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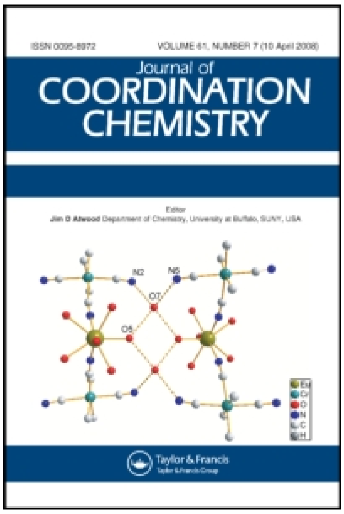

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SYNTHESIS AND X-RAY MOLECULAR STRUCTURE ANALYSIS OF SOME Au–Co, Au–Mn, AND Hg–Co BONDED COMPOUNDS

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The reaction of $NaCo(CO)_{4-x}(PR_3)_x$ ($x = 0, 1$) with $Au(PR_3)Cl$ was examined in THF. The products were characterized by single crystal X-ray analysis and/or XPS spectroscopy. When the THF solution of $NaCo(CO)_{4-x}(PR_3)_x$ which was in situ prepared by the reduction of the corresponding cobalt carbonyl dimer with Na amalgam was filtered, the main product was $(R_3P)Au–Co(CO)_4$ and $(R_3P)Au–Co(CO)_{4-x}(PR_3)_x$ ($x = 1, 2$); phosphine migration from the Au to the Co site was observed for bulky phosphines during the recrystallization process. When the THF solution of $NaCo(CO)_{4-x}(PR_3)_x$ was not filtered, the main product had the composition of $M[Co(CO)_3(PR_3)]_2$. The element M was clearly determined to be Hg by XPS spectroscopy. The reaction of $NaMn(CO)_5$ with $Au(PR_3)Cl$, however, afforded $R_3PAu–Mn(CO)_5$. The bonding parameters such as Au–M and Hg–Co bond-lengths were interpreted in terms of the electronic nature of the R group of the monodentate PR_3 ligand.

Keywords: Au–M bond; CF_3-substituted aryl phosphine; X-ray structure; XPS spectrum

INTRODUCTION

Heteronuclear Au–M clusters have been the subject of increasing interest [1–22], not only because of their intriguing physical properties [1,23], but also for their unique structures and/or chemical reactivities [24–26]. Recently a new facet of this class of clusters has appeared, i.e., dendrimers, on which surface heteronuclear cluster composed from Au–M bond(s) are attached, have been exquisitely designed [27,28]. In our previous paper we reported on our attempt to construct a new supra structure by

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incorporating metal clusters into a Au(I)-phosphine complex [29]. Among new clusters the synthesis of $Au_4Co_2(CO)_7L_3$ and the mechanism of its formation in the reaction of $Au(PPh_3)Cl$ with $Co(CO)_4^-$ are quite interesting, because this cluster was overlooked in the early study by Nyholm *et al.* [30]. The important effect of the bulkiness of the phosphine ligand on Au cluster size has now been well established [31]. Therefore, we were tempted to examine similar reactions of $Au(PR_3)Cl$ with $Co(CO)_4^-$ where R denotes a CF_3^- substituted phenyl group such as *m*-$F_3CC_6H_4$ and *p*-$F_3CC_6H_4$. This article reports on the synthesis and X-ray molecular structure analysis for R_3P–Au–$Co(CO)_{4-x}(PR_3)_x$ ($x = 0$–2), $Hg[Co(CO)_3(PR_3)]_2$, and R_3P–Au–$Mn(CO)_5$ compounds.

EXPERIMENTAL

Materials and General Procedures

Synthesis and manipulations were done under an argon atmosphere with standard Schlenk-line techniques. Solvents were dried by standard procedures before use. (*m*-$F_3CC_6H_4)_3P$, (*p*-$F_3CC_6H_4)_3P$, and $\{3,5\text{-}(CF_3)_2C_6H_3\}_3P$ were synthesized by the Grignard method from the corresponding bromide in THF [32]. $[Co(CO)_3L]_2$ (L = (*m*-$F_3CC_6H_4)_3P$, (*p*-$F_3CC_6H_4)_3P$, and $(MeO)_3P$) was synthesized by the literature method [33]. $NaCo(CO)_3L$ was obtained by Na amalgam reduction of the corresponding cobalt carbonyl dimer. $Au(PR_3)Cl$ was prepared according to our previous paper [32].

