

Ionic complexes $[\text{Au}_2(\text{P-P})_2][\text{Co}(\text{CO})_4]_2$ as intermediates in the synthesis of compounds containing a Co_2Au_2 core

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Abstract

The pathway for the formation of $[\text{Co}_2\text{Au}_2(\text{CO})_6(\mu\text{-dppm})_2]$ (**3**) from dppm and $[(\text{CO})_4\text{CoAu}_2(\mu\text{-dppm})]$ (**2a**) seems to involve the intermediate complex $[\text{Au}_2(\mu\text{-dppm})_2][\text{Co}(\text{CO})_4]_2$ which, although undetected in tetrahydrofuran, was isolated in toluene. This mechanism was confirmed by isolation of the analogous ionic complex $[\text{Au}_2(\mu\text{-dppip})_2][\text{Co}(\text{CO})_4]_2$ (**6**) from the reaction between $[(\text{ClAu})_2(\mu\text{-dppip})]$ (dppip = diphenylphosphinoisopropane) and $\text{Na}[\text{Co}(\text{CO})_4]$, and its crystal structure has been determined by X-ray diffraction methods. The crystals are triclinic, space group *P1* with *Z* = 1 in a unit cell of dimensions *a* = 11.242(5) Å, *b* = 12.003(2) Å, *c* = 13.564(5) Å, α = 97.13(2)°, β = 103.94(3)°, γ = 103.73(2)°. The structure has been solved from diffractometer data by direct and Fourier methods and refined by full-matrix least-squares. Final *R* = 0.027.

Keywords: Au; Co; Heterometallic clusters; Mechanism of formation; X-ray crystal structure

1. Introduction

For fewer square planar metal clusters are known than those adopting butterfly or tetrahedral metal geometries. Recently, we have shown that the appropriate use of bidentate ligands, such as dppm (dppm = diphenylphosphinomethane), may force the metal atoms to adopt square planar arrangements [1]. For example, whereas the Fe_2Cu_2 cluster exhibits a butterfly metal core [2], the Fe_2Au_2 skeleton of the anion $[\text{Fe}_2\text{Au}_2(\text{CO})_8(\mu\text{-dppm})]^-$ has been found to display a slightly distorted metal square planar arrangement [1]. In the light of these findings, we became interested in extending the study of metal clusters, adopting the latter geometry to other transition metals; specifically, our investigations have been developed in the area of mixed metal clusters containing cobalt and gold. As a result, in this paper we report the synthesis of the unexpected $[\text{Co}_2\text{Au}_2(\text{CO})_6(\mu\text{-dppm})_2]$, together with attempts to rationalize the pathway for its formation. A preliminary account of part of this work has been published elsewhere [3].

