	x/a	y/b	z/c	B_{iso} [b]
Hg(1)	0.12616(2)	0.18026(5)	0.54213(2)	[a]
Hg(2)	0.35166(3)	−0.00968(5)	0.64904(2)	[a]
Co(1)	0.23601(8)	0.0884(2)	0.59139(6)	[a]
Co(2)	0.29559(8)	0.1264(2)	0.68965(7)	[a]
Co(3)	0.01561(9)	0.2887(2)	0.50878(7)	[a]
Co(4)	0.4347(1)	−0.1656(2)	0.65465(7)	[a]
C(1)	0.2036(6)	0.059(1)	0.6446(5)	2.0(2)
C(2)	0.1964(7)	0.155(1)	0.6738(5)	2.5(2)
C(3)	0.2245(6)	0.256(1)	0.6634(4)	2.0(2)
C(4)	0.2555(2)	0.236(1)	0.6280(5)	2.8(3)
C(11)	0.2712(7)	0.124(1)	0.5469(5)	2.5(3)
C(12)	0.2102(8)	−0.046(1)	0.5612(6)	3.1(3)
C(21)	0.3699(7)	0.209(1)	0.7193(5)	2.9(3)
C(22)	0.3146(7)	0.034(1)	0.7432(5)	2.7(3)
C(31)	−0.0620(8)	0.357(1)	0.4813(6)	3.4(3)
C(32)	0.0403(7)	0.321(1)	0.4585(5)	2.3(2)
C(33)	0.0525(8)	0.365(2)	0.5700(6)	4.1(3)
C(34)	−0.0145(8)	0.147(1)	0.5136(6)	3.3(3)
C(41)	0.3814(8)	−0.165(1)	0.5879(6)	3.3(3)
C(42)	0.4893(7)	−0.051(1)	0.6815(5)	2.7(3)
C(43)	0.4929(9)	−0.268(2)	0.6535(7)	4.9(4)
C(44)	0.4042(9)	−0.233(2)	0.6963(7)	4.7(4)
C(51)	0.1776(6)	−0.057(1)	0.6515(4)	1.9(2)
C(52)	0.1093(8)	−0.063(1)	0.6429(6)	3.6(3)
C(53)	0.0837(8)	−0.173(1)	0.6461(6)	3.7(3)
C(54)	0.1210(7)	−0.269(1)	0.6541(6)	3.3(3)
C(55)	0.1856(7)	−0.266(1)	0.6622(5)	2.6(3)
C(56)	0.2150(7)	−0.159(1)	0.6599(5)	2.9(3)
C(61)	0.2863(6)	0.338(1)	0.6134(4)	2.1(2)
C(62)	0.3458(7)	0.330(1)	0.6083(5)	2.7(3)
C(63)	0.3733(7)	0.422(1)	0.5934(5)	3.1(3)
C(64)	0.3371(9)	0.525(2)	0.5829(7)	3.9(3)
C(65)	0.2836(9)	0.535(2)	0.5894(6)	3.9(3)
C(66)	0.2530(7)	0.442(1)	0.6027(5)	3.1(3)
O(11)	0.2926(5)	0.1459(9)	0.5168(4)	3.3(2)
O(12)	0.1896(5)	−0.135(1)	0.5398(4)	3.6(2)
0921)	0.4149(5)	0.267(1)	0.7378(4)	4.0(2)
O(22)	0.3246(6)	−0.032(1)	0.7768(4)	4.2(2)
O(31)	−0.1152(6)	0.406(1)	0.4615(4)	5.1(3)
O(32)	0.0531(3)	0.356(1)	0.4253(4)	4.0(2)
O(33)	0.0769(6)	0.421(1)	0.6073(4)	4.3(2)
O(34)	−0.0388(6)	0.070(1)	0.5228(5)	5.3(3)
O(41)	0.3446(6)	−0.169(1)	0.5437(4)	4.2(2)
O(42)	0.5256(7)	0.022(1)	0.6971(5)	5.8(3)
O(43)	0.529(1)	−0.340(2)	0.6532(7)	9.5(5)
O(44)	0.3856(7)	−0.282(1)	0.7234(5)	5.7(3)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg(1)	1.98(2)	3.20(3)	2.49(2)	0.33(2)	0.76(2)	0.25(2)
Hg(2)	2.05(2)	2.88(3)	2.48(2)	0.36(2)	1.06(2)	0.05(2)
Co(1)	1.97(8)	3.03(9)	2.12(7)	0.12(7)	1.00(6)	−0.07(6)
Co(2)	2.48(8)	2.92(9)	2.03(7)	0.08(7)	1.16(6)	0.10(6)
Co(3)	1.87(7)	3.7(1)	2.75(8)	0.51(7)	0.94(6)	0.29(7)
Co(4)	2.53(8)	3.2(1)	3.27(9)	0.81(7)	1.16(7)	−0.21(7)