Synthesis of $\{3,5\text{-}(CF_3)_2C_6H_3\}_3P$–Au–$Co(CO)_4$ (1)

The synthesis of $\{3,5\text{-}(CF_3)_2C_6H_3\}_3P$–Au–$Co(CO)_4$ (**1**) described below as a typical procedure was adopted for all other R_3P–Au–$Co(CO)_4$ compounds. 0.27 g of $Co_2(CO)_8$ (0.78 mmol) in 20 mL of THF was stirred over 1% Na amalgam for 2 h. The resulting yellow–gray solution was filtered by use of filter-paper and the filtrate was collected in a dropping funnel. This was added slowly to an ice-cooled THF solution (60 mL) of $\{3,5\text{-}(CF_3)_2C_6H_3\}_3PAuCl$ (1.06 g, 1.18 mmol) and the mixture was stirred at this temperature for 1 h. Then the temperature was gradually raised to room temperature during overnight stirring. The resulting solution was filtered and the solvent was vacuum-stripped to leave dark-red oil. The oil was first extracted with each 10 mL of hexane three-times and the solvent was rotary-evaporated. The yellow–brown product was recrystallized from CH_2Cl_2–hexane to give pale-brown crystals of $\{3,5\text{-}(CF_3)_2C_6H_3\}_3P$–Au–$Co(CO)_4$ (**1**). Yield 0.58 g, 47%, IR(ν(CO))/(KBr disk): 2059 (w), 1989 (m), 1947 (vs), 1917 (s). An unidentified yellow–brown product was extracted with THF from the extraction residue of **1**. IR data of the unidentified product is 1996 (w), 1931 (vs), 1917 (vs) for a KBr disk. IR data suggests that this product is perhaps $\{3,5\text{-}(CF_3)_2C_6H_3\}_3P$–Au–$Co(CO)_3P\{3,5\text{-}(CF_3)_2C_6H_3\}_3$. (*m*-$F_3CC_6H_4)_3P$–Au–$Co(CO)_4$ (**2**) was similarly synthesized in 84% yield. IR(ν(CO))/(KBr disk): 2056 (w), 1988 (s), 1957 (vs). A small amount of (*m*-$F_3CC_6H_4)_3P$–Au–$Co(CO)_3P(C_6H_4CF_3$-*m*$)_3$ (**3**) was obtained as a byproduct from the mother liquor after crystals of **2** were collected on a filter.

Synthesis of (*m*-$F_3CC_6H_4)_3P$–Au–Co$(CO)_3P(C_6H_4CF_3$-*m*$)_3$ (3) and (*m*-$F_3CC_6H_4)_3P$–Au–Co$(CO)_2[P(C_6H_4CF_3$-*m*$)_3]_2$ (4)

As a general procedure, the reaction of AuP($C_6H_4CF_3$-*m*$)_3$Cl with NaCo$(CO)_3P(C_6H_4$-CF_3-*m*$)_3$ is described. 2.29 g (2 mmol) of [Co$(CO)_3P(C_6H_4CF_3$-*m*$)]_2$ was dissolved in 30 mL of THF and this solution was treated with 1% Na amalgam for 2 h. The supernatant yellow–gray solution was filtered by use of filter-paper and the filtrate was collected in a dropping funnel. This was added slowly to an ice-cooled THF solution (120 mL) of AuP($C_6H_4CF_3$-*m*$)_3$Cl (2.10 g, 3 mmol) and the mixture was stirred at this temperature for 1 h. Then the temperature was gradually raised to room temperature during overnight stirring. The resulting solution was filtered and the solvent was vacuum-stripped to leave dark-red oil. The oil was extracted first with hexane (30 mL). Distillation of hexane and recrystallized from hexane-pentate yielded yellow–brown crystals of **3** (870 mg). Second extraction of the dark-red oil product was made with ether (30 mL). The extract was partially concentrated to give yellow powder of the unreacted parental cobalt carbonyl derivative (950 mg). The solvent was distilled off from the mother liquor to leave a red oil. The oil was subjected to column chromatography over silica-gel. The red band was first eluted with benzene from which 210 mg of **3** was obtained; total yield of **3** was 27%. IR(ν(CO))/(KBr disk): 1999 (w), 1925 (vs), 1917 (s). XPS:84 ev for $4f_{7/2}$ which is characteristic for Au(I) compounds [34–36]. Then a brown band was eluted with benzene from which pale-brown crystals of (*m*-$F_3CC_6H_4)_3P$–Au–Co$(CO)_2[P(C_6H_4CF_3$-*m*$)_3]_2$ (**4**) (180 mg, 3.5%) were obtained. IR(ν(CO))/(KBr disk): 2018(w), 1932 (vs), 1873 (vs). A small amount of crystals of **4** was also obtained from the mother liquor after crystals of **3** were collected on a filter.