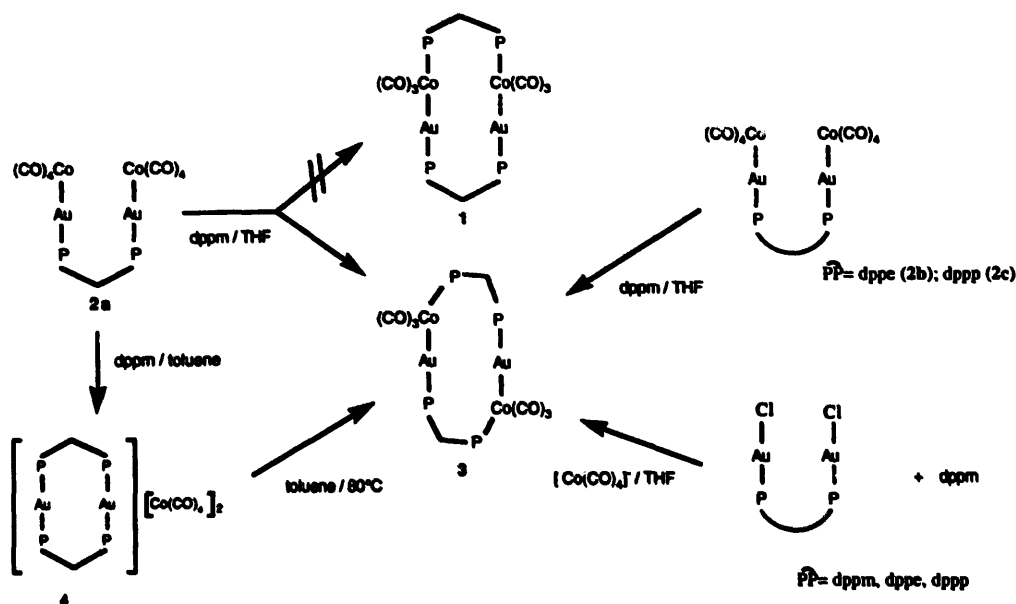
2. Results and discussion

The object of this work was to synthesize the square cluster $[\text{Co}_2\text{Au}_2(\text{CO})_6(\mu\text{-dppm})_2]$ (**1**) in order to compare the more relevant structural features with those reported for the similar anion $[\text{Fe}_2\text{Au}_2(\text{CO})_8(\mu\text{-dppm})]^-$. For this reason, the tetranuclear compound $[(\text{CO})_4\text{CoAu}_2(\mu\text{-dppm})]$ (**2a**), which is obtained by the reaction between $[(\text{ClAu})_2(\mu\text{-dppm})]$ and $\text{Na}[\text{Co}(\text{CO})_4]$, was believed to be its precursor, bearing in mind that two carbonyl groups, attached to different cobalt atoms, could easily be displaced by a diphosphine ligand (Scheme 1). However, we found that the final product of this reaction was **3** instead of **1**.

The structure of **3** consists of a 10-atom cycle containing the Co_2Au_2 metal framework in a *Z*-skew form, with the Co–Au bonds in reverse order to that expected. It should be noted that the geometry around the cycle is highly distorted as a consequence of the moderate Au–Au (2.977 Å) interaction [3].

Given the unexpected nature of **3**, we attempted to elucidate the pathway for its formation. Firstly, we investigated the reaction between a THF solution of $\text{Na}[\text{Co}(\text{CO})_4]$ and a mixture of $[(\text{ClAu})_2(\mu\text{-dppm})]$ and dppm, and we found that **3** was obtained as a major

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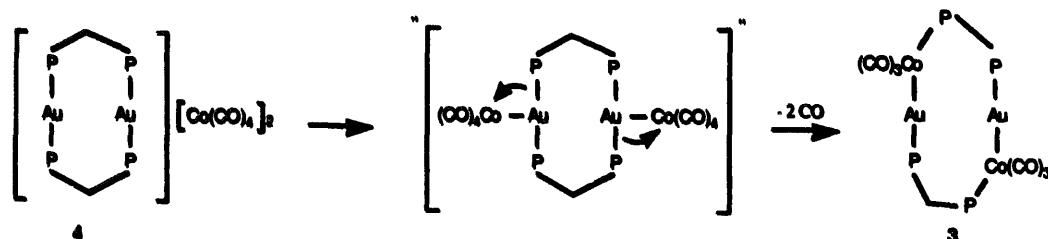
Scheme 1.

product. Interestingly, in reacting the cobalt anion with a mixture formed by $[(\text{ClAu})_2(\mu\text{-dippe})]$ or $[(\text{ClAu})_2(\mu\text{-dppp})]$ (dippe = diphenylphosphinoethane; dppp = diphenylphosphinopropane) and dppm, **3** was again formed in both cases, indicating that a rapid phosphine exchange occurs in solution. This substitution was also observed when dppm reacted with the complexes $[(\text{CO})_4\text{CoAu}_2(\text{P-P})]$ (P-P = dippe (**2b**) and dppp (**2c**)). Fortunately, when the reaction between **2a** and dppm was run in toluene, we were able to isolate a white crystalline solid in good yield. Although all attempts to grow crystals for an X-ray structure determination failed, it was tentatively formulated as $[\text{Au}_2(\mu\text{-dppm})_2][\text{Co}(\text{CO})_4]_2$ (**4**) according to its $\nu(\text{CO})$ IR spectrum (only one strong band at 1890 cm^{-1}), ^{31}P NMR spectrum (one singlet at $\delta = 32\text{ ppm}$) and elemental analyses. The most important point was that, when this complex was heated in toluene to 80°C , it afforded a yellow solution from which **3** was precipitated after addition of hexane.

All these results suggest that, as shown in Scheme 1, complex **4** is the undetected intermediate in the formation of **3** in THF, which undergoes a rapid intramolecular reorganization involving the migration of phospho-

rus from the gold atom to the $\text{Co}(\text{CO})_4$ units with loss of two carbonyl groups (Scheme 2).

