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1,1'-Bis(diphenylphosphino)ferrocene complexes of gold(I). Polymeric $[AuCl(\mu\text{-dppf})]_n$ and dimeric $[Au_2(dppf\text{-}P,P')_2(\mu\text{-dppf})](NO_3)_2$

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Abstract

Addition of molar equivalent of $[Au_2Cl_2(\mu\text{-dppf})]$ to $[Fe(C_5H_4PPh_2)_2]$ (dppf) gives an intermediate complex $[AuCl(dppf)]_x$(**1**) which readily polymerises in solution to give $[AuCl(dppf)]_n.nCH_2Cl_2$(**2**). X-ray diffraction analysis of **2** revealed a repeating unit of [AuCl(dppf)] propagating one-dimensionally along the *c* axis to give a zigzag chain. Complex **1** metathesises with $AgNO_3$ to give $[Au(NO_3)(dppf)]_x$ which reacts with HCO_2Na to give $[Au_2(dppf\text{-}P,P')_2(\mu\text{-dppf})](NO_3)_2.2H_2O$ (**3**) as one of the products. The X-ray structure of **3** shows a centrosymmetric dimeric framework with two {Au(dppf)} chelates bridged by a dppf ligand. Both **2** and **3** show negligible inter- or intramolecular Au ··· Au interactions.

Key words: Gold; Iron; Ferrocene; Diphosphine; Phosphine; Polymer

1. Introduction

Diphosphine complexes of gold(I) have attracted much interest because of the intricate relationship between the coordinate modes of the ligand and the inter- and intramolecular Au ··· Au interactions [1]. This relationship is in turn possibly linked to the therapeutic [2], photophysical [3] and electrochemical [4] properties of these Au^I complexes. Recent studies of the coordination behaviour of a ferrocenyl diphosphine, $Fe(C_5H_4PPh_2)_2$ (dppf), has unveiled a variety of bonding modes made possible by the facile torsional twist of the Cp rings [5]. When the metal coordination geometry also changes with the ligand coordination mode, the problem becomes very intriguing and the resultant species can display a variety of nuclearities and unusual bonding modes of the supporting ligands [6]. In order to substantiate this mutual dependency of metal and ligand coordination behaviour, we examined the interaction between dppf and Au^I. The latter is well known to show a variety of coordination geometries [7]. Since dppf is also known to display an array of coordination modes under very similar conditions, the structures of the resultant complexes are essentially unpredictable. These "self-assembled" complex structures could give useful information on some "natural" coordination modes of dppf and the geometries of Au^I with diphosphines as ligands.

While we were investigating the chemistry of Ag^I and dppf, Hill *et al.* reported the first dppf complex of Au^I, $[Au_2Cl_2(\mu\text{-dppf})]$, from a 2 : 1 mixture of $AuCl[S(C_2H_4OH)_2]$ and dppf [8]. For comparison, we studied Au^I/dppf interactions under other stoichiometries. When the dppf ligand concentration is doubled, *i.e.* the ratio is 2:2, an array of coordination possibilities is envisaged based on many reported bridging [9] and terminal [10] chloro, and bridging [11] and chelating [12] diphosphine structures for Au^I. Even the unidentate mode cannot be ignored since it has precedence in other metal complexes [5b,13]. In this paper, we report a self-assembled polymeric structure with a Au : dppf ratio of 2 : 2 and dimeric structure at a ratio of 2 : 3. While this project was in progress, Silver *et al.*

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[14] proposed a dimeric structure for the [2:2] complex based on Mössbauer and ^{31}P-NMR data. The apparent discrepancy between these findings and the structures presented here emphasize the complexity of the dppf chemistry of Au^I.

