Journal of Organometallic Chemistry, 456 (1993) 305–312

JOM 23601

Reactivity of ketonylgold(III) complexes. Crystal and molecular structure of SP-4-4-[Au(2-$C_6H_4N_2Ph$){$CH_2COC_6H_2(OMe)_3$-3,4,5}Cl(PPh_3)] and SP-4-4-[Au(2-$C_6H_4N_2Ph$)(CH_2COMe)Cl(PPh_3)]

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(Received January 5, 1993)

Abstract

Ketonyl complexes [Au(η^2-pap)(η^1-CH_2COR)Cl][η^2-pap = 2-(phenylazo)phenyl-C^1,$N^{2'}$] react i) with various salts [AgAc, Ac = $MeCO_2$, or NaI] to give neutral complexes [Au(η^2-pap)(η^1-CH_2COMe)X] [X = Ac (**1**), I (**2**)], ii) with PPh_3 to give [Au(η^1-pap)(η^1-CH_2COR)Cl(PPh_3)] (R = Me (**3**), $C_6H_2(OMe)_3$-3,4,5 (**4**)], iii) with PPh_3 and KCN to give [Au(η^1-pap)(η^1-CH_2COMe)CN(PPh_3)] (**5**), iv) with $Ph_2P(CH_2)_2PPh_2$ (dppe) (1:1) to give [Au(η^1-pap)(η^1-CH_2COMe)(μ-dppe)]$_2$ Cl_2 (**6a**) which in turn reacts with $NaClO_4$ to give [Au(η^1-pap)(η^1-CH_2COMe)(μ-dppe)]$_2$ $(ClO_4)_2$ (**6b**), v) with $PhNH_2$ to give [Au(η^2-pap)(η^1-CH_2C(=NPh)Me)Cl] (**7**), or vi) with $AgClO_4$ or $Ag(CF_3SO_3)$ to give [Au(η^2-pap)(η^2-CH_2COMe)]X [X = ClO_4 (**8a**), CF_3SO_3 (**8b**)]. The complex [Au(η^1-pap)(η^1-CH_2COMe)Cl(PPh_3)] shows dynamic behaviour in solution. Low-temperature crystal structures have been determined for complexes **3** and **4**. **3** crystallizes in the triclinic space group $P\bar{1}$ with a = 10.389(3), b = 11.269(3), c = 14.482(3), α = 89.20(2), β = 72.95(2), γ = 63.43(2)°, U = 1436.0 Å^3, Z = 2, 4399 observed reflections [$F > 4.0\sigma(F)$], R = 4.6%, and wR = 5.7%. Complex **4** crystallizes in the monoclinic space group $P2_1$ with a = 11.151(3) Å, b = 18.468(5) Å, c = 17.780(3) Å, β = 92.11(2)°, U = 3659.2(15) Å^3, Z = 4, 9657 observed reflections [$F > 4.0\sigma(F)$], R = 2.62%, and wR = 2.61%. Both complexes show a square-planar coordination around the gold atom with chloride *trans* to aryl. The ketonyl group is unambiguously bonded through the carbon atom in complex **4**, but may be disordered in complex **3**.

1. Introduction

Metallated ketones play a very important role in organic synthesis [1]. They can be prepared by direct metallation of the ketone, oxidation-addition reactions (with α-halogenocarbonyl compounds or epoxides), or transmetallation reactions, *etc.* [1,2]. We have recently reported that an unusual [3] C–H activation of acetone occurs by intramolecular co-operation between the metal [Au^{III}] and a ligand attached to it [4]. Thus, [Au(η^2-pap)Cl_2][η^2-pap = 2-(phenylazo)phenyl-C^1, $N^{2'}$] when treated in acetone with various reagents such as Tl(acac) (Hacac = acetylacetone), KCN, $AgClO_4$, 1,10-phenanthroline, [HgR_2] (R = C_6F_5, pap), [PdR_2] (R = $C_6H_4NO_2$-2], gives [Au(η^2-pap)(η^1-CH_2COMe)Cl]. Some intermediates in this process (see Scheme 1) were isolated. We have also studied the C–H activation of other ketones [5]. We now report the study of the reactivity of the new ketonylcomplexes and X-ray structural studies of some phosphine derivatives.

2. Results

The complex [Au(η^2-pap)(η^1-CH_2COMe)Cl] [η^2-pap = 2-(phenylazo)phenyl-C^1,$N^{2'}$], obtained by C–H activation of acetone (see Scheme 1) [4], reacts with AgAc (Ac = $MeCO_2$) in equimolar proportions, or with an excess of NaI, to give the corresponding substitution products [Au(η^2-pap)(η^1-CH_2COMe)X] [X = Ac (**1**) or I (**2**)] (see Scheme 2).

PPh_3 reacts readily with ketonyl complexes [Au(η^2-pap)(η^1-CH_2COR)Cl] to give the corresponding

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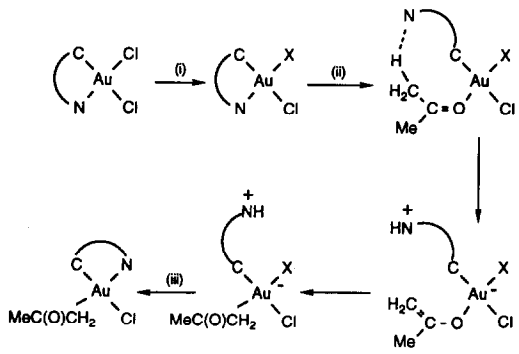


Scheme 1. Proposed reaction pathway for the carbon–hydrogen activation process of ketones with 2-(phenylazo)phenylgold(III) complexes, CN = $C_6H_4N_2$Ph-2: (i) X = acac-C, CN, $C_6H_4N_2$Ph-2, C_6F_5, or $C_6H_4NO_2$-2; (ii) + Me_2CO; (iii) − XH.