Confirmation of the pathway for the formation of **3** was provided by use of the diphosphine dppip (dppip = bisdiphenylphosphinoisopropane) as a bidentate ligand. This diphosphine shows a similar bite angle to that exhibited by dppm, but the presence of two methyl groups bonded to the central carbon atom, along with its higher basicity, could prevent the opening of the $\text{C}_2\text{P}_2\text{Au}_2$ cycle and consequently, favour the stabilization of the dppip analogous to **4**. Indeed, the mixed Co/Au cluster $[(\text{CO})_4\text{Co-Au}_2(\mu\text{-dppip})]$ (**5**), obtained by reaction of $\text{Na}[\text{Co}(\text{CO})_4]$ and $[(\text{ClAu})_2(\mu\text{-dppip})]$ in THF at 0°C , reacted with dppip at room temperature to give a pale yellow crystalline solid which, according to its spectroscopic data (IR: $\nu(\text{CO})$: 1884 cm^{-1} ; ^{31}P NMR: $\delta = 59\text{ ppm}$), almost identical to those found for **4**, can be formulated as $[\text{Au}_2(\mu\text{-dppip})_2][\text{Co}(\text{CO})_4]_2$ (**6**). The nature of **6** has been unambiguously confirmed by an X-ray crystal study. Interestingly, this complex was also obtained by reacting the di-gold complex $[(\text{ClAu})_2(\mu\text{-dppip})_2]$ with $\text{Na}[\text{Co}(\text{CO})_4]$ in THF at -15°C . It is remarkable that the treatment of this ionic compound in toluene at different temperatures did not



produce a species analogous to **3** because of the steric hindrance due to the two methyl substituents.

In conclusion, the structural characterization of **6** and its chemical behaviour reinforces the mechanism suggested for the formation of **3** through the complex **4** as intermediate. All these results demonstrate that for this four-metal system, Co_2Au_2 , the dppm ligand does not ensure the maintenance of a preformed geometry which is needed as part of a general strategy to build clusters using dppm-assisted dinuclear building blocks.

3. X-ray crystal structure determination of **6**

The molecular structure of **6** is shown in Fig. 1 together with the atomic numbering scheme. Selected bond and angle parameters are listed in Table 1 while the crystallographic parameters are summarized in Table 2.

The crystal contains well separated $[\text{Co}(\text{CO})_4]^-$ and $[\text{Au}_2(\mu\text{-dppip})_2]^{2+}$ ions without short interionic contacts. The cobalt atom in the anion presents a tetrahedral coordination of the carbonyl groups as expected. The cation possesses approximately C_1 symmetry and it is formed by an eight-atom cycle, of which the atoms P(1), Au, P(2), P(1'), Au', and P(2') lie basically in the same plane (Fig. 2). The angle between the planes containing P(1), Au, Au', P(1') and P(2), Au, Au', P(2') is 2.49° . It can therefore be considered as a planar array

Table 1
Selected bond distances (Å) and angles ($^\circ$) for **6**. Atoms labelled with prime have symmetry operation $-x, 1-y, -z$

Au–Au	2.9275(10)		
P1–Au	2.3289(11)	P1–C1'	1.876(4)
P2–Au	2.3340(11)	P2–C22	1.812(4)
P1–C10	1.831(4)	P2–C16	1.817(3)
P1–C4	1.812(3)	P2–C1	1.867(4)
P1–Au–P2	176.27(3)	C4–P1–Au	113.32(13)
P1–Au–Au'	93.14(3)	C4–P1–C10	106.1(2)
P2–Au–Au'	89.64(3)	C16–P2–Au	110.75(13)
P2–C1–P1'	108.7(2)	C22–P2–Au	109.46(14)
C1–P2–Au	110.35(11)	C2–C1–C3	108.3(3)
C1'–P1–Au	108.64(12)	C10–P1–C1'	106.0(2)
C10–P1–Au	109.90(13)	C22–P2–C1	106.1(2)

with the isopropyl groups of the diphosphine out of plane. Each gold atom is bonded to a phosphorus atom of each bridging dppip ligand. The Au–P bonds in **6** (Au–P(1) = 2.3289(11) and Au–P(2) = 2.3340(11) Å) are similar to those reported for $[(\text{ClAu})_2(\mu\text{-dppm})]$ (2.327 and 2.288 Å) [4]. The short Au–Au separation (2.9275(10) Å) is comparable with that observed for **3** (2.977(10) Å) [3], $[(\text{ClAu})_2(\mu\text{-dppm})_2]$ (2.962(1) Å), $[\text{Au}_2(\mu\text{-}(\text{PPh}_2)_2\text{C}(\text{AuPPh}_3)_2)_2]$ (2.920(2) Å) [5] and $[\text{Fe}_2\text{Au}_2(\text{CO})_8(\mu\text{-dppm})]^-$ (2.915(1) Å) [1] and slightly longer than that found in metallic gold (2.884 Å) [6], consequently a bonding interaction should be assumed.