2. Results and discussion

Addition of a molar equivalent of $[Au_2Cl_2(\mu\text{-dppf})]$ to a THF solution of dppf gives an orange complex analysed as $[AuCl(dppf)]_x$ (**1**) whose solid-state structure is unknown. In $CDCl_3$ solution, **1** slowly deposits orange yellow crystals of $[AuCl(dppf)]_n$ (**2**). X-ray analysis of **2** revealed a polymeric structure based on a repeating unit of [AuCl(dppf)], Fig. 1(a). One-dimensional propagation occurs via the singly-bridging dppf ligand. A molecular packing of the polymeric chain is illustrated in Fig. 1(b). A large torsional twist of the phosphinocyclopentadienyl (Cp) rings (C(1)–Cp1–Cp2–C(6)) (τ 153.1°) (Cp1 and Cp2 are the centres of the rings composed of C(1)–C(5) and C(6)–C(10) respectively) promotes this propagation and precludes any possible intramolecular Au ··· Au contacts [Au(1) ··· Au(1b) 6.577 Å]. The inter-chain Au ··· Au distance (12.714 Å) also indicates negligible metal contacts. This behaviour contradicts that of the other diphosphines which are reported to give dimeric $[Au(\mu\text{-P-P})]_2^{2+}$ [11g,15] or $[AuCl(\mu\text{-P-P})]_2$ [10c,16] and trimeric $[Au_3Cl_2(\mu\text{-P-P})_2]^+$ [10b] or $[Au_3(\mu\text{-P-P})_2]^{3+}$ [17] (P-P = diphosphines) species, all of which are supported by prominent Au ··· Au contacts. While this contrast could be attributed to a longer P ··· P bite distance for dppf, we must not assume that (a) the dppf ligand cannot support a metal–metal bond, or that (b) the metallocyclic ring $[M(\mu\text{-dppf})]_2^{2+}$ cannot be sustained. Recent results have identified some dppf-bridged M–M bonds, *e.g.* $[Co_3(\mu_3\text{-CMe})(CO)_7(\mu\text{-dppf})]$ [Co–Co 2.520(1) Å] [5k,18], $[M_3(CO)_{10}(\mu\text{-dppf})$ [M = Ru, 2.9284(5) [19]; M = Fe, 2.553(2) Å] [5j] and $[Au_2Ru_4(\mu_6\text{-B})(\mu\text{-H})(CO)_{12}(\mu\text{-dppf})]$ [Au–Au 2.818(2) Å] [20], and a doubly-bridging dimer in $[Ag(NO_3)(\mu\text{-dppf})]_2$ [6]. This ability of the dppf ligand to accommodate a wide range of M–M distances distinguishes it from the other common diphosphines. The lack of Au ··· Au contacts in **2** is in contrast to the relativistic effects shown for Au^I in many dimeric and oligomeric species [21]. It also suggests that Au^I does not necessarily seek M–M stabilisation actively unless prompted electronically or spatially by a more rigid ligand. A similar trigold complex with bridging dppf derivatives [22] also experiences negligible Au ··· Au contacts.

(a)

(b)