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[a] Anisotropic temperature factors for 1, Å^2. [b] Atomic scattering factors multiplied by $\exp(-B_{iso}\sin^2\theta/\lambda^2)$.

Table 7

Fractional coordinates and temperature factors, Å², for the non-hydrogen atoms of compound **2**

Atom	x/a	y/b	z/c	U_{iso} [b]
Hg(1)	0.000(0)	0.000(0)	0.000(9)	[a]
Hg(2)	0.8620(2)	0.3972(1)	0.2896(1)	[a]
Co(1)	0.9392(5)	0.1904(4)	0.1416(5)	[a]
Co(2)	0.8169(5)	0.2353(4)	0.3960(4)	[a]
Co(3)	0.8424(6)	0.6039(4)	0.2957(5)	[a]
C(1)	0.990(4)	0.102(3)	0.278(3)	0.09(1)
C(2)	0.903(3)	0.057(3)	0.343(3)	0.074(9)
C(3)	0.782(3)	0.099(3)	0.318(3)	0.08(1)
C(4)	0.772(3)	0.179(3)	0.225(3)	0.09(1)
C(11)	0.871(3)	0.265(3)	0.022(3)	0.08(1)
C(12)	0.098(4)	0.187(3)	0.069(3)	0.09(1)
C(21)	0.646(5)	0.329(4)	0.487(4)	0.12(1)
C(22)	0.867(5)	0.267(4)	0.536(5)	0.15(2)
C(31)	1.002(4)	0.532(3)	0.178(4)	0.11(1)
C(32)	0.831(4)	0.598(4)	0.468(5)	0.12(1)
C(33)	0.710(5)	0.617(4)	0.237(4)	0.13(2)
C(34)	0.828(5)	0.744(4)	0.298(4)	0.13(2)
C(41)	0.127(4)	0.061(3)	0.296(3)	0.09(1)
C(42)	0.185(4)	0.125(3)	0.328(4)	0.10(1)
C(43)	0.308(5)	0.092(4)	0.340(4)	0.12(1)
C(44)	0.385(5)	0.955(4)	0.308(5)	0.14(2)
C(45)	0.335(5)	0.889(4)	0.276(4)	0.13(4)
C(46)	0.204(4)	0.933(3)	0.266(4)	0.10(1)
C(51)	0.648(4)	0.227(3)	0.192(3)	0.09(1)
C(52)	0.608(4)	0.142(4)	0.140(4)	0.12(1)
C(53)	0.492(5)	0.192(4)	0.098(5)	0.13(2)
C(54)	0.433(5)	0.302(5)	0.102(5)	0.14(2)
C(55)	0.463(5)	0.383(4)	0.151(5)	0.15(2)
C(56)	0.584(4)	0.342(4)	0.190(4)	0.11(1)
O(11)	0.836(3)	0.304(2)	−0.064(3)	0.122(9)
O(12)	0.202(3)	0.181(2)	0.020(3)	0.114(8)
O(21)	0.540(4)	0.385(3)	0.545(3)	0.16(1)
O(22)	0.916(3)	0.276(3)	0.617(3)	0.14(1)
O(31)	1.109(3)	0.482(3)	0.104(3)	0.14(1)
O(32)	0.817(3)	0.596(3)	0.582(3)	0.15(1)
O(33)	0.626(3)	0.623(3)	0.189(3)	0.14(1)
O(34)	0.808(3)	0.841(3)	0.293(3)	0.15(1)