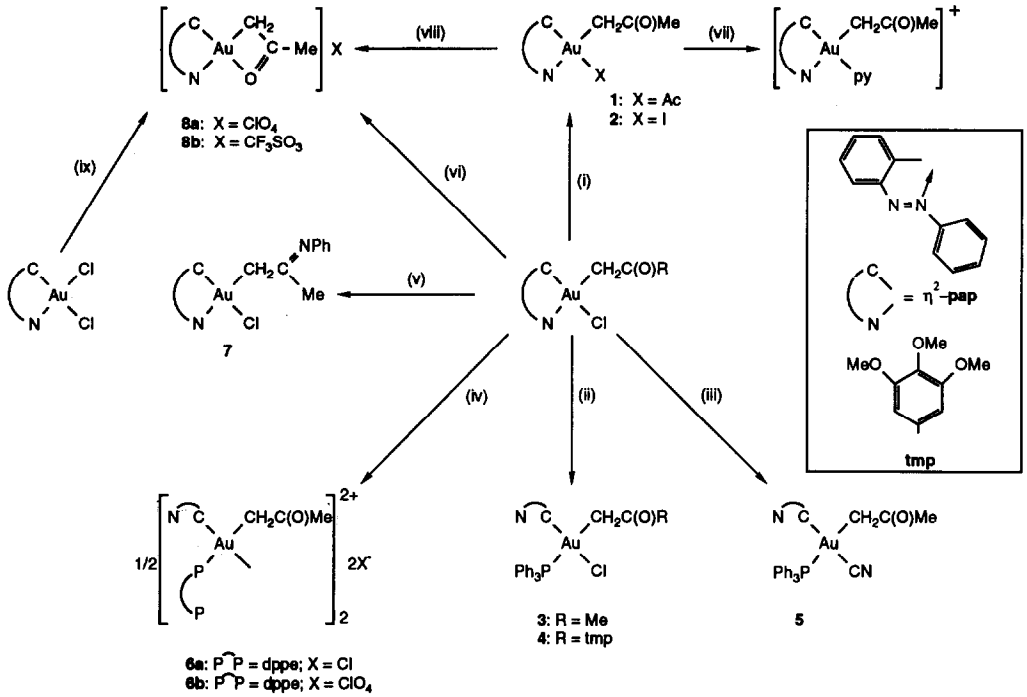
adducts [Au(η^1-pap)(η^1-CH_2COR)Cl(PPh_3)] [R = Me (**3**) or R = $C_6H_2(OMe)_3$-3,4,5(tmp) (**4**)]. The related species [Au(η^1-pap)(η^1-CH_2COMe)CN(PPh_3)] (**5**) was prepared to compare its solution behaviour with that of **3** (see below) by adding PPh_3 (1:1) and then, after 30 min, KCN (1:1:5), to [Au(η^2-pap)(η^1-CH_2COMe)Cl].

1,2-bis(diphenylphosphino)ethane (dppe) reacts with [Au(η^2-pap)(η^1-CH_2COMe)Cl] (1:1) to give [Au(η^1-pap)(η^1-CH_2COMe)(μ-dppe)]$_2Cl_2$ (**6a**), which in turn reacts with $NaClO_4$ (1:1) to give [Au(η^1-pap)(η^1-CH_2COMe)(μ-dppe)]$_2(ClO_4)_2$ (**6b**).

Reaction of [Au(η^2-pap)(η^1-CH_2COMe)Cl] with $PhNH_2$ yields the imine complex [Au(η^2-pap)(η^1-CH_2C(=NPh)Me}Cl] (**7**). [Au(η^2-pap)(η^1-CH_2CO-Me)(Ac)] reacts with aqueous $HClO_4$ to give [Au(η^2-pap)(η^2-CH_2COMe)]ClO_4 (**8a**) and with (pyH)ClO_4 (py = pyridine) to give the known complex [Au(η^2-pap)(η^1-CH_2COMe)(py)]ClO_4 [5]. An alternative preparation of **8a** is the reaction between [Au(η^1-pap)(η^1-CH_2COMe)(bipy)]ClO_4 [5] (bipy = 2,2′-bipyridine) and $AgClO_4$. However, the most direct method consists in reaction of [Au(η^2-pap)Cl_2] with $AgClO_4$ (1:2) in acetone. In this way, [Au(η^2-pap)(η^1-CH_2COMe)Cl] is formed at first [4,5], and then reacts with $AgClO_4$ to give **8a**. Because **8a** is too unstable in solution to yield a ^{1}H NMR spectrum, we isolated [Au(η^2-pap)(η^2-CH_2COMe)]CF_3SO_3 (**8b**), which is slightly more stable in solution, by reaction of [Au(η^2-pap)(η^1-CH_2COMe)Cl] with $AgCF_3SO_3$.

3. Discussion

The reactions between the ketonylgold(III) complexes and PPh_3 are fast and are accompanied by a change from yellow to orange-red, presumably due to the change of coordination of the aryl ligand from di- to mono-hapto (see Scheme 2). This behaviour is similar to that found for [Au(η^2-pap)Cl_2] [6]. [Au(η^2-



Scheme 2. Synthesis of complexes **1**–**8**: (i) + AgAc − AgCl or + NaI − NaCl; (ii) + PPh_3; (iii) + PPh_3 + KCN − KCl; (iv) + dppe or + dppe + $NaClO_4$; (v) + $PhNH_2$ − H_2O; (vi) + AgX − AgCl; (vii) + $HClO_4$ − HAc; (ix) + 2 $AgClO_4$ + Me_2CO − 2 AgCl − $HClO_4$.

pap)(η^1-CH_2COMe)Cl] also resembles [Au(η^2-pap)Cl_2] in its reactions with some more labile donors, such as $AsPh_3$, $SbPh_3$ and pyridine because, although the same colour change in solution was observed, the starting products were recovered unchanged, probably because of an equilibrium between the starting complex and the neutral adducts [6].