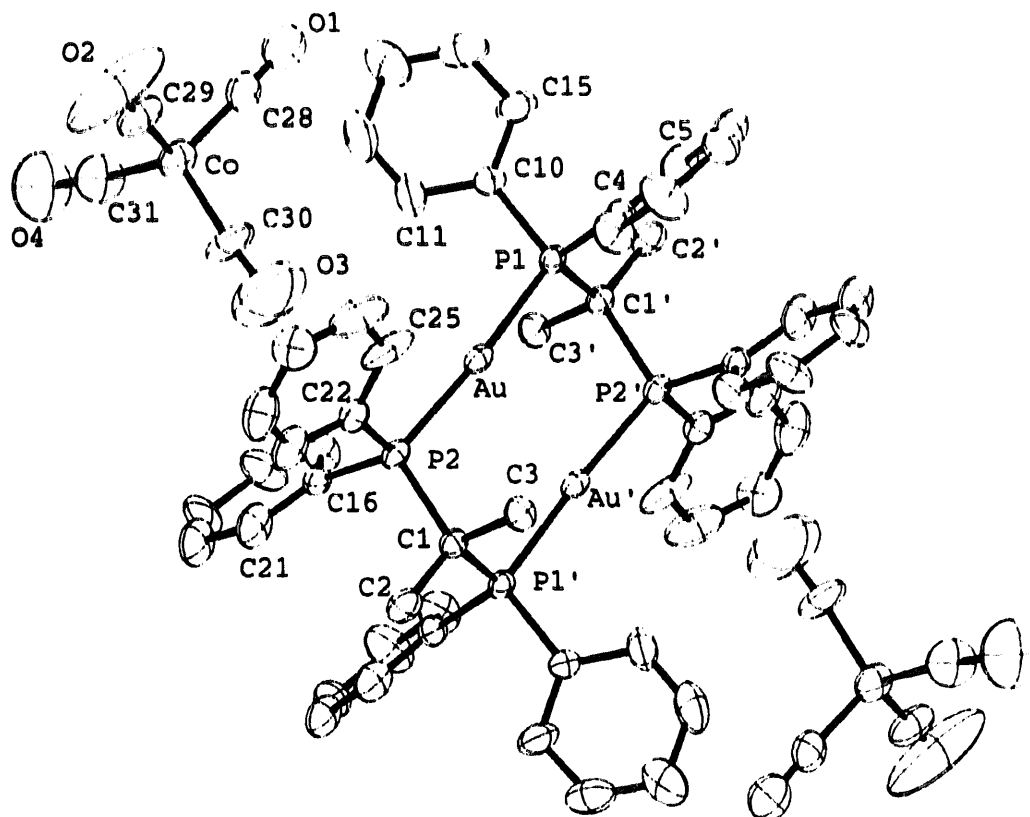


Fig. 1. ORTEP view of the molecular structure of the complex $[\text{Au}_2(\mu\text{-dppip})_2][\text{Co}(\text{CO})_4]_2$ (**6**) together with the atomic numbering scheme.

Table 2
Crystallographic data for 6

Formula	C ₆₂ H ₅₂ Au ₂ Co ₂ O ₈ P ₄
F _w	1560.71
Space group	P1
a (Å)	11.242(5)
b (Å)	12.003(2)
c (Å)	13.564(5)
α (°)	97.13(2)
β (°)	103.94(3)
γ (°)	103.73(2)
V (Å ³)	1693.4(10)
Z	1
D _{calc} (g cm ⁻³)	1.530
μ (Mo K α) (mm ⁻¹)	4.941
T (°C)	293(2) K
λ (cm ⁻¹)	0.71069
R	0.027

The P–Au–Au angles are almost right (P(2)–Au–Au' = 89.64(3)° and P(1)–Au–Au' = 93.14(3)°), whereas each gold atom seems almost linearly coordinated to the two phosphorus atoms as indicated by the P–Au–P angles (176.27(3)°). This contrasts with the P–Au–P angle of 155.9° observed for [(ClAu)₂(μ-dppm)₂]. In this case, the presence of a chlorine atom increases the coordination number at gold centres, which explains this distortion.