Synthesis of Hg[Co$(CO)_3P(C_6H_4CF_3$-*p*$)_3]_2$ (5)

Synthesis of Hg[Co$(CO)_3P(C_6H_4CF_3$-*p*$)_3]_2$ (**5**) is described as a typical procedure for Hg[Co-$(CO)_3PR_3]_2$ (R = *p*-$F_3CC_6H_4$, *m*-$F_3CC_6H_4$, OCH_3). 130 mg (0.20 mmol) of [Co$(CO)_3P(C_6H_4CF_3$-*p*$)]_2$ was dissolved in 30 mL of THF and this solution was treated with 1% Na amalgam for 2 h. The supernatant yellow–gray solution which should contain finely dispersed mercury particles was transferred to a dropping funnel by use of a syringe. This solution was added slowly to an ice-cooled THF solution (20 mL) of AuP($C_6H_4CF_3$-*p*$)_3$Cl (140 mg, 0.20 mmol) and the mixture was stirred at this temperature for 1 h. The temperature was gradually raised to room temperature during overnight stirring. The resulting solution was filtered and the solvent was vacuum-stripped to leave dark-red oil. The oil was washed with hexane two times (each 10 mL) and the residue was extracted with acetone (10 mL × 2). Small amount of yellow–brown product, which is presumably (*p*-$F_3CC_6H_4)_3P$–Au–Co$(CO)_3P(C_6H_4CF_3$-*p*$)_3$ was obtained from the hexane washing. The solvent was vacuum-stripped from the acetone extracts to leave yellow–brown solid. The product was recrystallized from acetone : hexane (1 : 1) to give orange–yellow crystals of **5**. Yield 60 mg, 45%. IR(ν(CO))/(KBr disk): 1999 (w), 1951 (vs), 1917 (m). The existence of Hg instead of Au in **5** was determined by XPS spectroscopy; $4f_{7/2}$ resonance was observed at 100.63 eV and $4f_{5/2}$ resonance at 104.5 eV, which are characteristic for Hg(II). Similarly Hg[Co$(CO)_3P(C_6H_4CF_3$-*m*$)_3]_2$ (**6**) and Hg[Co$(CO)_3P(OMe)_3]_2$ (**7**) were synthesized. The yield of **6** was 45%. Anal. Calc. For $C_{48}H_{24}F_{18}HgO_6P_2$: C, 40.59; H, 1.70. Found: C, 40.57; H, 1.55%. IR(ν(CO))/(KBr disk): 2008 (w), 1961(vs), 1923 (m). The yield of **7** was 30%. IR(ν(CO))/(KBr disk): 1995 (w), 1955 (vs), 1943 (m). In each synthesis of **6** and **7**, a small amount of yellow–brown product was obtained from the hexane-washing, which is expected to be (m-$F_3CC_6H_4)_3P$–Au–$Co(CO)_3P(C_6H_4CF_3$-$m)_3$ and $(MeO)_3P$–Au–$Co(CO)_3P(OMe)_3$ respectively for each synthesis.

Synthesis of (m-$F_3CC_6H_4)_3P$–Au–$Mn(CO)_5$ (8)

0.39 g of $Mn_2(CO)_{10}$ (1 mmol) in 20 mL of THF was stirred over 1% Na amalgam for 2 h. The resulting yellow–gray solution was filtered to another three-necked flask. A THF solution (50 mL) of (m-$CF_3C_6H_4)_3PAuCl$ (1.05 g, 1.5 mmol) was added slowly to this solution and the mixture was stirred overnight. The resulting solution was filtered and the solvent was vacuum-stripped to leave a brown solid. The solid was extracted four-times with 20 mL of benzene and the solvent was rotary-evaporated from the combined extracts. The yellow product was recrystallized from CH_2Cl_2–hexane to give golden-yellow crystals of (m-$F_3CC_6H_4)_3P$–Au–$Mn(CO)_5$ (**8**). Yield 0.58 g, 45%. IR(ν(CO))/(KBr disk): 2045 (s), 2013 (vs), 1982 (m).

X-ray Crystallography

Crystals suitable for X-ray studies were obtained by recrystallization from CH_2Cl_2–hexane and/or benzene–hexane. Selected crystals were glued to the top of a fine glass rod. Accurate cell dimensions were obtained by least-squares refinements of 20–25 reflections on a MAC MXC^3 and/or a Bruker SMART-1000/CCD diffractometer with graphite-monochromated Mo K_α radiation. The reflection data were collected at −60°C for **1** on the Bruker SMART-1000/CCD and those for **3**–**5**, **7**, and **8** were obtained on the MAC MXC^3 diffractometer at 298 K. Complete crystal data are given in Table I. The structures of these crystals were solved by direct methods using the teXsan (Dirdif) and Sir92, Dirdif and/or SHELXS 86 in a Crystan-GM program package. The crystal of **1** belongs to the hexagonal space group R-3. However, neither Au nor Co are located on a special position. The same hexagonal space group R-3 is assigned to **5**. In this crystal, Hg is located at the origin and thus only 1/3 of the molecule is refined. The Hg atom is located at the origin for **7** and 1/2 of the molecule was refined. Refinements with anisotropic thermal parameters were made by full-matrix least-squares programs in a Crystal-GM and/or a Crystan program package provided by MAC Science except **1**: SHELXTL-PC ver. 5.10 was used for **1**. An analytical absorption correction was applied at the final stage of all refinements [19]. The final R and R_w values are given in Table I. A disorder was observed for one F_3C methyl carbon in the (m-$F_3CC_6H_4)_3P$ ligand which was coordinated to the cobalt atom *trans* to Au in **4**. The molecular structure of **6** was refined with a severely disordered CH_2Cl_2 molecule. Tables for atomic coordinates, thermal parameters, and bond-lengths and angles are available as supporting informations. Selected bond-lengths and angles are tabulated in Table II.