Atom	Y_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Hg(1)	11.0(2)	6.7(1)	6.7(1)	0.4(1)	−3.6(1)	−4.2(1)
Hg(2)	12.6(1)	6.13(8)	7.8(1)	1.30(7)	−4.3(1)	−4.46(9)
Co(1)	10.4(3)	5.9(2)	6.8(2)	0.9(2)	−3.5(2)	−3.9(2)
Co(2)	11.9(4)	7.3(3)	6.4(3)	1.3(2)	−3.5(3)	−4.8(3)
Co(3)	14.3(5)	6.3(3)	8.0(3)	1.5(2)	−4.3(3)	−4.6(3)

[a] Anisotropic temperature factors for **2**. ($U_{ij} \times 100$ Å²). [b] Atomic scattering factors multiplied by $\exp(-8\pi^2 U_{iso} \sin^2\theta/\lambda^2)$.

to **3** in the region 1900 to 1850 cm^{-1}. The solution was filtered through a "fine" porosity frit and the solvent was removed by trap-to-trap vacuum distillation (TTVD). Hexane (75 ml) was distilled onto the residue and, after stirring for 3 h, the solution was filtered, and the volume was reduced to 60 ml by TTVD. A red-orange precipitate formed quickly and was redissolved by heating the solution in a warm water bath. The solution was transferred by decantation under argon into a 80 ml SRV, which was then placed in a small dewar flask inside a larger dewar flask. Dry Ice was placed in the outer dewar flask, and the assembly was covered. On standing overnight, the temperature in the inner dewar flask fell to −45°C. A substantial mass of orange-brown powder was formed together with a small quantity of poorly formed red-orange crystals. The solid was redissolved in 100 ml of hexanes. The resulting solution was cooled slowly over a period of 3 d to −50°C, producing a mass of large red-orange plates and a small amount of orange-brown powder. The supernatant solution was removed by cannula and the crystals were washed with cold hexanes. After drying under vacuum, **4** was obtained as red-orange rectangular crystals (0.204 g, 18%), m.p. 112–113°C. Anal.: Found: C, 64.40, 64.82; H, 4.13, 4.02; Co, 14.44. $C_{21}H_{15}CoO_4$ calcd.: C, 64.63; H, 3.87; Co, 15.10%. IR (KBr): 3975vw, 3905vw, 3089w, 3033w, 3009vw, 2912vw, 2005vs, 1943vs, 1934w, 1773s, 1607w, 1582vw, 1529w, 1480w, 1453w, 1425vw, 1386w, 1369m, 1328w, 1318w, 1267w, 1196s, 1175s, 1072w, 1037vw, 1025w, 1013vw, 1000vw, 915vw, 893vw, 883m, 853m, 848(sh), 787w, 769s, 760w, 714w, 700s, 619m, 603w, 577sh, 552m, 529m, 511vw, and 482w cm^{-1}. ^1H NMR (DMSO-d_6) δ 2.23 (s, 3H, $C(O)CH_3$), 5.73 (s, 2H, $CHCH$), 7–8 (m, 10H, C_6H_5); ^{13}C NMR: 203.8, CO; 168.4, $C(O)CH_3$; 131.0, 128..5, 127.9, 127.8, 126.7, C_6H_5; 118.7, C–O–C(O); 98.4, C–C_6H_5; 77.5, 77.4, $CHCH$; 20.3, $C(O)CH_3$.