4. Experimental

All manipulations were performed under an atmosphere of prepurified N₂ with use of standard Schlenk techniques, and all solvents were distilled from appropriate drying agents. Elemental analysis of C and H were carried out at the Institut de Bio-Orgànica de Barcelona. Infrared spectra were recorded on an FT-IR 520 Nicolet spectrophotometer. ¹H and ³¹P{¹H} NMR

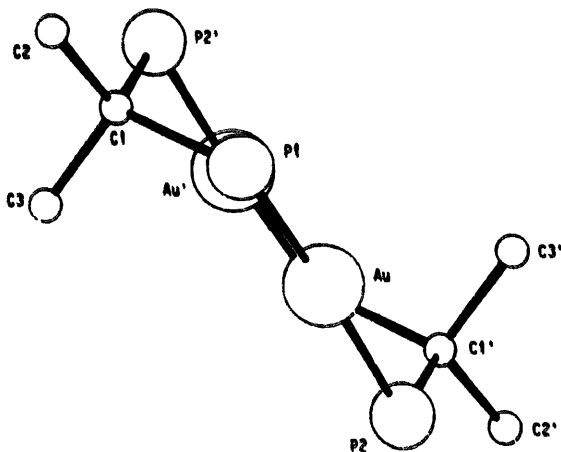


Fig. 2. Drawing of the planar skeletal core of the cation of complex 6.

spectra were obtained on a Bruker WP 80SY spectrometer ($\delta(85\% \text{H}_3\text{PO}_4) = 0.0 \text{ ppm}$). Fast atom bombardment (FAB) mass spectra were recorded on an Auto SPEC U, Cs⁺, 30 kV mass spectrometer using a 3-nitrobenzylalcohol (NBA) matrix. Compounds [(AuCl)₂(μ-PP)] (PP = dppm, dppe, dppp, dppip) were synthesized and isolated as solids from AuCl(tht) [7] solutions by adding the appropriate amount of the corresponding diphosphine.

4.1. Preparation of [(CO)₄CoAu₂(PP)] (PP = dppm (2a), dppe (2b), dppp (2c), dppip (5))

Details of the synthesis of 2a apply also to 2b, 2c, and 5.

A solution of Na[Co(Co)₄] (0.64 g, 3.30 mmol) in THF (100 ml) at 0°C was treated with the stoichiometric quantity of solid [(ClAu)₂(PP)]. After 30 min of stirring, the solution was evaporated to dryness. The residue was extracted with toluene (2 × 25 ml) and filtered, and the pale yellow solution was concentrated to 10 ml. After addition of 10 ml of hexane, white crystals (green for 5) were obtained in ca. 60–70% yield.

Spectroscopic data and analysis for 2a. IR (THF, cm⁻¹): ν(CO) 2052 s, 2023 m, sh, 1978 s, 1957 vs. ¹H NMR (25°C, acetone-*d*₆): δ 7.2–7.9 (m, 20H, Ph), 4.5 (t, 2H, J(H–P) = 12 Hz) ³¹P{¹H} NMR (25°C, toluene): δ 24.6. Anal. Found: C, 35.41; H, 2.01. C₃₃H₂₂Au₂Co₂O₈P₂. Calc.: C, 35.37; H, 1.98%.

Spectroscopic data and analysis for 2b. IR (THF, cm⁻¹): ν(CO) 2053 s, 1982 m, 1955 vs. ¹H NMR (25°C, CDCl₃): δ 7.4–7.7 (m, 20H, Ph), 3.1 (s, br, 4H, PCH₂CH₂P). ³¹P{¹H} NMR (25°C, toluene): δ 37.4. Anal. Found: C, 36.09; H, 2.20. C₃₄H₂₄Au₂Co₂O₈P₂. Calc.: C, 36.00; H, 2.13%.