XPS Measurements

XPS spectra were obtained on an ULVAC-PHI ESCA-5700MC spectrometer with Mg K_α exciting radiation. Finely ground powders of cobalt carbonyl products and BN

TABLE I Crystal data

Compound	$\{3,5\text{-}(F_3C)_2C_6H_3\}_3$ $PAuCo(CO)4$ (**1**)	$(m\text{-}F_3CC_6H_4)_3PAuCo(CO)_3$ $P(m\text{-}F_3CC_6H_4)_3$ (**3**)	$(m\text{-}F_3CC_6H_4)_3PAuCo(CO)_2$ $[P(m\text{-}F_3CC_6H_4)_3]_2$ (**4**)
Formula	$C_{28}H_9AuCoF_{24}O_4P$	$C_{45}H_{24}AuCoF_{18}O_3P_2$	$C_{65}H_{36}AuCoF_{27}O_2P_3$
Formula weight	1152.2	1272.5	1710.8
Crystal system	Rhombohedral	Monoclinic	Triclinic
Space group	$R\bar{3}$	$P2_1/n$	$P\bar{1}$
a/Å	37.5575(13)	22.986(5)	12.363(2)
b/Å	37.5575(13)	20.889(3)	15.191(4)
c/Å	12.0395(6)	10.207(3)	19.107(4)
α/deg	90	90	83.22(2)
β/deg	90	99.01(2)	82.08(1)
γ/deg	120	90	71.31(2)
V/Å^3	14707.3(10)	4840(2)	3356(1)
Z	18	4	2
d_{calcd}/g cm^{-3}	2.342	1.747	1.69
Crystal dimensions/mm^3	$0.3 \times 0.3 \times 0.10$	$0.7 \times 0.6 \times 0.6$	$0.8 \times 0.8 \times 0.40$
μ(Mo K$_\alpha$)/cm^{-1}	52.15	36.6	27.2
Scan type	ϕ and ω	$2\theta - \omega$	$2\theta - \omega$
Scan range		$1.20 + 0.35 \tan\theta$	$1.13 + 0.35 \tan\theta$
Scan speed/deg min^{-1}		7.0	7.0
$2\theta_{max}$/deg	55.0	50.0	45.0
Temperature (K)	213	298	298
Unique reflections	7469	9606	8788
Reflections with $\lvert Fo\rvert > n\sigma(\lvert Fo\rvert)$	4880 ($n = 3$)	5198 ($n = 3$)	7048 ($n = 3$)
No. of parameters refined	637	727	970
R (R_w)	0.0299 (0.068)	0.082 (0.094)	0.081 (0.049)
Compound	$Hg[Co(CO)_3P$ $(C_6H_4CF_3\text{-}p)_3]_2$ (**5**)	$Hg[Co(CO)_3P$ $(OMe)_3]_2$ (**7**)	$(m\text{-}F_3CC_6H_4)_3$ $PAuMn(CO)_5$ (**8**)
Formula	$C_{48}H_{24}Co_2HgF_{18}O_6P_2$	$C_9H_{18}Co_2Hg_8O_9P_2$	$C_{26}H_{12}AuMnF_9O_5P_1$
Formula weight	1419.1	734.7	858.2
Crystal system	Rhombohedral	Triclinic	Monoclini
Space group	$R\bar{3}$	$P\bar{1}$	$P2_1/n$
a/Å	13.172(2)	6.920(6)	15.298(3)
b/Å	13.170(2)	8.362(5)	19.091(3)
c/Å	25.968(4)	10.381(7)	9.987(2)
α/deg	90	91.11(5)	90
β/deg	90	93.34(7)	95.2(2)
γ/deg	120	94.52(7)	90
V/Å^3	3901(1)	597.6(7)	2904.6(9)
Z	3	1	4
d_{calcd}/g cm^{-3}	1.81	2.04	1.96
Crystal dimensions/mm^3	$0.8 \times 0.5 \times 0.5$	$0.8 \times 0.45 \times 0.15$	$0.65 \times 0.65 \times 0.45$
μ(Mo K$_\alpha$)/cm^{-1}	37.5	87.8	58.0
Scan type	$2\theta - \omega$	$2\theta - \omega$	$2\theta - \omega$
Scan range	$1.15 + 0.35 \tan\theta$	$1.15 + 0.35 \tan\theta$	$1.10 + 0.35 \tan\theta$
Scan speed/deg min^{-1}	5.0	6.0	6.0
$2\theta_{max}$/deg	55.0	55.0	52.0
Temperature (K)	298	298	298
Unique reflections	1977	2734	5712
Reflections with $\lvert Fo\rvert > n\sigma(\lvert Fo\rvert)$	1367 ($n = 3$)	1548 ($n = 3$)	3821 ($n = 3$)
No. of parameters refined	162	157	434
R (R_w)	0.060(0.070)	0.085(0.066)	0.087 (0.119)