The reaction between [Au(η^2-pap)(η^1-CH_2COMe)Cl] and dppe leads to the dimer **6a** even using a 2:1 ratio. In this case, a mixture of **6a** and the starting gold(III) complex was obtained. This result contrasts with that previously described [6] for [Au(η^2-pap)Cl_2], which, upon reaction with dppe (2:1 or 1:1), gave the neutral dimer with a bridging diphosphine, *cis*-[Au_2(η^1-pap)$_2Cl_4$(μ-dppe)].

The condensation reaction giving complex **7** occurs under very mild conditions which contrasts with the fact that ketones add primary amines only at high temperatures [7]. The difference may be attributed to the increase in electrophilic character of the carbonyl carbon atom on substitution of a hydrogen in acetone by the Cl(pap)Au^{III} moiety.

3.1. *Structure and spectroscopic properties of the complexes*

A strong absorption corresponding to ν(CO) appears at *ca.* 1675 cm^{-1} in the ketonyl complexes **1–6**. In the cationic chelating ketonyls **8** this band shifts to *ca.* 1580 cm^{-1} as a result of the coordination of the carbonyl oxygen to the metal. Complex **1** shows two strong absorptions at *ca.* 1625 and 1300 cm^{-1} due to $\nu_{asym}(CO_2)$ and $\nu_{sym}(CO_2)$, respectively, of the acetate. Complex **7** shows ν(CN) as a medium band at 1620 cm^{-1}. The ν(AuCl) band appears around 300 cm^{-1} in chloro-complexes **3**, **4** and **7**, indicating that the chloro ligands are *trans* to the phenyl group, consistent with the X-ray structure of **3** and **4** (see below) and other related complexes [4].

The ^{1}H NMR spectra of ketonyl complexes **1** and **2** show CH_2 resonances as a singlet in the range 3.2–3.8 ppm, consistent with the coordination of the ketonyl group through the CH_2 carbon atom [4,5]. Complexes **8a,b** rapidly decompose in solution and only the ^{1}H NMR spectrum of **8b** could be recorded, showing a singlet at 3.5 ppm. Complexes **3** and **4** show the CH_2 resonance as a broad peak and a singlet, respectively, indicating dynamic behaviour in solution, while **5** shows a doublet at 3.2 ppm (^3J(HP) = 14.7 Hz).

A conductivity study of complex **6b** in nitromethane gives the values expected for a 1:2 electrolyte [8]. The *cis* geometry is based on the ^{31}P NMR spectrum.

As far as we are aware, **7**, **8a,b** are the only complexes containing a dihapto-acetonyl and a monohapto CH_2C(=NPh)Me ligand. In the complex [W(η^5-Cp)$(CO)_2$(η^3-CH_2COMe)], the acetonyl is assumed to be coordinated as η^3-oxaallyl [2a].

An interesting feature of the phosphine complex **3** is that it undergoes slow spontaneous reductive elimination to give [AuCl(PPh_3)] and the coupling product pap-CH_2COMe. The synthesis and characterization of these new C–C coupling derivatives are currently under study. We have recently described [9] a family of substituted biphenyls, Ar–Ar', prepared by reaction of complexes [Au(Ar)(Ar')Cl] with PPh_3.

The X-ray diffraction studies of complexes **3** and **4** (see Tables 1 and 2, Figs. 1 and 2) reveal the expected square-planar geometry at the metal atom, with the ketonyl groups *trans* to the phosphine (as indicated by the IR and low-temperature NMR data). The ketonyl group in **3** displayed relatively high displacement parameters for a low-temperature structure (*ca.* 0.1 $Å^2$), and the hydrogen atoms were not located. However, no such problems were encountered in the structure of **4**, where the hydrogen atoms were all located and the coordination of the ketonyl group through the carbon atom thus confirmed.

The two independent molecules of **4** display similar molecular dimensions, the main difference being in the Au–Cl bond lengths of 2.372, 2.382(1) Å. These values are similar to that of **3** [2.368(3) Å], but surprisingly, much longer than the 2.347(1) Å observed *trans* to the aryl in [Au(η^2-mpap)Cl_2] [5] [η^2-mpap = 2-(4'-methylphenylazo)-5-methylphenyl-C^1,$N^{2'}$]. This may be due to a larger *cis* influence of ketonyl and phosphine ligands compared with chloro and azo-N, but *cis* influences in gold complexes have not been studied in any detail.

The Au–C(aryl) bond lengths in **3**, **4**, [Au(η^2-mpap)Cl_2], and [Au(η^2-mpap)(η^1-CH_2COMe)(py)]-ClO_4 [5] are very similar [range 2.011(5)–2.033(11) Å], despite the different *trans* ligands (Cl in the first three complexes, acetonyl C in the latter).

The C(ketonyl)–Au bonds in **4** [2.100, 2.114(6) Å] are longer than in [Au(η^2-mpap)(η^1-CH_2COMe)(py)]-

TABLE 1. Selected bond lengths (Å) and angles (°) for compound **3**

Au–P	2.383(2)	Au–Cl	2.368(3)
Au–C(1)	2.194(11)	Au–C(11)	2.033(11)
P–C(31)	1.836(9)	P–C(41)	1.816(11)
P–C(51)	1.819(9)	C(1)–C(2)	1.278(28)
C(2)–C(3)	1.503(24)	C(2)–O	1.347(28)
N(1)–N(2)	1.259(12)		
P–Au–Cl	90.3(1)	P–Au–C(1)	173.2(4)
Cl–Au–C(1)	95.0(5)	P–Au–C(11)	91.3(2)
Cl–Au–C(11)	178.2(2)	C(1)–Au–C(11)	83.4(5)
Au–C(1)–C(2)	115.3(13)	C(1)–C(2)–C(3)	119.7(18)
C(1)–C(2)–O	123.2(17)	C(3)–C(2)–O	117.0(18)
N(2)–N(1)–C(12)	113.7(9)	N(1)–N(2)–C(21)	112.9(10)