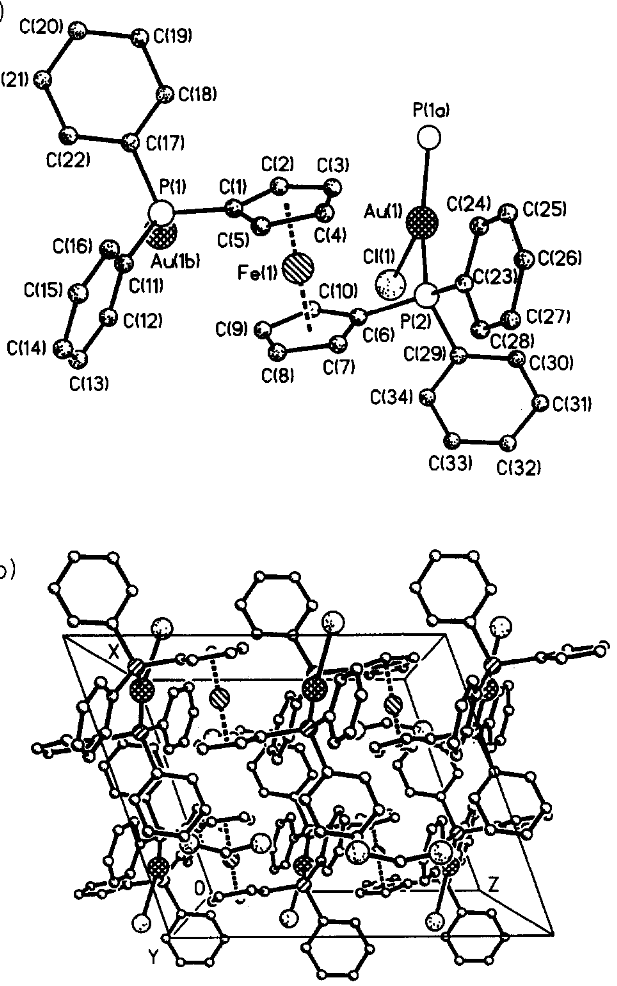

Fig. 1. (a) Structure of the [AuCl(dppf)] repeating unit in $[AuCl(\mu\text{-dppf})]_n$(**2**) with atom labelling. The *c* glide links the units into a polymeric zigzag chain running parallel to the *c* axis. (b) Molecular packing in polymeric $[AuCl(\mu\text{-dppf})]_n.nCH_2Cl_2$. The origin of the unit cell lies at the lower left corner, with *a* pointing upwards, *b* towards the reader, and *c* from left to right.

The freshly prepared solution of **1** in $CDCl_3$ shows an intense resonance at 28.4 and a weaker one at 26.5 ppm both of which are slightly broad. Upon standing, the former signal gradually weakens and the latter intensifies. This is accompanied by the gradual deposition of microcrystals of **2** which, when isolated, slowly redissolve in $CDCl_3/CH_2Cl_2$ mixture and give a ^{31}P NMR resonance at 29.2 ppm which is also slightly broad. The absence of high field resonance rules out the possibility of unicoordination for dppf in any of the above species. Based on the MW data in $CHCl_3$ (of a freshly prepared sample), **1** is monomeric in solution, possibly trigonal [AuCl(dppf)]. The ready conversion of **1** to **2**, and precipitation of the latter, is attributed to polymerisation. The present data cannot determine with certainty the species X which is responsible for the resonance at 26.5 ppm. Since it is unlikely that a polymeric species like **2**, which is deposited easily from $CDCl_3$ solution, is soluble enough to give an intense

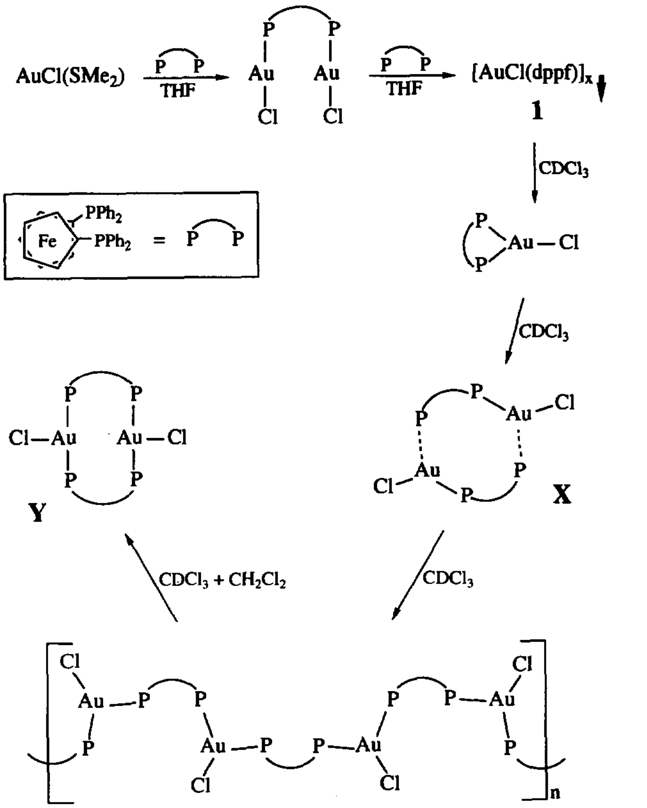

Fig. 2. A schematic representation showing the formation of $[AuCl(\mu\text{-dppf})]_n$(2) from $[Au_2Cl_2(\mu\text{-dppf})]$.