Spectroscopic data and analysis for 2c. IR (THF, cm⁻¹): ν(CO) 2053 s, 1981 m, 1954 vs. ¹H NMR (25°C, CDCl₃): δ 7.3–7.6 (m, 20H, Ph), 2.8 (m, 4H, PCH₂) 1.95 (m, 2H, PCH₂CH₂). ³¹P{¹H} NMR (25°C, toluene): δ 31.3. Anal. Found: C, 36.93; H, 2.35. C₃₅H₂₆Au₂Co₂O₈P₂. Calc.: C, 36.60; H, 2.28%.

Spectroscopic data and analysis for 5 IR (THF, cm⁻¹): ν(CO) 2053 m, 1982 m, 1956 vs. ¹H NMR (25°C, acetone-*d*₆): δ 7.4–8.0 (m, 20H, Ph), 1.7 (t, 6H, J(H–P) = 15 Hz). ³¹P{¹H} NMR (25°C, toluene): δ 55.6. FAB mass spectrum: *m/z* 1171 [M + Na]⁺, 1064 [M–3CO]⁺, 977 [M–Co(CO)₄]⁺. Anal. Found: C, 36.83; H, 2.38. C₃₅H₂₆Au₂Co₂O₈P₂. Calc. C, 36.60; H, 2.28%.

4.2. Preparation of [Co₂Au₂(CO)₆(μ-dppm)₂] (3)

A solution of 2a (0.1 g, 0.09 mmol) in THF (100 ml) at room temperature was treated with 0.034 g (0.09 mmol) of solid dppm. After 15 min of stirring, the mixture was evaporated to dryness. The residual solid

was treated with 10 ml of dichloromethane and filtered, and after addition of 15 ml of methanol, bright yellow microcrystals of **1** were obtained in ca. 40–60% yield.

IR (KBr, cm^{-1}): $\nu(\text{CO})$ stretch 1992 m, 1990 vs, 1912 m, 1896 s, 1872m, $^{31}\text{P}\{^1\text{H}\}$ NMR (240 K, CH_2Cl_2): δ 57.2 (dd), 27.1 (dd, $^{2+3}J(\text{P}-\text{P}) = 107$ Hz). ^1H NMR (25°C, CD_2Cl_2): δ 7.1–8.0 (m, 40H, Ph), 3.50 (t, 4H, $J(\text{H}-\text{P}) = 10.1$ Hz). Anal. Found C, 46.17; H, 3.13. $\text{C}_{56}\text{H}_{44}\text{Au}_2\text{Co}_2\text{O}_6\text{P}_4$. Calc.: C, 46.43; H, 3.06%.

4.3. Preparation of diphenylphosphinoisopropane (dp-pip)

Solid PPh_3 (19.7 g, 0.075 mol) was added slowly to a stirred suspension of finely divided lithium (1.45 g, 0.2 mol) in THF (100 ml) at room temperature. After 20 h of stirring, the solution was filtered and cooled to -78°C . Ammonium bromide (7.45 g, 0.075 mol) was added and, after 15 min of stirring at -78°C , the mixture was allowed to warm to room temperature. After 1 h of stirring, the deep orange solution obtained was added very slowly to a cooled solution (-78°C) of 3.9 ml (0.037 mol) of 2,2-dichloropropane in 10 ml of THF. The resulting solution was stirred for 20 h at room temperature. It was then cooled to -78°C and, by careful addition of 150 ml of ethanol followed by 125 ml of distilled water, a white precipitate was obtained. The mixture was filtered and the solid was dried *in vacuo*. The solid product was dissolved in ethyl ether and the solution obtained was filtered, concentrated to half volume and cooled overnight (-30°C). Colourless crystals of dppip were obtained in 45% yield. M.p. $106\text{--}110^\circ\text{C}$. $^{31}\text{P}\{^1\text{H}\}$ NMR (25°C, CH_2Cl_2): δ 12.5 ppm. ^1H NMR (25°C, CDCl_3): 7.2–8.2 (m, 20H, Ph), 1.2 (t, 6H, $J(\text{H}-\text{P}) = 20$ Hz).

4.4. Preparation of $[(\text{ClAu})_2(\mu\text{-dppip})_2]$

A suspension of dppip (0.008 g, 0.19 mmol) in ethanol (10 ml) at 40°C was added to a suspension of $[(\text{ClAu})_2(\mu\text{-dppip})]$ (0.17 g, 0.19 mmol) in ethanol (15 ml). The mixture was stirred for 20 min at room temperature. The colourless solution was filtered and evaporated to dryness. A pale green solid was obtained in 95% yield. $^{31}\text{P}\{^1\text{H}\}$ NMR (210 K, CH_2Cl_2): δ 59 ppm. ^1H NMR (240 K, acetone- d_6): 7.2–7.8 (m, 40H, Ph), 1.7 (s, br, 12H). Anal. Found C, 50.84; H, 4.17. $\text{C}_{54}\text{H}_{52}\text{Au}_2\text{Cl}_2\text{P}_4$. Calc.: C, 50.30; H, 4.06%.