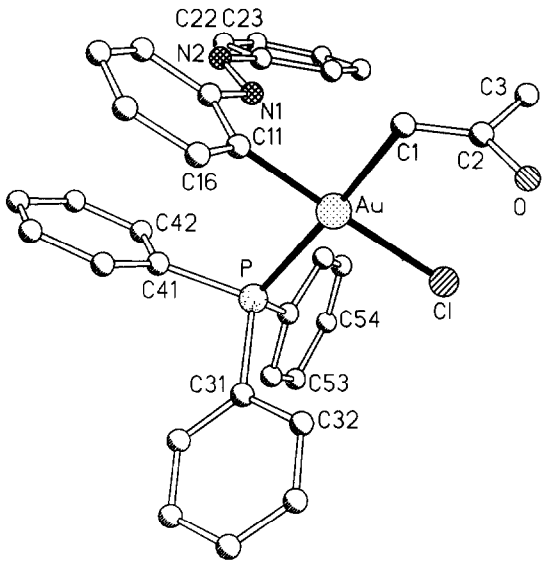


Fig. 1. The structure of complex 3 in the crystal.

ClO_4 [2.061(6) Å], [5] because the *trans* ligand in the latter is an azo-N atom. Other bond lengths of the ketonyl in both compounds are similar, and are consistent with C–metal bonding [*e.g.* C=O 1.217(7)–1.229(7), C–CH_2 1.481(7)–1.487(9) Å]. The bond lengths of the ketonyl in **3** do not fit this pattern because C=O is 1.35(3) and C–CH_2 is 1.28(3) Å; the structure of **3** is in any case imprecise, and a static disorder involving superposition of *O*- and *C*-bonded ketonyl cannot be ruled out.

4. Experimental section

The IR spectra, the C, H, N and Au analyses, conductance measurements, melting point determinations, NMR spectra and general reaction conditions were as described elsewhere [10]. The starting complexes [Au(pap)(CH_2COR)Cl] and [Au(η^1-pap)(η^1-CH_2COMe)(bipy)]ClO_4 [4,5] were prepared as reported.

4.1. [Au(η^2-pap)(η^1-CH_2COMe)X] [X = Ac (1) or I (2)]

To an acetone solution of [Au(η^2-pap)(CH_2COMe)Cl] (0.1 mmol) solid AgAc (0.1 mmol), or NaI (0.3 mmol) was added and the suspension stirred for 5 h or 5 min respectively. The solvent was removed to dryness and the residue extracted with CH_2Cl_2 and filtered through $MgSO_4$. The solution was concentrated (1 cm^3), whereupon addition of Et_2O/hexane (10 cm^3) and recrystallization from Et_2O/hexane gave the complexes as yellow solids. Yields: 70 (**1**); 79 (**2**)%. M.p. (°C): 148 (**1**); 150 (decomp.) (**2**). ν(CO) (cm^{-1}) 1670 (**1**), (**2**). ^{1}H NMR ($CDCl_3$) (**1**): δ 7.7 (m, 9H, Ph), 3.2 (s, 2H, CH_2); 2.3 (s, 3H, Me), 1.9 (s, 3H, Me(Ac) ppm; ^{1}H NMR ($CDCl_3$) (**2**): δ 7.6 (m, 9H, Ph), 3.8 (s, 2H, CH_2), 2.4 (s, 3H, Me) ppm. ^{13}C NMR ($CDCl_3$) (**1**): δ 207.4 (CO), 176.7 (CO_2), 38.1 (CH_2), 31.0 [Me(Ac)], 24.6 (Me) ppm. Anal. Calc. for $C_{17}H_{17}AuN_2O_3$ (**1**): C, 41.3; H, 3.5; N, 5.7; Au, 39.8. Found: C, 41.4; H, 4.0; N, 5.9; Au, 39.1%. Anal. Calc. for $C_{15}H_{14}AuIN_2$ (**2**): C, 32.0; H, 2.5; N, 5.0; Au, 35.0. Found: C, 32.5; H, 2.8; N, 4.6; Au, 34.6%.

4.2. [Au(η^1-pap)(η^1-CH_2COR)Cl(PPh_3)] [R = Me (3) or R = tmp (4)]

To a CH_2Cl_2 (15 cm^3) solution of [Au(pap)(CH_2COMe)Cl] (0.1 mmol), solid PPh_3 (0.1 mmol) was added and the resulting solution stirred for 1 h. The solution was concentrated (1 cm^3) and hexane (5 cm^3) added to

TABLE 2. Selected bond lengths (Å) and angles (°) for compound **4**

	Mol. 1	Mol. 2		Mol. 1	Mol. 2
Au(1)–Cl(1)	2.382(1)	2.372(1)	Au(1)–P(1)	2.386(2)	2.390(2)
Au(1)–C(11)	2.020(6)	2.020(5)	Au(1)–C(30)	2.100(6)	2.114(6)
P(1)–C(41)	1.808(6)	1.824(6)	P(1)–C(51)	1.812(6)	1.807(6)
P(1)–C(61)	1.811(6)	1.817(6)	N(1)–N(2)	1.248(7)	1.255(7)
C(30)–C(37)	1.489(8)	1.487(9)	C(31)–C(37)	1.503(9)	1.489(9)
C(37)–O(4)	1.222(7)	1.229(7)			
Cl(1)–Au(1)–P(1)	91.2(1)	91.8(1)	Cl(1)–Au(1)–C(11)	174.1(2)	176.3(2)
P(1)–Au(1)–C(11)	92.2(2)	90.9(2)	Cl(1)–Au(1)–C(30)	90.8(2)	90.9(2)
P(1)–Au(1)–C(30)	174.9(2)	177.3(2)	C(11)–Au(1)–C(30)	86.2(2)	86.4(2)
C(12)–N(1)–N(2)	113.5(5)	114.7(5)	N(1)–N(2)–C(21)	112.3(5)	115.6(5)
Au(1)–C(30)–C(37)	112.1(4)	111.7(4)	C(30)–C(37)–C(31)	120.2(5)	120.9(5)
C(30)–C(37)–O(4)	120.6(6)	119.2(6)	C(31)–C(37)–O(4)	119.2(5)	119.9(6)