resonance, X is possibly an intermediate of a di- or oligomeric complex formed in the process of chain propagation. The dimeric complex $[AuCl(\mu\text{-dppf})]_2$, Y, proposed by Silver *et al.* resonates at 30.06 ppm. This difference of ≈ 3.6 ppm is significant which has led us to conclude that the structure of X may be related but different from that of Y. X may thus be an oligomer $[AuCl(\mu\text{-dppf})]_m$. Interestingly, allowing for the effect of solvent on the NMR shifts, the ^{31}P shift of Y is practically identical to that of the species formed when 2 is dissolved in a mixture of $CDCl_3$ and CH_2Cl_2 (29.2 ppm). Since it is unlikely that 2, which was precipitated from solution in $CDCl_3$, can redissolve in chlorinated solvents without structural reorganisation, we may suggest that 2 slowly depolymerises to give Y in the solvent mixture. These conversions are summarised in Fig. 2. The similarity in the shifts of all these complexes suggest that the trigonal planar geometry is maintained in the course of polymerisation and depolymerisation.

The observed P–Au–P angle [155.2(1)°] is substantially larger than that of $AuCl(PPh_3)_2$ [132.1(1)°] [23]. In the absence of reliable data for the cone angle of PPh_2Fc in dppf, this gives the most reasonable estimate of the steric demand of dppf. Trigonal planar $[Au^IL_2X]$ complexes have variable L–Au–L angles but angles substantially larger than 120° are usually associated with bulky ligands. This high spatial demand of two dppf groups co-planar with the chloro ligand must have contributed to the further weakening of the Au–Cl bond [2.709(2) Å] compared to those of $[AuCl(PPh_3)]$ [2.290(3) Å] [24], $\{AuCl[P(2\text{-}MeC_6H_4)_3]\}$ [2.281(3) Å] [25] and $[AuCl(PPh_3)_2]$ [2.500(4), 2.526(10) Å] [23]. In fact, this length is comparable to that found in the tetrahedral complex $[AuCl(PPh_3)_3]$ [2.710(2) Å] [26]. Complex 2 was initially obtained from a mixture of $[AuCl(SMe_2)]$, CH_3CO_2Na and dppf (1:1:1) in an attempt to study anionic exchange. This absence of acetato coordination demonstrates that the Au–Cl bond, albeit weak, is significant in the stabilisation of the polymeric structure. Carboxylato phosphine complexes of Au[I] have been reported [27].

Anionic exchange of 1 with $AgNO_3$ gives $[Au(NO_3)\text{-}(dppf)]_x$ which does not metathesise with RCO_2Na (R = Me, Ph) but with HCO_2Na to give, among other products presently unidentified, a complex analysed as $[Au_2(dppf)_3](NO_3)_2]$ (3). The ionic nitrate is established in its IR spectrum. Its ^{31}P-NMR spectrum at room temperature resembles that of $[Cu_2(dppf\text{-}P,P')_2(\mu\text{-dppf})](BF_4)_2$ [28] at −25°C in CD_3NO_2. Whilst an AB_2 pattern can be identified, hence suggesting an isomorphous relationship of 3 with its Cu analogue, there are at least two minor species in solution. But

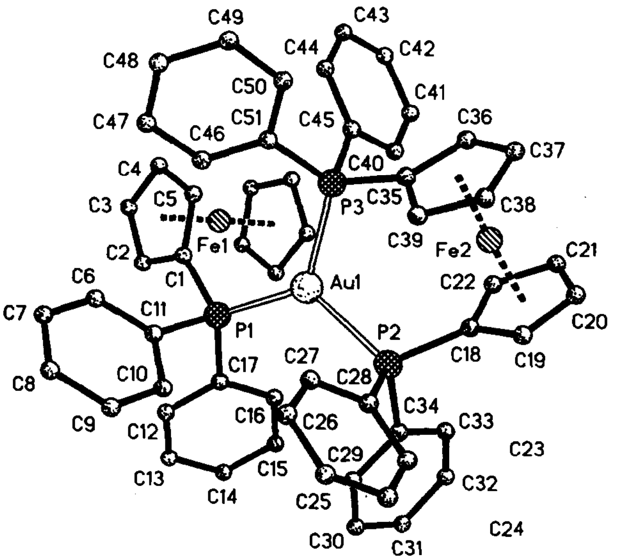

Fig. 3. Perspective view of the structure of $[Au_2(dppf\text{-}P,P')_2(\mu\text{-}dppf)](NO_3)_2 \cdot 2H_2O$ ignoring the uncoordinated anion and solvent molecules and showing only half of the molecule which is centrosymmetric at the iron centre Fe(1) of the bridging dppf ligand.

