Synthesis, Structure and Reactivity of [(acac)AuCH(PPh$_2$AuPPh$_2$)$_2$CHAu(acac)], a Complex Containing the Tridentate Ligand [HC(PPh$_2$)$_2$]$^-$

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The complex [(acac)AuCH(PPh$_2$AuPPh$_2$)$_2$CHAu(acac)] (**1**) is obtained by various procedures: a) by reaction of [Ph$_3$PAuCH(PPh$_2$AuPPh$_2$)$_2$CHAuPPh$_3$](ClO$_4$)$_2$ with NBu$_4$[Au(acac)Cl], b) by reaction of [ClAuCH(PPh$_2$AuPPh$_2$)$_2$CHAuCl] with [Au(acac)PPh$_3$] or with Tl(acac) and c) by reaction of [ClAuPPh$_2$CH$_2$PPh$_2$AuCl] with Tl(acac). The acetylacetonato ligand can act as deprotonating agent; thus, complex **1** reacts with (phosphane)gold complexes, [Au(C$_6$F$_5$)$_2${(PPh$_2$)$_2$CH$_2$}]ClO$_4$, [Au(C$_6$F$_5$)$_3$(PPh$_2$CH$_2$PPh$_2$)] or [Au(PPh$_3$)$_2$]ClO$_4$, to give the hexanuclear complexes [(C$_6$F$_5$)$_2$Au{(PPh$_2$)$_2$CH}AuCH(PPh$_2$AuPPh$_2$)$_2$CHAu{CH(PPh$_2$)$_2$}Au(C$_6$F$_5$)$_2$](ClO$_4$)$_2$, [(C$_6$F$_5$)$_3$Au(PPh$_2$CHPPh$_2$)AuCH(PPh$_2$AuPPh$_2$)$_2$CHAu(PPh$_2$CHPPh$_2$)Au(C$_6$F$_5$)$_3$] or [(Ph$_3$PAu)$_2$C(PPh$_2$AuPPh$_2$)$_2$C(AuPPh$_3$)$_2$](ClO$_4$)$_2$, respectively. The crystal structure of **1** has been established by X-ray crystallography and displays two independent eight-membered rings with inversion symmetry and short transannular gold–gold contacts. The first ab initio results for a transannular Au^I–Au^I interaction are reported.

(Acetylacetonato)gold complexes, such as [Au(acac)PPh$_3$], [N(PPh$_3$)$_2$][Au(acac)Cl] or [N(PPh$_3$)$_2$][Au(acac)$_2$], have been used for the synthesis of ylide[1] and methanide[2] complexes of gold. They are excellent precursors for abstracting one or two protons from CH or CH$_2$ groups, thus leaving one or two free coordination sites. The acac ligand is displaced as acetylacetone.

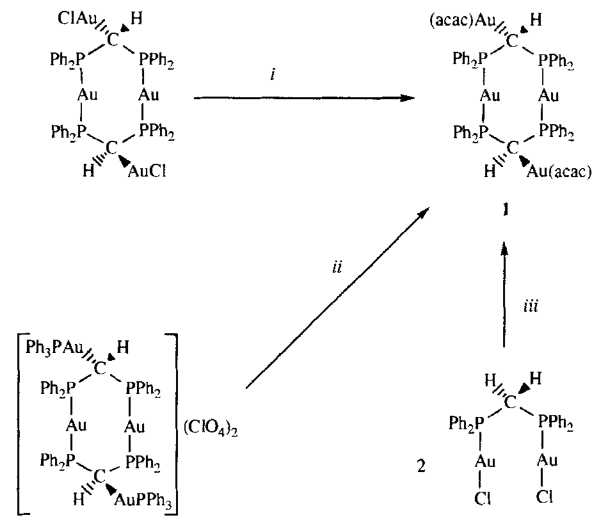
Here, we have studied the preparation of the tetranuclear compound [(acac)AuCH(PPh$_2$AuPPh$_2$)$_2$CHAu(acac)] (**1**) and its reactivity as a deprotonating agent of (diphosphane)gold derivatives. The structure of **1** has been established by single-crystal X-ray analysis.