Mo K$_\alpha$ radiation ($\lambda = 0.71073$ Å); $R = \sum \lvert\lvert Fo\rvert - \lvert Fc\rvert\rvert / \lvert Fo\rvert$; $R_w = [\sum(\lvert Fo\rvert - \lvert Fc\rvert)^2 / \sum w(Fo)^2]^{1/2}$ where $w = 1/\sigma^2(F)$.

TABLE II Selected bond-lengths and angles

Compound	$\{3,5\text{-}(CF_3)_2C_6H_3\}_3PAuCo(CO)_4$ **(1)**	$(m\text{-}F_3CC_6H_4)_3PAuCo(CO)_3P(m\text{-}F_3CC_6H_4)_3$ **(3)**	$(m\text{-}F_3CC_6H_4)_3PAuCo(CO)_2[P(m\text{-}F_3CC_6H_4)_3]_2$ **(4)**
«bond-length(Å)»			
Au–Co	2.4654(7)	2.461(2)	2.475(2)
Au–P	2.252(1)	2.246(5)	2.259(3)
Co–P		2.173(5)	2.186(3)(P2) 2.170(3)(P3)
Co–C1	1.780(7)	1.72(2)	1.74(1)
Co–C2	1.779(6)	1.76(2)	1.75(2)
Co–C3	1.795(6)	1.74(2)	
Co–C4	1.773(7)		
C1–O1	1.136(8)	1.19(3)	1.17(2)
C2–O2	1.148(7)	1.16(2)	1.16(2)
C3–O3	1.135(7)	1.17(2)	
C4–O4	1.141(7)		
P1–C		1.83(2), 1.83(2), 1.82(2)	1.81(2), 1.82(1), 1.84(1)
P2–C	1.825(5), 1.814(5), 1.822(5)	1.81(2), 1.84(2), 1.81(2)	1.86(1), 1.86(1), 1.85(2)
P3–C			1.84(1), 1.86(1), 1.83(1)
«bond-angle(°)»			
P–Au–Co	176.38(4)	175.7(1)	172.8(1)
Au–Co–P		175.0(2)	91.48(9)(P2), 158.6(1)
P–Co–P			109.6(1)
Au–Co–C1	178.0(2)	75.6(6)	73.3(4)
Au–Co–C2	78.4(2)	82.6(7)	77.1(4)
Au–Co–C3	79.0(2)	81.8(8)	
Au–Co–C4	78.4(2)		
C–Co–C	115.7(3), 118.8(3), 114.0(3)	114.0(9), 122.3(9), 115(1)	126.6(6)
Co–C–O	178.4(6), 177.8(6), 177.8(6), 177.4(6)	177(2), 177(2), 177(2)	175(1), 178(1)
P–Co–C		99.9(9), 101.4(7), 99.0(7)	115.1(5)(P2), 109.0(4)(P2), 93.7(4)(P3), 98.6(4)
Au–P–C	113.3(2), 115.0(2), 112.0(2)	111.3(5), 112.4(4), 114.9(5)	116.8(4), 114.6(4), 108.7(4), 114.4(4)
Compound	$Hg[Co(CO)_3P(C_6H_4CF_3\text{-}p)_3]_2$ **(5)**	$Hg[Co(CO)_3P(OMe)_3]_2$ **(7)**	$(m\text{-}F_3CC_6H_4)_3PAuMn(CO)_5$ **(8)**
«bond-length(Å)»			
Hg–Co	2.498(2)	2.514(2)	
Au–Mn			2.545(3)
Au–P			2.278(4)
Co–P	2.193(3)	2.135(5)	
M–C1	1.781(9)	1.75(2)	1.78(2)
M–C2		1.73(2)	1.81(2)
M–C3		1.75(2)	1.78(2)
M–C4			1.85(3)
M–C5			1.82(2)
C–O	1.14(1)	1.16(2), 1.16(2), 1.15(2)	1.18(3), 1.16(3), 1.15(3), 1.11(4), 1.14(3)
P–C	1.830(6)		1.84(2), 1.84(2), 1.82(2)
P–O		1.55(1), 1.55(2), 1.52(3), 1.75(3), 1.77(4)	

(*continued*)