The peaks at δ 168.4 ppm and at 20.3 ppm are assigned to the acyl carbon and the methyl carbon of the acetyl group, respectively, by comparison with the spectrum of ethyl acetate [37]. The relatively weak peak at δ 118.7 ppm is assigned to the single carbon at the cyclopentadienyl 1 position by comparison with that of methoxyferrocene [38]. The peak at δ 203.8 ppm is assigned to the two terminal CO's by analogy with the ^{13}C spectrum of dicarbonyl 1-ethyl-2,3,4,5-tetramethylcyclopentadienylcobalt in which the terminal carbonyls were found at δ 208.0 ppm [39]. The peak at δ 98.4 ppm is assigned to the 2- and 5-cyclopentadienyl positions and the peaks at δ 77.5 and 77.4 ppm to the 3- and 4-cyclopentadienyl positions; values of $^1J(CH)$ for sp^2 carbons occur in the range of 155 to 205 Hz [40]. The peaks at δ 128.5 and 126.7 ppm are assigned to the four *ortho* carbons and to the four *meta* carbons of the phenyl groups on the basis of their intensity. The peak at δ 127.9 ppm is assigned to the two *para* carbons on account of its greater intensity than the peak at δ 131.0 ppm, assigned to the *ipso* carbon of the phenyl ring. MS(70 eV, EI, Probe temp. 120°C) m/z 390 (M^+), 391($M+1$); metastable peaks: 308, 253–254, and beneath the small peaks at 237 and 238.

Reaction of the sodium salt of 3 with trifluoroacetic acid. To a solution of 2.02 g (1.72 mmol) of **1** in THF (35 ml) was added sodium amalgam (from 0.8 g of sodium and 10 ml of mercury). After stirring for 5 h, the solution was evaporated to dryness by TTVD. Diethyl ether (60 ml) was distilled into the vessel, and the resulting mixture was stirred for 12 h. The solution was removed by cannula, and the residue was washed with a second 50 ml portion of ether transferred by cannula. It was found to contain only a small amount of tetracarbonylcobaltate anion as judged by the amount of solid formed on exposure to air.

Diethyl ether (60 ml) was distilled onto the residue, and 0.26 ml (3.4 mmol) of trifluoroacetic acid was added by gas-tight syringe. The diethyl ether was removed by TTVD. Toluene (80 ml) was distilled into the SRV and after stirring for several hours, the solution was filtered through Celite filter aid. The toluene was removed from the filtrate by TTVD. Hexanes (50 ml) was collected in the SRV and the contents were stirred overnight. The red solution was filtered and the filtrate was immersed in a Dry Ice bath. This produced a light red precipitate, which was allowed to settle for 2.5 h. The supernatant solution was removed by cannula and the precipitate was dried by evacuation leaving 90 mg of a red powder, **5**. ^{1}H NMR (C_6D_6): δ 7.6–7.5 (m, 4H, C_6H_5); 7.2–7.1 (m, 6H, C_6H_5); 4.50 (s, 1H, $CHCH$); 4.48 (s, 1H, $CHCH$); 4.08 (s, 1H, OH) ppm. IR (KBr): 3453w(sh), 3388vw(br), 3038w, 3005(sh), 1997vs, 1942vs, 1605m, 1580w, 1529w, 1469w, 1447w, 1428m, 1374w, 1305w, 1185w, 1154vw, 1125vw, 1085vw, 1069w, 1025w, 998vw, 977w, 873vw, 835w, 767s, 749w(sh), 723m, 701w(sh), 696s, 646m, 564m, 541m, 510vw, 468w cm^{-1}. MS (EI, 180 °C): m/z 348 (M^+), 320 ($M-$CO), 292 ($M-$2CO).

A similar experiment employing trifluoroacetic acid-*d*, prepared by a literature method [41], was carried out to make the deuterium analogue. IR (KBr): ν(O–D), 2569 cm^{-1}.

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