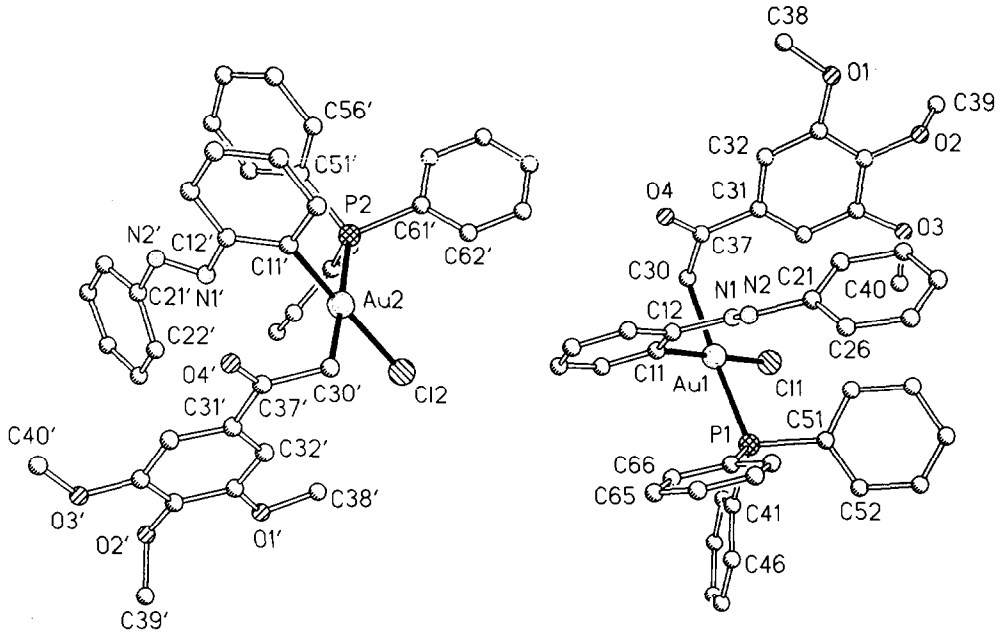


Fig. 2. The structures of the two independent molecules of complex **4**.

give orange precipitates. Recrystallization was from Et_2O/hexane. Yields: 86 (**3**); 85 (**4**)%. M.p. (°C): 126 (**3**); 138 (**4**). ν(CO) (cm^{-1}) 1675 (**3**), 1640 (**4**). ^1H NMR ($CDCl_3$) (**3**): room temperature δ 7.5 (m, 24H, Ph), 3.2 (s, 2H, CH_2), 2.0 (s, 3H, Me) ppm. AB part of the ABX system: 250 K: $\delta(H_A)$ 3.2 ppm, $\delta(H_B)$ 3.1 ppm, $^2J(HH) = 5.3$ Hz, $^3J(HP) = 14.6$ Hz; 270 K: $\delta(H_A)$ 3.2 ppm, $\delta(H_B)$ 3.1 ppm, $^2J(HH) = 5.8$ Hz, $^3J(HP) = 14$ Hz, ^1H NMR ($CDCl_3$) (**4**): δ 7.4 (m, 26H, Ph), 3.9 (s, 3H, OMe), 3.8 (s, 6H, OMe), 3.7 (s, 2H, CH_2) ppm. ^{13}C NMR ($CDCl_3$) (**3**): δ 208.0 (CO), 46.9 (CH_2), 31.2 (Me) ppm. ^{13}C NMR ($CDCl_3$) (**4**): δ 198.0 (CO), 61.0 (OMe), 56.0 (OMe), 41.2 (CH_2) ppm. ^{31}P NMR ($CDCl_3$) (**3**): δ 29.9 ppm; ^{31}P NMR ($CDCl_3$) (**4**): δ 34.9 ppm. Anal. Calc. for $C_{33}H_{29}AuClN_2OP$ (**3**): C, 54.1; H, 4.0; N, 3.8; Au, 26.9. Found: C, 53.7; H, 3.7; N, 3.4; Au, 26.1%. Anal. Calc. for $C_{41}H_{37}AuClN_2O_4P$ (**4**): C, 55.6; H, 4.2; N, 3.2; Au, 22.3. Found: C, 55.1; H, 4.5; N, 2.6; Au, 23.1%.

4.3. X-ray structure determination of compound 3

4.3.1. Crystal data

$C_{33}H_{29}AuClN_2OP$, M = 733.0, triclinic, space group $P\bar{1}$, $a = 10.389(3)$, $b = 11.269(3)$, $c = 14.482(3)$ Å, $\alpha = 89.20(2)$, $\beta = 72.95(2)$, $\gamma = 63.43(2)°$, $U = 1436.0$ Å^3, $Z = 2$, $D_x = 1.695$ Mg m^{-3}, λ(Mo Kα) = 0.71069 Å, $\mu = 5.3$ mm^{-1}, $T = 178$ K, $F(000) = 720$.

4.3.2. Data collection and reduction

An orange tablet 0.3 × 0.35 × 0.1 mm was mounted in inert oil on a glass fibre and transferred to the cold gas stream of the diffractometer (Siemens R3 with LT-2 low temperature attachment). Data were collected to $2\theta_{max} = 50°$ with monochromated Mo Kα radiation. Cell constants were refined from diffractometer angles of 50 reflections in the 2θ range 20–23°. An absorption correction was applied (after isotropic refinement, see below) using the program DIFABS [11] with transmission factors 0.78–1.30. Of 5307 reflections, 5028 were unique (R_{int} 0.025) and 4399 > 4$\sigma(F)$ used for all calculations (program system Siemens SHELXTL PLUS).