TABLE II Continued

Compound	*Hg[Co(CO)$_3$ P(C$_6$H$_4$CF$_3$-p)$_3$]$_2$* (**5**)	*Hg[Co(CO)$_3$ P(OMe)$_3$]$_2$* (**7**)	*(m-F$_3$CC$_6$H$_4$)$_3$ PAuMn(CO)$_5$* (**8**)
«bond-angle(°)»			
Hg–Co–P	180	175.4(2)	
Hg–Co–C	84.0(2)	83.2(6), 81.3(6), 88.7(6)	
Au–Mn–C			83.6(8), 76.2(8), 79.9(8), 87.7(8), 174.1(7)
P–Au–Mn			174.5(1)
P–Co–C	96.0(2)	97.7(6), 94.5(6), 94.8(6)	
Co–C–O	179(1)	174(2), 174(2), 177(2)	
Mn–C–O			176(2), 176(2), 173(2), 174(2), 177(2)

TABLE III XPS data for metal 4f$_{7/2}$ and 4f$_{5/2}$ core levels (eV)

Compound	*Binding energies* (eV)					
	Au	*4f$_{7/2}$*	*4f$_{5/2}$*	*Hg*	*4f$_{7/2}$*	*4f$_{5/2}$*
3		84.0	87.7			
5					100.63	104.5
6					99.2	103.3

standard were pressed into a disk. The disk was mounted on a stub. The 4f$_{7/2}$ and 4f$_{5/2}$ binding energies of Hg(II) and Au(I) were calibrated *vs.* the B 1s or N 1s lines of a sample base [37]. The energies for **3, 5,** and **6** are shown in Table III.

RESULTS AND DISCUSSION

The reaction of R$_3$PAuCl with NaCo(CO)$_4$ or NaCo(CO)$_3$PR$_3$ has been believed to yield R$_3$P–Au–Co(CO)$_4$ or R$_3$P–Au–Co(CO)$_3$PR$_3$ [30]. An initial TLC test with a silica-gel plate showed, however, that a few spots are observed on a TLC plate for the reaction mixtures of Au{(*m*-F$_3$CC$_6$H$_4$)$_3$}PCl and/or Au{(*p*-F$_3$CC$_6$H$_4$)$_3$}PCl with an unfiltered THF solution of NaCo(CO)$_4$. Therefore, we have pursued the products first. Elemental analysis and preliminary single crystal X-ray analysis for **5** have shown that it has a M[Co(CO)$_3$P(C$_6$H$_4$CF$_3$-*p*)$_3$]$_2$ composition. We at first imagined that M was Au with the oxidation state II; in this oxidation state Au(II) should have an odd electron configuration (Xe · 5d^9). However, this species was ESR-silent. Therefore, the product was subjected to an XPS measurement to determine the element M. The XPS spectrum showed two peaks at 100.63 and 104.5 eV for **5**, which correspond to 4f$_{7/2}$ and 4f$_{5/2}$ binding energies of Hg(II) (Table III). The XPS spectrum of **6** was also composed from two peaks at almost the same energy region; detailed discussion on XPS data will appear below. Thus products with the M[Co(CO)$_3$P(C$_6$H$_4$CF$_3$)$_3$]$_2$ composition should be Hg(II) derivatives. Similar Hg(II) derivative **7** was also synthesized and single crystal X-ray analyses for **5** and **7** have been refined as a Hg(II) derivative. When the THF solution in which the cobalt carbonyl dimer was treated with Na amalgam was filtered before reacting with

$Au(PR_3)Cl$, the yield of Hg derivatives was reduced to a great extent. Instead, the yield of Au–Co bonded derivatives **2–4** was significantly improved. No such Hg derivative was obtained when $Mn_2(CO)_{10}$ was used. Another interesting finding is that phosphine ligand migration occurs easily from Au(I) to the cobalt carbonyl site during the recrystallization process for bulky F_3C-substituted aryl phosphines. For instance, (m-$F_3CC_6H_4)_3P$–Au–$Co(CO)_3P(C_6H_4CF_3$-$m)_3$ (**3**) was obtained with a significant yield in the reaction of $AuP(C_6H_4CF_3$-$m)_3Cl$ with $NaCo(CO)_4$ as was described in the Synthesis section. Similar phosphine migration from Au to cobalt is deemed operative for the formation of (m-$F_3CC_6H_4)_3P$–Au–$Co(CO)_2[P(C_6H_4CF_3$-$m)_3]_2$ (**4**). However, phosphine migration does not occur for the manganese carbonyl. These synthetic results suggest that the PR_3-type monodentate phosphine ligand, at least for bulky phosphines, prefers Co to Au(I), but the preference is not strong for Mn. This tendency may be interpreted in terms of the basicity of metal carbonyl anions [38]. Two possible mechanisms are presumed for the formation of $Hg[Co(CO)_3PR_3]_2$. The first one is that Hg is oxidized to Hg(II) by AuCl after migration of PR_3 from Au(I) to $Co(CO)_4^-$ and then Hg(II) reacts with $NaCo(CO)_3PR_3^-$ to yield $Hg[Co(CO)_3PR_3]_2$; Au may be converted to gold colloids in this case. In fact, we found the deposition of a small amount of insoluble grey powder. The second possible mechanism is that the metal exchange occurs from Au to Hg after $Au[Co(CO)_3PR_3]_2$ is formed. However, latter one requests a rather rare oxidation state of Au(II) at first. Therefore, we suppose that the first mechanism is more plausible for the formation of $Hg[Co(CO)_3PR_3]_2$.