Synthesis and Properties of the Complexes

NBu$_4$[Au(acac)Cl] reacts with [Ph$_3$PAuCH(PPh$_2$AuPPh$_2$)$_2$CHAuPPh$_3$](ClO$_4$)$_2$, but no deprotonation of the methanide CH groups is observed; instead a mixture of the acetylacetonato complex **1**, [AuCl(PPh$_3$)] and NBu$_4$(ClO$_4$) is formed (Scheme 1). The mononuclear chloro complex is partially soluble in diethyl ether and can be separated by washing the mixture with this solvent; complex **1** can then be obtained free of NBu$_4$(ClO$_4$) by passing a dichloromethane solution of the mixture through a 3-cm column of Al$_2$O$_3$.

Complex **1** can also be obtained in other ways. The reaction of [ClAuCH(PPh$_2$AuPPh$_2$)$_2$CHAuCl] with [Au(acac)PPh$_3$] (molar ratio 1:2) leads to the substitution of the chloro ligand by acetylacetonate; a mixture of **1** and [AuCl(PPh$_3$)] is obtained, which can be separated as above using ether. The substitution of the chloro ligand in [ClAuCH(PPh$_2$AuPPh$_2$)$_2$CHAuCl] can also be achieved by reaction with Tl(acac). The reaction of [ClAuPPh$_2$CH$_2$PPh$_2$AuCl] with Tl(acac) (molar ratio 1:2) leads to the precipitation of TlCl and complex **1** is obtained from the solution.

Scheme 1[a]

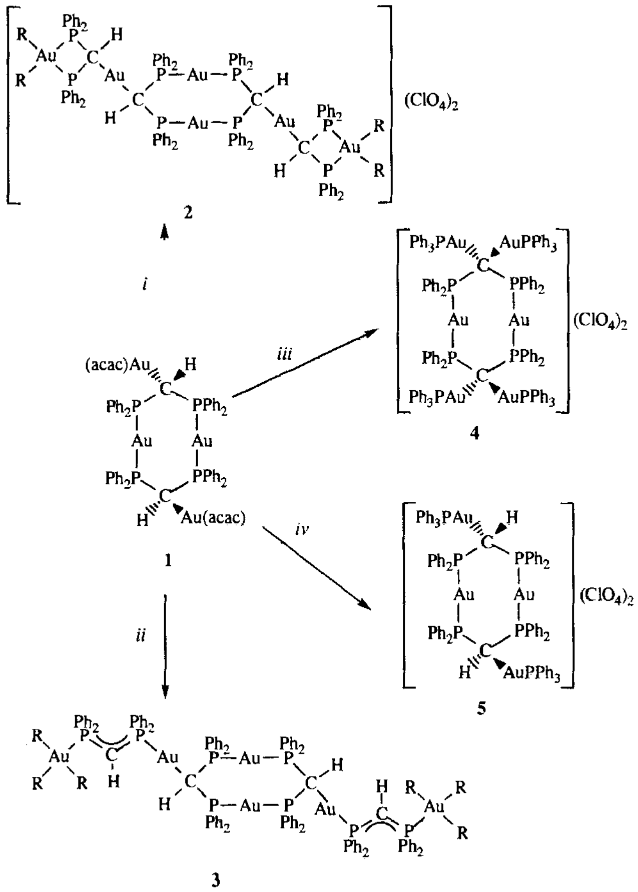


[a] i) + 2 Tl(acac) (or 2 [Au(acac)PPh$_3$]), −2 TlCl (or 2 [AuCl(PPh$_3$)]. – ii) + 2 Bu$_4$N[Au(acac)Cl], −2 Bu$_4$NClO$_4$, −2 [AuCl(PPh$_3$)]. – iii) + 4 Tl(acac), −4 TlCl, −2 acacH.