4.3.3. Structure solution and refinement

The structure was solved by the heavy-atom method. Au, P, and Cl atoms were refined anisotropically. Hydrogen atoms were included using a riding model, except for those of the acetonyl, which were not located. Refinement proceeded to R 0.046, wR 0.057. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002F^2$. 172 parameters; S 2.4; max. Δ/σ 0.007; max. $\Delta\rho$ 2.9×10^{-6} e pm^{-3}. Final atomic coordinates are given in Table 3.

4.4. X-ray structure determination of compound 4

4.4.1. Crystal data

$C_{41}H_{37}AuClN_2O_4P$, M = 885.1, monoclinic, space group $P2_1$, $a = 11.151(3)$, $b = 18.468(5)$, $c = 17.780(3)$ Å, $\beta = 92.11(2)°$, $U = 3659.2$ Å^3, $Z = 4$, $D_x = 1.607$ Mg m^{-3}, λ(Mo Kα) = 0.71069 Å, $\mu = 4.2$ mm^{-1}, $T = 178$ K, $F(000) = 1760$.

TABLE 3. Atomic coordinates ($\times 10^4$) for compound 3

Atom	x	y	z
Au	1577.5(4)	4952.5(3)	3013.8(2)
P	3798(2)	2849(2)	2713(1)
Cl	3081(3)	6078(2)	2760(2)
C(1)	−602(15)	6788(13)	3422(9)
C(2)	−507(21)	7881(18)	3393(13)
C(3)	−383(16)	8490(14)	2461(10)
O	−565(16)	8561(14)	4174(10)
N(1)	931(8)	3731(7)	1488(5)
N(2)	975(9)	3095(7)	762(5)
C(11)	236(10)	4036(8)	3219(6)
C(12)	114(10)	3522(8)	2400(6)
C(13)	−771(11)	2866(9)	2517(6)
C(14)	−1513(11)	2698(9)	3415(6)
C(15)	−1374(11)	3207(9)	4246(7)
C(16)	−522(10)	3882(9)	4150(6)
C(21)	1810(11)	3317(9)	−154(6)
C(22)	2291(13)	2383(11)	−943(7)
C(23)	3093(13)	2529(11)	−1855(8)
C(24)	3398(13)	3584(10)	−1961(8)
C(25)	2872(12)	4540(10)	−1176(7)
C(26)	2069(12)	4413(10)	−270(7)
C(31)	4503(9)	2558(7)	3761(5)
C(32)	4175(10)	3662(8)	4382(6)
C(33)	4683(11)	3475(9)	5177(6)
C(34)	5491(11)	2213(9)	5368(6)
C(35)	5857(12)	1109(10)	4740(7)
C(36)	5326(11)	1299(9)	3948(6)
C(41)	3499(9)	1423(8)	2496(5)
C(42)	3921(10)	805(9)	1556(6)
C(43)	3563(12)	−198(10)	1402(7)
C(44)	2798(11)	−610(9)	2185(6)
C(45)	2342(11)	18(9)	3113(6)
C(46)	2707(10)	1029(8)	3273(6)
C(51)	5333(10)	2698(9)	1637(6)
C(52)	6837(13)	1843(11)	1554(8)
C(53)	7974(17)	1725(13)	662(9)
C(54)	7506(15)	2375(12)	−72(9)
C(55)	6108(14)	3153(11)	−14(8)
C(56)	4981(11)	3332(9)	856(6)

4.4.2. Data collection and reduction

As for **3**, with the following differences; orange prism $0.25 \times 0.2 \times 0.2$ mm, absorption correction based on ψ-scans, with transmission factors 0.63–0.87. Of 11545 reflections, 10709 were unique (R_{int} 0.020) and $9657 > 4\sigma(F)$ used for all calculations.

4.4.3. Structure solution and refinement

The structure was solved by the heavy-atom method. All non-H atoms were refined anisotropically. Hydrogen atoms were included using a riding model. The absolute structure was determined by an η refinement, with $\eta = +1.022(8)$. Refinement proceeded in two blocks (each independent molecule separately) to R 0.026, wR 0.026. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0002F^2$. 900 parameters (451 per block); S 1.1; max. Δ/σ 0.011; max. $\Delta\rho$ 1.6×10^{-6} e pm^{-3}. Final atomic coordinates are given in Table 4.

4.5. *[Au(η^1-pap)(η^1-CH_2COMe)CN(PPh_3)] (5)*

To an acetone solution of [Au(pap)(CH_2COMe)Cl] (80 mg, 0.17 mmol), solid PPh_3 (49 mg, 0.17 mmol) was added and after stirring for 30 min solid KCN (11 mg, 0.17 mmol) was added. After 52 h the solvent was removed to dryness and the residue extracted with CH_2Cl_2. Filtration through $MgSO_4$, concentration to 1 cm^3 and addition of hexane gave an orange solid. Yield: 65%. M.p. 151°C; ν(CO) 1670 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.4 (m, 24H, Ph), 3.2 [d, 2H, CH_2, ^3J(HP) 14.7 Hz], 2.1 (s, 3H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ 29.9 ppm. Anal. Calc. for $C_{34}H_{29}AuN_3OP$: C, 56.4; H, 4.0; N, 5.8; Au, 27.2. Found: C, 57.1; H, 4.4; N, 6.0; Au, 27.3%.

4.6. *[Au(η^1-pap)(η^1-CH_2COMe)(μ-dppe)]$_2Cl_2$ (6a)*

To an acetone solution of [Au(η^2-pap)(CH_2COMe)Cl] (34 mg, 0.07 mmol) solid dppe (29 mg, 0.07 mmol) was added and the solution stirred for 40 min. The solution was concentrated (1 cm^3) whereupon addition of Et_2O (5 cm^3) and recrystallization from CH_2Cl_2/Et_2O gave an orange solid **6a**. Yield: 85%. M.p. 282°C. ν(CO) 1665 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.5 (m, 29H, Ph), 3.0 [m, 6H, CH_2CH_2 (dppe) + $AuCH_2$], 1.3 (s, 3H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ 51.6, 48.6 ppm. Anal. Calc. for $C_{82}H_{76}Au_2Cl_2N_3O_2P_4$: C, 56.7; H, 4.4; N, 3.2; Au, 22.7. Found: C, 55.9; H, 4.6; N, 2.8; Au, 23.0%.