4.5. Preparation of $[\text{Au}_2(\mu\text{-dppip})_2][\text{Co}(\text{CO})_4]$, (**6**)

4.5.1. Method(a) **5** + dppip

A solution of **5** (0.2 g, 0.17 mmol) in 100 ml of THF was treated with solid dppip (0.071 g, 0.17 mmol). The initial green solution became brown immediately. The

mixture was stirred for 20 min and filtered. The solution was concentrated and a brown solid precipitated. The mixture was filtered and the solid was dried *in vacuo*. Yield 50%.

4.5.2. Method(b) $[(\text{ClAu})_2(\mu\text{-dppip})_2] + \text{Na}[\text{Co}(\text{CO})_4]$

A solution of $\text{Na}[\text{Co}(\text{CO})_4]$ (0.21 g, 1.08 mmol) in THF (50 ml) was added to a solution of $[(\text{ClAu})_2(\mu\text{-dppip})_2]$ (0.69 g, 0.54 mmol) in THF (25 ml) at -15°C . After 1 h of stirring, the mixture was allowed to warm to room temperature. The solution was filtered and concentrated to 10 ml. Pale brown crystals of **6** were obtained in 50–60% yield.

Table 3

Atomic coordinates ($\times 10^4$; Au, Co and P atoms $\times 10^5$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) with esds in parentheses for the non-hydrogen atoms of compound **6**

Atom	x	y	z	U_{eq}
Au	5169(2)	45368(2)	9082(2)	41(1)
Co	-38826(6)	-5387(6)	24015(1)	65(1)
P(1)	-4296(8)	55245(7)	19456(8)	38(1)
P(2)	14272(7)	34413(7)	-833(8)	39(1)
O(1)	-5041(5)	865(4)	3557(4)	108(2)
O(2)	-1503(16)	-694(19)	3816(16)	341(15)
O(2')	-1727(14)	-681(13)	3865(12)	303(11)
O(3)	-3137(8)	728(7)	879(6)	276(3)
O(4)	-5569(16)	-2930(14)	1663(14)	183(4)
O(4')	-5849(26)	-2612(22)	1452(27)	343(20)
C(1)	1891(3)	4228(3)	-1096(3)	39(1)
C(2)	2643(4)	3626(4)	-1705(4)	56(1)
C(3)	2753(3)	5448(3)	-528(3)	51(1)
C(4)	655(3)	6861(3)	2771(3)	44(1)
C(5)	292(4)	7682(4)	3315(4)	67(1)
C(6)	1205(5)	8679(4)	3959(4)	77(2)
C(7)	2433(6)	8838(4)	4028(4)	76(2)
C(8)	2833(5)	8053(6)	3488(5)	97(2)
C(9)	1932(5)	7057(5)	2831(5)	77(2)
C(10)	-991(3)	4604(3)	2813(3)	47(1)
C(11)	-1093(6)	3436(4)	2607(5)	80(2)
C(12)	-1511(7)	2723(6)	3243(7)	104(2)
C(13)	-1798(6)	3154(7)	4099(6)	99(2)
C(14)	-1663(6)	4268(8)	4302(5)	94(2)
C(15)	-1270(6)	5036(6)	3676(4)	78(2)
C(16)	340(3)	2000(3)	-663(3)	43(1)
C(17)	-901(4)	1795(4)	-584(4)	71(1)
C(18)	-1768(5)	717(5)	-1017(5)	90(2)
C(19)	-1433(6)	-145(4)	-1515(5)	83(2)
C(20)	-225(6)	35(4)	-1577(5)	87(2)
C(21)	658(5)	1104(4)	-1164(5)	74(2)
C(22)	2890(3)	3286(3)	732(3)	48(1)
C(23)	3491(4)	2463(4)	456(5)	72(1)
C(24)	4597(5)	2382(5)	1135(6)	90(2)
C(25)	5086(4)	3091(6)	2072(5)	84(2)
C(26)	4538(6)	3929(8)	2351(5)	107(2)
C(27)	3419(5)	3999(6)	1682(4)	89(2)
C(28)	-4596(5)	326(4)	3090(5)	72(1)
C(29)	-2505(6)	-644(5)	3250(5)	81(2)
C(30)	-3493(8)	167(8)	1445(7)	100(2)
C(31)	-4960(6)	-1933(6)	1908(6)	100(2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Spectroscopic data and analysis for **6**. IR (KBr, cm^{-1}): $\nu(\text{CO})$ 1884 vs. ^1H NMR (25°C, acetone- d_6): δ 7.4–8.0 (m, 40H, Ph), 1.7 ppm (t, 12H, $J(\text{H}-\text{P}) = 12$ Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (240 K, acetone- d_6): δ 59.2 ppm. Anal. Found: C, 48.05; H, 3.43. $\text{C}_{62}\text{H}_{52}\text{Au}_2\text{Co}_2\text{O}_8\text{P}_4$. Calc. C, 47.70; H, 3.36%.