Complex **1** is an air- and moisture-stable yellow solid that can be heated to over 250°C without decomposition. The IR spectrum displays a vibration at $\tilde{\nu}$ = 1629 cm^{-1} (vs) for $\nu(C{=}O)$[3], consistent with the coordination of the acac ligand through the carbon atom. The $^{31}P\{^1H\}$-NMR spectrum shows a singlet at $\delta = 37.5$ and the ^1H-NMR spectrum displays a triplet at $\delta = 3.55$ [J(PH) = 3.47 Hz] for the methine proton (as a consequence of the coupling with two equivalent phosphorus atoms) and two singlets at δ = 4.23 and 1.83 (intensity ratio 1:6) for the acetylacetonato ligand bonded through the carbon atom[4].

Since the acac ligand can act as a deprotonating agent, we decided to study the reactions of complex **1** with other (phosphane)gold derivatives. The reaction of **1** with 2 equivalents of $[Au(C_6F_5)_2\{(PPh_2)_2CH_2\}]ClO_4$ leads to the deprotonation of the CH_2 group and formation of the hexanuclear complex **2** (see Scheme 2).

Scheme 2[a]



[a] R = C_6F_5. – i) + 2 $[AuR_2(dppm)]ClO_4$, –2 acacH. – ii) + 2 $[AuR_3(dppm)]$, –2 acacH. – iii) + 2 $[Au(PPh_3)_2]ClO_4$, –2 acacH. – iv) + 2 $[Ag(PPh_3)_2]ClO_4$, –2 $[Ag(acac)PPh_3]$.

Complex **2** is an air- and moisture-stable white solid. It behaves as a 1:2 electrolyte in acetone solution (275 Ω^{-1} cm^2 mol^{-1}). The IR spectrum shows bands at $\tilde{\nu}$ = 1100 (vs, br.) and 620 cm^{-1}, which arise from the ClO_4^- ion, and also at $\tilde{\nu}$ = 1508 (vs), 964 (vs), 800 (sh) and 784 cm^{-1} (m), consistent with the presence of C_6F_5 groups linked to a gold(III) centre, the last two confirming the *cis* disposition[5]. The band at $\tilde{\nu}$ = 592 cm^{-1} (m) is assigned to ν(Au–C) of the methanide groups[6,7].

The ^{19}F-NMR spectrum shows signals arising from equivalent pentafluorophenyl rings {three resonances at $\delta = -121.5$ (m, *o*-F), -155.4 [t, J(FF) = 19.3 Hz, *p*-F] and -160.1 (m, *m*-F)}. In the $^{31}P\{^1H\}$-NMR spectrum the two different phosphorus atoms bonded to gold(I) and gold(III) give rise to singlets at $\delta = 41.2$ and -28.3, respectively. The signals of the two different CH groups appear in the ^1H-NMR spectrum as triplets at $\delta = 4.47$ [J(PH) = 3.42 Hz] and 4.67 [J(PH) = 13.67 Hz]. The first signal, which has a coupling constant similar to that found in complex **1**, can be assigned to the CH groups of the eight-membered ring, and the second to the CH groups of the four-membered rings[8].

A different result is observed in the reaction of complex **1** with two equivalents of $[Au(C_6F_5)_3(PPh_2CH_2PPh_2)]$ (Scheme 2). Deprotonation of the CH_2 group of the diphosphane ligand is also observed, but the coordination to the gold(I) centre is through the free phosphorus and not the methanide carbon atom (complex **3**).

Complex **3** is an air- and moisture-stable yellow solid. The IR spectrum shows bands at $\tilde{\nu}$ = 1506 (vs), 966 (vs) and 790 (m) cm^{-1} which arise from the C_6F_5 groups. A band at $\tilde{\nu}$ = 1187 (m) cm^{-1} is characteristic of the PPh_2CHPPh_2 system when not coordinated through the carbon atom, and has been observed in other methanide complexes[9]. The ^{19}F-NMR spectrum, as expected, shows signals of two types of pentafluorophenyl groups, with an intensity ratio 1:2 (*cis*:*trans*). The $^{31}P\{^1H\}$-NMR spectrum corresponds to an ABX_2 system with $\delta_A = 18.7$, $\delta_B = 28.3$, $\delta_X = 42.3$ and $J(P_AP_B) = 81.2$ Hz.