4.7. *[{Au(η^1-pap)(η^1-CH_2COMe)(μ-dppe)}$_2$](ClO_4)$_2$ (6b)*

To an acetone solution of **6a** (50 mg, 0.06 mmol) solid $NaClO_4 \cdot H_2O$ (8 mg, 0.06 mmol) was added and the solution stirred for 50 min. Concentration of the solution (1 cm^3) gave **6b** as an orange precipitate. Yield: 82%. M.p. 130°C; ν(CO) 1665 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.0 (m, 29H, Ph), 3.0 [m, 6H, CH_2CH_2 (dppe) + $AuCH_2$], 1.3 (s, 3H, Me) ppm. ^{31}P NMR ($CDCl_3$): δ 51.6, 48.0 ppm. Anal. Calc. for $C_{82}H_{76}Au_2Cl_2N_3O_{10}P_4$: C, 52.8; H, 4.1; N, 3.0; Au, 21.1. Found: C, 52.7; H, 4.6; N, 2.6; Au, 21.3%.

4.8. *[Au(η^2-pap){η^1-CH_2C(=NPh)Me}Cl] (7)*

To a CH_2Cl_2 solution of [Au(η^2-pap)(CH_2COMe)Cl] (50 mg, 0.11 mmol) $PhNH_2$ (2 cm^3) was added and the mixture stirred over molecular sieves. After 1 h the solution was filtered through $MgSO_4$, the solvent evaporated to 1 cm^3 and hexane (5 cm^3) added to obtain a yellow solid that was recrystallized from CH_2Cl_2/hexane. Yield: 62%. M.p. 123°C. ν(CN) 1620 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.7 (m, 14H, Ph), 4.9 (s, 2H, CH_2), 2.4 (s, 3H, Me) ppm. Anal. Calc. for $C_{21}H_{19}AuClN_3$: C, 46.2; H, 3.5; N, 7.7; Au, 36.1. Found: C, 45.6; H, 3.1; N, 7.4; Au, 36.8%.

TABLE 4. Atomic coordinates ($\times 10^4$) for compound **4**

Atom	x	y	z
Au(1)	1784.0(2)	5000	4904.6(1)
Cl(1)	1437(1)	5357(1)	6165.6(7)
P(1)	2291(1)	3801(1)	5303.7(8)
C(11)	2196(5)	4784(3)	3831(3)
C(12)	1410(6)	4393(3)	3346(3)
C(13)	1761(6)	4229(3)	2614(3)
C(14)	2866(6)	4440(3)	2390(3)
C(15)	3651(6)	4812(4)	2861(3)
C(16)	3315(5)	4987(4)	3583(3)
N(1)	295(5)	4182(3)	3650(3)
N(2)	−236(5)	3698(3)	3279(3)
C(21)	−1354(6)	3486(4)	3606(4)
C(22)	−2086(7)	3952(4)	3962(4)
C(23)	−3128(7)	3690(5)	4276(5)
C(24)	−3395(7)	2967(5)	4229(5)
C(25)	−2663(8)	2500(5)	3856(5)
C(26)	−1659(8)	2753(5)	3527(4)
C(30)	1201(6)	6015(3)	4504(3)
C(31)	−1098(6)	5874(3)	4277(3)
C(32)	−2068(6)	6016(3)	3776(4)
C(33)	−3230(6)	5933(3)	4005(3)
C(34)	−3442(5)	5716(4)	4733(3)
C(35)	−2475(6)	5583(4)	5242(3)
C(36)	−1311(5)	5669(3)	5012(3)
C(37)	137(6)	5955(3)	3977(3)
C(38)	−4069(6)	6328(4)	2821(3)
C(39)	−5156(7)	6147(5)	5331(4)
C(40)	−1881(6)	5185(4)	6488(3)
O(1)	−4241(4)	6082(3)	3571(2)
O(2)	−4604(4)	5573(3)	4940(2)
O(3)	−2792(4)	5362(3)	5936(2)
O(4)	257(4)	5961(3)	3296(2)
C(41)	3649(6)	3671(3)	5875(3)
C(42)	4084(6)	4227(4)	6346(4)
C(43)	5079(7)	4114(4)	6823(4)
C(44)	5677(6)	3465(4)	6828(4)
C(45)	5256(6)	2922(4)	6359(4)
C(46)	4254(6)	3012(4)	5892(3)
C(51)	1057(6)	3455(3)	5833(3)
C(52)	1250(6)	2957(4)	6406(3)
C(53)	263(7)	2635(4)	6742(4)
C(54)	−869(7)	2801(4)	6522(4)
C(55)	−1081(6)	3300(4)	5948(4)
C(56)	−103(6)	3622(4)	5605(4)
C(61)	2399(6)	3144(4)	4553(3)
C(62)	1524(7)	2628(4)	4413(4)
C(63)	1597(9)	2168(5)	3808(4)
C(64)	2508(10)	2203(5)	3351(4)
C(65)	3427(9)	2710(5)	3464(4)
C(66)	3376(7)	3203(4)	4073(3)
Au(2)	5227.7(2)	5338.5(2)	19.5(1)
Cl(2)	5720(1)	5073(1)	1299.2(7)
P(2)	4740(1)	6564(1)	315.5(8)
C(11′)	4749(5)	5503(3)	−1074(3)
C(12′)	5526(6)	5847(3)	−1542(3)
C(13′)	5160(6)	6010(3)	−2280(3)
C(14′)	4034(6)	5839(4)	−2544(3)
C(15′)	3238(6)	5495(4)	−2077(3)
C(16′)	3592(5)	5317(4)	−1342(3)
N(1′)	6656(5)	6059(3)	−1207(3)
N(2′)	7245(5)	6491(3)	−1594(3)