XPS spectra for **3, 5,** and **6** are crucial to determine the element of M in R_3P–M–$Co(CO)_{4-x}(PR_3)_x$ ($x = 0$–2) and $M[Co(CO)_3(PR_3)]_2$ (Table III). The binding energies of $4f_{7/2}$ and $4f_{5/2}$ for **3** are typical for Au(I) derivatives [39] and those for **5** and **6** are typical for Hg(II) derivatives [40]. The binding energies of **5** are slightly higher than those of **6**. Presumably the presence of an electron-withdrawing substituent (CF_3 group) at the para position in **5** is responsible for these higher energy shifts than those of **6**.

Single crystal X-ray determinations and least-squares refinements for **1**, **3–5**, **7**, and **8** have been done with the aid of these XPS data. Molecular structures of **3–5**, **7**, and **8** have shown in Figs. 1–5. The substituent effect of the R group in the PR_3 ligand on the

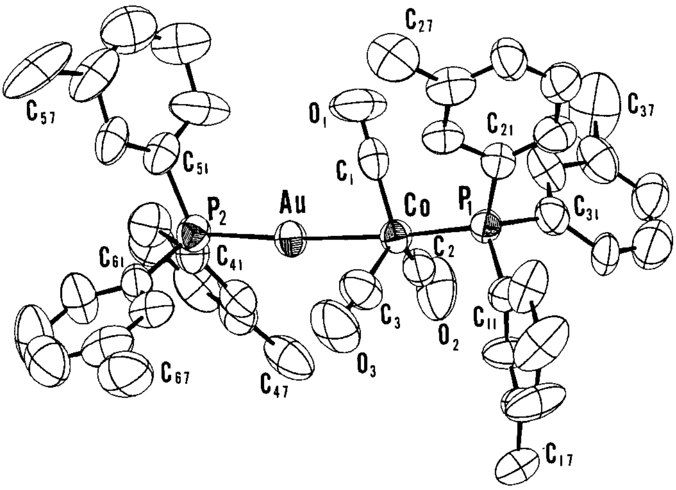

FIGURE 1 The ORTEP drawing of **3**. F atoms are omitted for clarity.

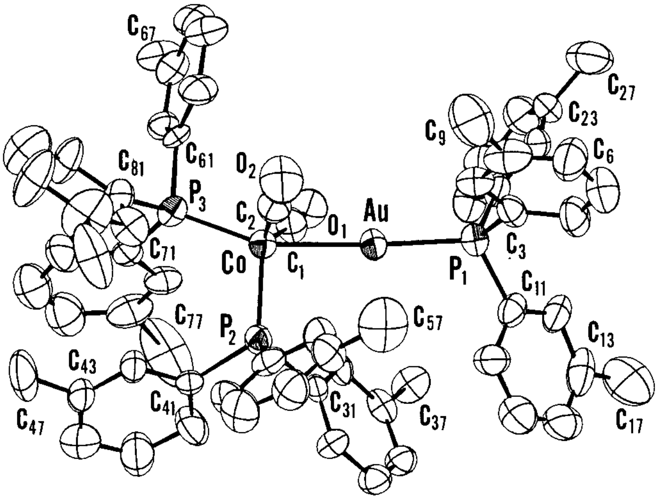

FIGURE 2 The ORTEP drawing of **4**. F atoms are omitted for clarity.

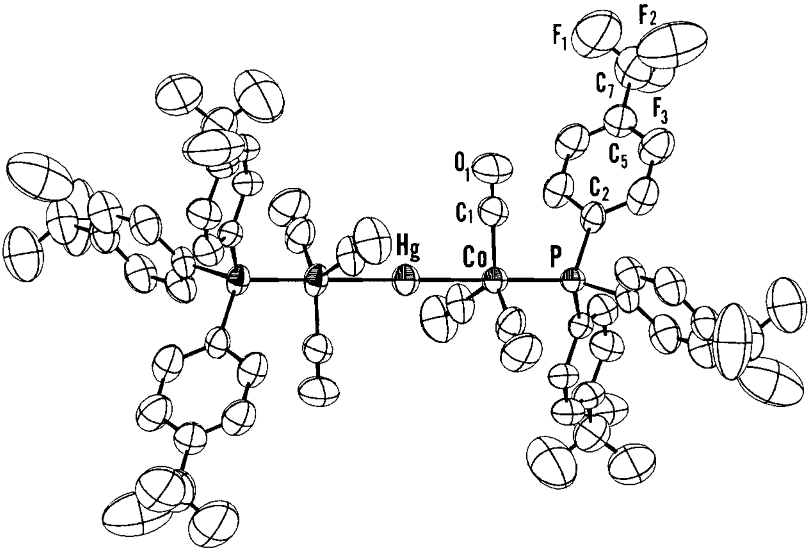

FIGURE 3 The ORTEP drawing of **5**.