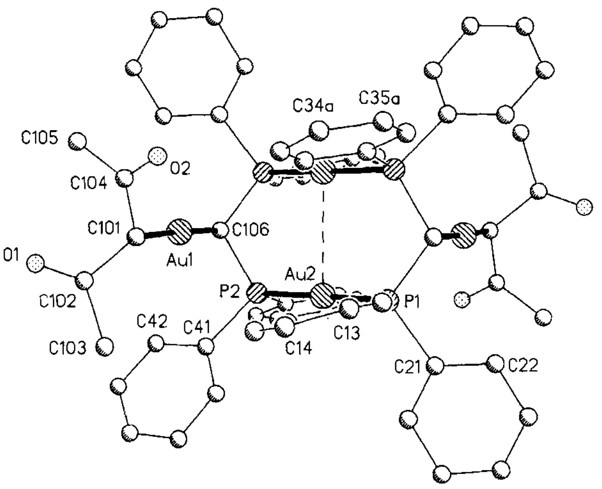
The reaction of complex **1** with two equivalents of $[Au(PPh_3)_2]ClO_4$ leads to the deprotonation of the CH groups in complex **1** and formation of the hexanuclear complex $[(Ph_3PAu)_2C(PPh_2AuPPh_2)_2C(AuPPh_3)_2](ClO_4)_2$ (**4**), previously described by us[10]. A different behaviour is observed with the silver derivative $[Ag(PPh_3)_2]ClO_4$, which reacts with **1** to give $[Ph_3PAuCH(PPh_2AuPPh_2)_2CHAuPPh_3](ClO_4)_2$ (**5**) and $[Ag(acac)(PPh_3)]$, but no deprotonation is observed. Complex **5** was previously prepared by us by another method[10].

Crystal Structure Determination of Complex 1

The molecular structure of complex **1** is shown in Figure 1. The asymmetric unit contains two half molecules lying across symmetry centres and two molecules of dichloromethane. The complete molecules display eight-membered $Au_2P_4C_2$ rings with a chair conformation, with one proton and one Au(acac) group bonded to each peripheral carbon atom. The intramolecular (transannular) gold–gold contacts, typical of this type of dinuclear gold complex, are Au(2)–Au(2*i*) 2.969(2) Å ($i = -x + 1, -y + 1, -z$) and Au(4)–Au(4*ii*) 3.001(2) Å ($ii = -x, -y, -z$), and there are also short intra- and intermolecular interactions between the peripheral and central gold atoms Au(1)–Au(2) 3.705(1) Å, Au(1)–Au(2*i*) 3.678(1) Å, Au(3)–Au(4)

3.599(1) Å and Au(3)−Au(4*ii*) 3.564(2) Å. Short Au−Au contacts have been attributed to relativistic effects in the valence orbitals of gold[11].

Figure 1. Structure of one of the two independent molecules of complex **1** in the crystal; radii are arbitrary; H atoms are omitted for clarity[a]



[a] Selected bond lengths [Å] and angles [°], including those of the second molecule: Au(1)−C(101) 2.12(2), Au(1)−C(106) 2.12(2), Au(2)−P(1) 2.308(4), Au(2)−P(2) 2.322(4), Au(2)−Au(2*i*) 2.969(2), Au(3)−C(107) 2.08(2), Au(3)−C(112) 2.106(14), Au(4)−P(3) 2.316(4), Au(4)−P(4) 2.325(5), Au(4)−Au(4*ii*) 3.001(2); C(101)−Au(1)−C(106) 178.0(7), P(1)−Au(2)−P(2) 175.4(2), P(1)−Au(2)−Au(2*i*) 89.10(12), P(2)−Au(2)−Au(2*i*) 91.55(12), C(107)−Au(3)−C(112) 177.7(8), P(3)−Au(4)−P(4) 179.1(2), P(3)−Au(4)−Au(4*ii*) 89.44(12), P(4)−Au(4)−Au(4*ii*) 91.31(13); symmetry operators: $i = -x + 1, -y + 1, -z$; $ii = -x, -y, -z$.