TABLE 4 (continued)

Atom	x	y	z
C(21′)	8355(6)	6732(4)	−1257(3)
C(22′)	9011(6)	6329(4)	−728(4)
C(23′)	10050(6)	6616(5)	−397(4)
C(24′)	10401(7)	7319(5)	−594(5)
C(25′)	9786(7)	7697(5)	−1144(4)
C(26′)	8735(7)	7403(4)	−1465(5)
C(30′)	5637(6)	4265(3)	−295(3)
C(31′)	7891(5)	4358(3)	−581(3)
C(32′)	8239(6)	4480(3)	172(3)
C(33′)	9440(5)	4598(4)	374(3)
C(34′)	10304(5)	4568(4)	−178(3)
C(35′)	9957(5)	4442(3)	−927(3)
C(36′)	8746(6)	4353(3)	−1129(3)
C(37′)	6620(6)	4242(3)	−837(3)
C(38′)	9001(6)	4885(5)	1647(3)
C(39′)	12174(6)	4117(4)	213(4)
C(40′)	10524(6)	4396(4)	−2199(3)
O(1′)	9872(4)	4726(3)	1098(2)
O(2′)	11487(4)	4717(3)	20(2)
O(3′)	10862(4)	4435(3)	−1420(2)
O(4′)	6374(4)	4116(3)	−1504(2)
C(41′)	5962(6)	6997(3)	856(3)
C(42′)	7126(6)	6766(4)	760(4)
C(43′)	8061(7)	7124(5)	1093(5)
C(44′)	7886(8)	7728(5)	1533(4)
C(45′)	6712(8)	7965(4)	1641(4)
C(46′)	5763(7)	7604(4)	1298(4)
C(51′)	4495(6)	7149(3)	−490(3)
C(52′)	5364(6)	7619(4)	−738(4)
C(53′)	5152(8)	8036(4)	−1377(4)
C(54′)	4077(8)	7989(4)	−1774(4)
C(55′)	3211(7)	7501(4)	−1555(4)
C(56′)	3405(6)	7085(4)	−915(3)
C(61′)	3382(5)	6638(3)	844(3)
C(62′)	2964(6)	6044(4)	1225(3)
C(63′)	1951(7)	6105(4)	1644(4)
C(64′)	1377(6)	6753(4)	1710(4)
C(65′)	1784(7)	7352(4)	1336(4)
C(66′)	2777(6)	7294(4)	899(4)

4.9. *[Au(η^2-pap)(η^2-CH_2COMe)]ClO_4 (8a)*

Method a: To an acetone solution of [Au(η^2-pap)Cl_2] (40 mg, 0.09 mmol) solid $AgClO_4$ (38 mg, 1.8 mmol) was added. After 30 min the solvent was removed to dryness and the residue extracted with CH_2Cl_2 (15 cm^3), filtered through $MgSO_4$ and the solution concentrated to 2 cm^3. Addition of Et_2O (7 cm^3) and recrystallization from CH_2Cl_2/Et_2O gave **8a**. Yield: 75%.

Method b: To an acetone solution of **1** (50 mg, 0.1 mmol) an excess of aqueous $HClO_4$ (conc.) was added. After 1 h the solvent was evaporated to 1 cm^3 and Et_2O added to obtain a yellow solid. Yield: 50%.

Method c: To an acetone solution of [Au(η^1-pap)-(η^1-CH_2COMe)(bipy)]ClO_4 (50 mg, 0.07 mmol) solid $AgClO_4$ (16 mg, 0.07 mmol) was added. After 15 min the suspension was filtered to obtain a white precipitate of Ag(bipy)ClO_4 (by IR) and an orange solution.

Concentration to 5 cm^3 and addition of Et_2O gave **8a**. Yield: 65%. M.p. 135°C (decomp.). $\Lambda_M = 134\ \Omega^{-1}\ cm^2\ mol^{-1}$ (2.5×10^{-4} mol dm^{-3} acetone). ν(CO) 1580 cm^{-1}. Anal. Calc. for $C_{15}H_{14}AuClN_2O_5$: C, 33.7; H, 2.6; N, 5.2; Au, 36.8. Found: C, 34.3; H, 2.7; N, 4.6; Au, 37.1%.

4.10. [Au(η^2-pap)(η^2-CH_2COMe)]CF_3SO_3 (8b)

To an acetone solution of [Au(η^2-pap)(η^1-CH_2COMe)Cl] (84 mg, 0.18 mmol) solid $Ag(CF_3SO_3)$ (46 mg, 0.18 mmol) was added. After 1 h the solvent was evaporated (1 cm^3). Addition of Et_2O (10 cm^3) gave **8b** as a yellow solid. Yield: 84%. M.p. 145°C. $\Lambda_M = 115\ \Omega^{-1}\ cm^2\ mol^{-1}$ (4.4×10^{-4} mol dm^{-3} acetone). ν(CO) 1580 cm^{-1}. ^1H NMR ($CDCl_3$): δ 8.2 (d, 1H, Ph), 7.9 (m, 2H, Ph), 7.8 (d, 1H, Ph), 7.5 (m, 5H, Ph), 3.5 (s, 2H, CH_2), 2.4 (s, 3H, Me) ppm. Anal. Calc. for $C_{16}H_{14}AuF_3N_2O_4S$: C, 32.9; H, 2.4; N, 4.8; Au, 33.7. Found: C, 33.5; H, 2.7; N, 4.2; Au, 33.6%.

5. Supplementary materials available

Further details of the structure determinations (complete bond lengths and angles, H atom coordinates, structure factors, temperature factors) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, W-7514 EggensteinLeopoldshafen 2, Germany. Any request for this material should quote a full literature citation and the reference number CSD-57304.

Acknowledgments

We thank Dirección General de Investigación Científica y Técnica (PB89-0430) and the Fonds der Chemischen Industrie for financial support.

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