4.6. X-ray structure determination of **6**

A summary of the crystal data is given in Table 2. A prismatic crystal ($0.2 \times 0.3 \times 0.2$ mm³) was selected and mounted on an Enraf-Nonius CAD4 four-circle diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($12 < \theta < 21^\circ$) and refined by the least-squares method. Intensities were collected with graphite monochromatized Mo K α radiation using the $\omega/2\theta$ scan technique. 7917 reflections were measured in the range $1.58 \leq \theta \leq 29.96$. 6432 reflections were assumed as observed, applying the condition $I > 2\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity control, and significant intensity decay was not observed. Lorentz-polarization and absorption corrections were made.

The structure was solved by Patterson synthesis, using the SHELXS computer program [8], and refined by the full-matrix least-squares method with SHELX93 [9] using 7867 reflections (very negative intensities were not assumed). The function minimized was $\sum w \| F_o^2 - |F_c|^2 \|^2$, where $w = [\sigma^2(I) + (0.1128P)^2 + 0.2982P]^{-1}$, and $P = (|F_o|^2 + 2|F_c|^2)/3$. f , f' , f'' were taken from *International Tables of X-ray Crystallography* [10]. O(2) and O(4) atoms were located in a disorder position. An occupancy factor of 0.5 was assumed according to the height of peaks in the Fourier map. The extinction coefficient was 0.00022. All H atoms were computed and refined with an overall

isotropic temperature factor using a riding model. The final R (on F) factor was 0.027 for reflections with $I > 2\sigma(I)$, wR (on $|F|^2$) 0.069 and goodness of fit 0.533 for all observed reflections. The number of refined parameters was 372. Max. shift/esd = 1.10. Mean shift/esd = 0.06. Max. and min. peaks in the final difference synthesis were 1.905 and -2.149 eÅ⁻³ respectively. The final atomic coordinates for the non-hydrogen atoms are given in Table 3. Tables of all distances and angles, final hydrogen parameters, anisotropic thermal parameters, and a list of structural factors can be obtained from the authors.

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References

- [1] S. Alvarez, O. Rossell, M. Seco, J. Valls, M.A. Pellinghelli and A. Tiripicchio, *Organometallics*, **10** (1991) 2309.
- [2] H. Deng and S.G. Shore, *Organometallics*, **10** (1991) 3486.
- [3] A. Pons, O. Rossell, M. Seco and A. Perales, *Organometallics*, **14** (1995) 555.
- [4] H. Schmidbaur, A. Wohlleben, U. Schubert, A. Frank and G. Huttner, *Chem. Ber.*, **110** (1977) 2751.
- [5] E.J. Fernández, M.C. Gimeno, P.G. Jones, A. Laguna, M. Laguna and J.M. López de Luzuriaga, *Angew. Chem., Int. Ed. Engl.*, **33** (1994) 87.
- [6] W.D. Pearson, *Lattice Spacings and Structure of Metals and Alloys*, Pergamon Press, London, 1957.
- [7] R. Usón and A. Laguna, *Organomet. Synth.*, **3** (1986) 324.
- [8] G.M. Sheldrick, *Acta Crystallogr., A*, **46** (1990) 467.
- [9] G.M. Sheldrick, in preparation.
- [10] *International Tables of X-ray Crystallography*, Vol. 4, Kynoch Press, Birmingham, UK, 1974, pp. 99–100 and 149.