All the gold atoms are linearly coordinated (maximum deviation 4.6°). The bond lengths from the gold atoms to the methanide or the acetylacetonato carbon atoms are very similar [2.08(2)−2.12(2) Å], cf. the Au−CH bond lengths in the related complex [(C$_6$F$_5$)AuCH(PPh$_2$AuPPh$_2$)$_2$CHAu(C$_6$F$_5$)] [2.109(12) Å][12]. The Au−P distances, which lie in the range 2.308(4)−2.325(5) Å are also similar to those in the latter complex [2.303(5)−2.309(5) Å]. The C−C bond lengths at one central acetylacetonato carbon atom (C101) differ by 0.14 Å (ca. 5σ), which, if significant, may indicate a slight disorder of this group.

ab initio Calculations

The size of the molecules under study necessitates the use of [CH$_2$(PH$_2$AuPH$_2$)$_2$CH$_2$]$^{2+}$ as a model for the theoretical calculations. All calculations were carried out using the GAUSSIAN 92 program package[13]. The molecular geometries were initially optimized, within appropriate molecular symmetry constraints (C_{2h}), at the Hartree-Fock self-consistent field (HF) level of theory, and electron correlation, keeping the core orbitals frozen, was included in further optimizations by using Møller-Plesset perturbation theory[14] with second-order corrections (MP2) employing Schlegel's analytical gradient procedure[15].

The procedures "LANL1MB" and "LANL1DZ" as implemented in GAUSSIAN 92 were employed. These involve for Au an 11-valence-electron quasirelativistic effective core potential (ECP) together with a 5d6s6p basis set, single-zeta for the former and double-zeta for the latter[16], for P a 5-valence-electron ECP together with a 3s3p basis set single- or double-zeta, respectively[16], and for C and H the STO-3G[17] and valence double-zeta[18] basis sets, respectively.

Table 1 shows the absolute energies and the most significant structural parameters obtained. Several features are noteworthy. At the HF/LANL1MB level, the Au−Au distance (4.254 Å) is far removed from the experimental value (about 3.0 Å for such complexes) and, concomitantly, internal P−Au−P angles are very low (155.2°). The experimental attraction is thus not well reproduced at this level of theory. Furthermore, the Au−P distance (2.684 Å) differs greatly from the experimental value (ca. 2.3 Å). The introduction of electron correlation at the MP2/LANL1MB level produces a shortening of the Au−Au distance (Δ = −0.196 Å) and an increase of the P−Au−P angle (Δ = +6.2°), but these changes are still insufficient to mirror the aurophilic attraction.

Table 1. Absolute energies [hartrees] and optimised structural parameters [Å, °] calculated for [CH$_2$(PH$_2$AuPH$_2$)$_2$CH$_2$]$^{2+}$

	HF/LANL1MB	MP2/LANL1MB	HF/LANL1DZ	MP2/LANL1DZ
Absolute energies	-173.136114	-173.432041	-174.231204	-174.808681
Au-Au	4.254	4.058	3.993	3.469
Au-P	2.684	2.672	2.512	2.476
P-C	1.955	1.985	1.896	1.916
Internal P-Au-P	155.2	161.4	160.7	174.9
Internal P-C-P	116.0	115.4	119.5	118.0

We next considered the split of the valence shell at the Hartree-Fock level. The distance Au−Au is reduced from 4.254 Å to 3.993 Å, Au−P from 2.684 Å to 2.512 Å and the angle P−Au−P is increased from 155.2° to 160.7°, but there is no essential change. However, the optimization at the MP2/LANL1DZ level of theory affords an Au−Au distance of 3.469 Å, an Au−P distance of 2.476 Å and internal P−Au−P angles of 174.9°, in reasonable agreement with the experimental findings; the appreciable reduction of 0.524 Å in the Au−Au distance when electron correlation is introduced shows that the experimental "aurophilic" attraction is at least partially reproduced. This conclusion is related to previous ab initio calculations[19].