Au–Co bond is easily examined by comparing the results of X-ray molecular structure analysis of **1** with those of $(C_6H_5)_3P$–Au–Co(CO)$_4$ [41]. The Au–Co length of **1** is 2.4654(7) Å, which is significantly shorter than that of $(C_6H_5)_3P$–Au–Co(CO)$_4$ (2.50(1) Å). The Au–Co bond-length of **3** which possesses a mono CF_3-substituent at a meta position (2.461(2) Å) is quite close to that of **1**. The Au–Co bond-length of **4** in which two carbonyl groups are replaced by two $P(C_6H_4CF_3\text{-}m)_3$ ligands (2.475(2) Å) is only slightly elongated compared with those of **1** and **3** to our surprise. Instead, the Au–Co–P_{ax} angle is significantly bent from linearity (158.6(1)°) because of the existence of two bulky phosphine ligands in close proximity.

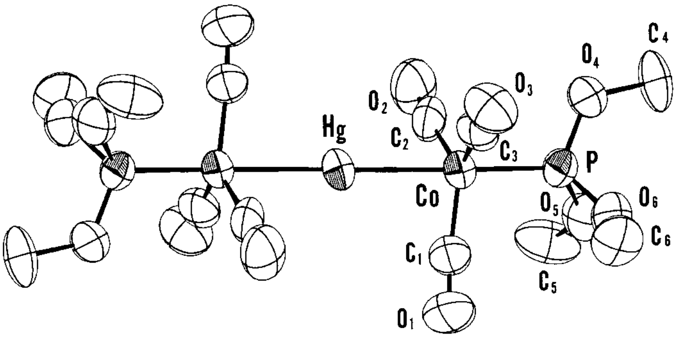

FIGURE 4 The ORTEP drawing of **7**.

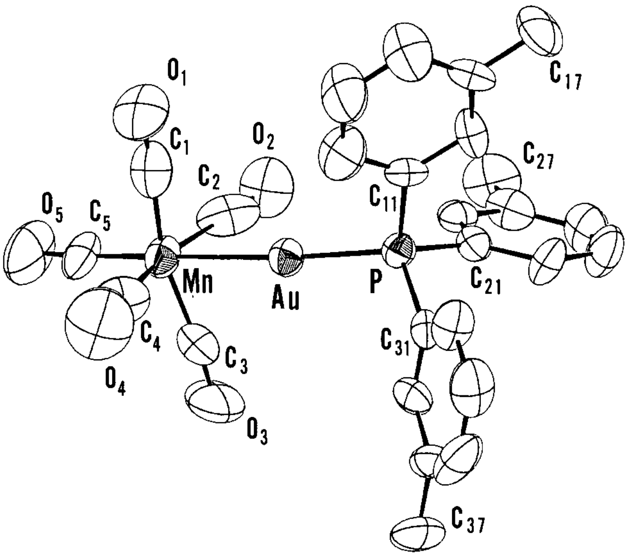

FIGURE 5 The ORTEP drawing of **8**. F atoms are omitted for clarity.

The substituent effect on the Au–Mn bond-length is investigated by comparing the result of **8** (2.545(3) Å) with those of Ph_3P–Au–$Mn(CO)_5$ (2.52(3) Å) [42] and of Ph_3P–Au–$Mn(CO)_4P(OPh)_3$ (2.573(7) Å) [43]. From the Au–Mn bond-length logic alone, $P(C_6H_4CF_3\text{-}m)_3$ seems to behave as an electron donor [44]. The Hg–Co bond-length of **7** is considerably longer than that of **5**. Electron-donating nature of $P(OMe)_3$ is deemed to be responsible for elongation of the Hg–Co bond of **7** than that of **5**. Au–P bond-lengths are in the normal range for Au(I) derivatives with a monodentate phosphine ligand [32], but that of **8** is slightly longer than those of Au–Co bonded derivatives. Co–P bond-lengths are also in the normal range for cobalt carbonyl phosphine derivatives, but that of **7** is considerably shorter than those of aryl phosphine derivatives. As $P(OMe)_3$ is small as a ligand, this phosphine can approach the cobalt atom closer than bulky ligands can.

CONCLUSION

It is worth pointing out that the phosphine migration from Au to Co has not been reported for the reaction of $Au_8(PPh_3)_7(NO_3)_2$ with $Li[Co(CO)_4]$ [8], that of $(Ph_3P)Au(NO_3)$ with $[FeCo(CO)_{12}]^-$ [10], and the formation of $Au_4Co_2(CO)_7(PPh_3)_3$ [29]. Another interesting point is that Hg is not useful to construct real heteronuclear gold clusters (no linear "open clusters" as in this study) for the present Au–phosphine system, although Hg is easily incorporated in gold clusters to afford new mixed-metal clusters [2–6].

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