In order to analyze the suggested 5d−6p correlation[19a], we omitted the Au-6p functions from LANL1DZ in the MP2 optimization. As a result, the metal−metal distance varied from 3.469 Å to 3.695 Å, confirming the importance of the 5d−6p correlation.

In summary, it is necessary to include correlation effects together with a split-valence basis set to account for the Au−Au attraction; a 5d−6p correlation is involved. More sophisticated calculations, such as the inclusion of polarization functions and a larger Au valence-electron space[19b], require a considerable computational effort. Since the MP2/LANL1DZ computations give reasonable geometries related to the experimental ones, we felt that such calculations were not justified in the present study. Further theoretical improvements are in progress.

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Experimental

IR: Range $\tilde{\nu}$ = 4000–200 cm^{-1}, Perkin-Elmer 559 or 883, Nujol mulls between polyethylene sheets. – C, H, and N analyses: Perkin-Elmer 240C microanalyser. – Conductivities: ca. $5 \cdot 10^{-4}$ M solutions, Phillips 9509 conductimeter. – ^{1}H and ^{31}P NMR: Varian UNITY 300 in CDCl$_3$ solutions, chemical shifts are quoted relative to SiMe$_4$ (^{1}H) and H$_3$PO$_4$ (external, ^{31}P). – All reactions were carried out at room temperature.

[(acac)AuCH(PPh$_2$AuPPh$_2$)$_2$CHAu(acac)] (**1**): a) To a suspension of [ClAuCH(PPh$_2$AuPPh$_2$)$_2$CHAuCl][12] (0.16 g, 0.1 mmol) in 20 ml of dichloromethane was added [Au(acac)(PPh$_3$)][20] (0.11 g, 0.2 mmol). After stirring the mixture for 5 h under N$_2$, the solution was filtered through a 1-cm pad of Celite. Concentration of the filtered solution to ca. 5 ml and addition of diethyl ether (15 ml) led to precipitation of a yellow solid, which was washed with diethyl ether (3 × 5 ml). Yield 0.16 g (92%).

b) To a suspension of [ClAuCH(PPh$_2$AuPPh$_2$)$_2$CHAuCl][12] (0.16 g, 0.1 mmol) in 20 ml of dichloromethane was added [Tl(acac)] (0.06 g, 0.2 mmol) and the mixture stirred for 4 h. The precipitated TlCl was filtered off on a 1-cm pad of Celite. The solution was concentrated to ca. 5 ml, and addition of diethyl ether (15 ml) gave complex **1** as a yellow solid. Yield 0.14 g (85%).

c) To a solution of [ClAu(PPh$_2$CH$_2$PPh$_2$)AuCl][21] (0.084 g, 0.1 mmol) in 20 ml of dichloromethane was added [Tl(acac)] (0.06 g, 0.2 mmol). Upon stirring for 5 h, the precipitated TlCl was filtered off. The solution was concentrated to ca. 5 ml, and addition of diethyl ether led to complex **1**. Yield 0.15 g (87%), m.p. > 250°C (dec.). – $C_{60}H_{56}Au_4O_4P_4$ (1752.8): calcd. C 41.1, H 3.2; found C 40.8, H 3.0.

[(C$_6$F$_5$)$_2$Au{(PPh$_2$)$_2$CH}AuCH(PPh$_2$AuPPh$_2$)$_2$CHAu{CH(PPh$_2$)$_2$}Au(C$_6$F$_5$)$_2$](ClO$_4$)$_2$ (**2**): To a solution of [Au(C$_6$F$_5$)$_2${(PPh$_2$)$_2$CH$_2$}]ClO$_4$[8] (0.20 g, 0.2 mmol) in 20 ml of dichloromethane was added complex **1** (0.175 g, 0.1 mmol). After stirring the mixture for 2 h under N$_2$, the solution was filtered through a 1-cm pad of Celite. The solution was concentrated to ca. 5 ml, and addition of diethyl ether (15 ml) gave complex **2** as a white solid. Yield 0.23 g (65%), m.p. 182°C (dec.). – $C_{124}H_{84}Au_6Cl_2F_{20}O_8P_8$ (3582.5): calcd. C 41.6, H 2.35; found C 41.5, H 2.2.

[(C$_6$F$_5$)$_3$Au(PPh$_2$CHPPh$_2$)AuCH(PPh$_2$AuPPh$_2$)$_2$CHAu(PPh$_2$CHPPh$_2$)Au(C$_6$F$_5$)$_3$] (**3**): To a solution of [Au(C$_6$F$_5$)$_3$(PPh$_2$CH$_2$PPh$_2$)][22] (0.21 g, 0.2 mmol) in 20 ml of dichloromethane was added complex **1** (0.175 g, 0.1 mmol) and the mixture stirred for 1 h under N$_2$. Concentration of the solvent to ca. 5 ml and addition of hexane (20 ml) gave complex **3**. Yield 0.23 g (73%). – $C_{136}H_{84}Au_6F_{30}P_8$ (3717.7): calcd. C 43.9, H 2.3; found C 43.3, H 2.3.

[(Ph$_3$PAu)$_2$C(PPh$_2$AuPPh$_2$)$_2$C(AuPPh$_3$)$_2$](ClO$_4$)$_2$ (**4**): To a solution of complex **1** (0.175 g, 0.1 mmol) was added [Au(PPh$_3$)$_2$]ClO$_4$ (0.164 g, 0.2 mmol). The reaction mixture was stirred for 8 h, concentrated to ca. 5 ml, and addition of diethyl ether (20 ml) led to complex **4** as a yellow solid. Yield 0.24 g (75%).

Crystal Structure Determination of Compound **1**: Crystals of **1** were grown from dichloromethane/hexane. – Crystal data: **1** · 2 CH$_2$Cl$_2$; $C_{62}H_{60}Au_4Cl_4O_4P_4$; M = 1922.65; monoclinic; $P2_1/c$; a = 22.832(6), b = 12.962(3), c = 22.033(7) Å; β = 102.02(3)°; V = 6378(3) Å^3; Z = 4; D_x = 2.002 Mgm^{-3}; $F(000)$ = 3632; μ = 9.5 mm^{-1}; T = −100°C. – Data collection and reduction: A colourless tablet of ca. 0.38 × 0.38 × 0.2 mm was mounted in inert oil on a glass fibre. A total of 11558 intensities were registered using monochromated Mo-K_α radiation (λ = 0.71073 Å, $2\Theta_{max}$ = 50°) on a Siemens P3 diffractometer with LT-2 low-temperature attachment; 11250 reflections were unique and 11225 used for all calculations. Cell constants were refined from setting angles of 50 reflections in the range 2Θ = 20–21°. An absorption correction was applied with the program SHELXA (transmissions 0.21–0.51). – Structure solution and refinement: The structure was solved by the heavy-atom method and refined anisotropically on F^2 using the program SHELXL-92[23]. Hydrogen atoms were included using a riding model. The methyl H atoms at C103 and C105 were not located, and therefore not included in the refinement. The final $wR(F^2)$ was 0.180 for all reflections, with a conventional $R(F)$ of 0.056 for 705 parameters and 544 restraints (to light-atom displacement parameters). Max. Δ/σ = 0.02, max. $\Delta\rho$ = 2.8 eÅ^{-3}, S = 1.03. – Further details of the structure determination have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference number CSD-401322.

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