unlike the Cu[I] reaction, there is no evidence for a unidentate mode of dppf as in [Au(dppf-*P*,*P'*)(dppf-*P*)]$^+$. An X-ray analysis confirmed the absence of anion coordination in the solid-state structure. It comprises a dinuclear frame with a dppf unit singly-bridging between two {Au(dppf)} chelates (Fig. 3). It is hence isomorphous with its Cu[I] [29] and Ag[I] [30] analogues. The crystallographically-imposed C_2 symmetry necessitates a perfect 180° torsional twist for the Cp rings of the bridging ligand. The chelate angle [109.2(1)°] is substantially smaller than an ideal 120° for a trigonal planar metal. This acuteness is translated into slightly weaker Au–P links [mean 2.389(3)° Å] compared to those of the bridge [2.335(3)° Å]. The general features of **3** resemble those of its congeneric analogues and need not be discussed further.

The common structural framework of $[M_2(dppf)_3]^{2+}$ (M = Cu, Ag, Au) allows an insight into some basic differences between dppm ($Ph_2PCH_2PPh_2$) and dppf in sustaining molecules of A-frame type. While the dppm ligand is known to form triply-bridged species $[M(\mu\text{-dppm})_3M]^{n+}$ [31], the analogous dppf complex is unknown. While the group 11 metals clearly prefer a bridge-chelate combination as in $[(dppf)M(\mu\text{-dppf})M(dppf)]^{2+}$, there is no evidence that dppm can sustain such a skeletal arrangement. The former contrast can be rationalised by the unfavourable steric interference among the ferrocenyl moieties when two planar metals are locked into close proximity by the ligands. The latter is explained by the unacceptable strain imposed by a trigonal planar metal on a 4-membered dppm chelate. Interchanges between these and other related structural isomers in solutions have been discussed elsewhere [30,31a,32].

Related to this work, $[Au_2Cl_2(\mu\text{-dppf})]$ exchanges with $AgNO_3$ to give $[Au_2(NO_3)_2(dppf)]$ (**4**) which metathesises further with $C_6H_5CO_2Na$ to give $[Au_2(O_2CC_6H_5\text{-}O)_2(\mu\text{-dppf})]$.

3. Experimental section

3.1. General comments

All procedures were routinely performed at room temperature under pure dry argon with standard Schlenk techniques. The general procedures and instruments used followed those described in our earlier reports [5a–c,6]. Continuous wave IR spectra were obtained with a Shimadzu IR-470 Infrared Spectrophotometer. Molecular weight measurements were carried out by vapour pressure osmometry at Galbraith Laboratories, Inc., Knoxville, TN, USA. $[AuCl(SMe_2)]$ was prepared according to a literature method [33]. $[Fe(C_5H_4PPh_2)_2]$ was obtained commercially or synthesised according to a published method [34].

3.2. Synthesis of $[Au_2Cl_2(\mu\text{-dppf})]$

The complex was prepared by modifying a literature method [8]. As a solution of dppf (1.367 g, 2.47 mmol) in a minimum of THF (*ca.* 50 ml) was added slowly to a rapidly stirred THF solution (15 ml) of $[AuCl(SMe_2)]$ (1.424 g, 4.83 mmol), an orange precipitate immediately formed. The resultant mixture was further stirred for 30 min before the orange precipitate was collected by filtration. It was redissolved in a minimum of CH_2Cl_2, filtered, and sufficient hexane was added until just before the onset of precipitation. Upon standing at −20°C overnight, microcrystals of $[Au_2Cl_2(\mu\text{-dppf})]$ were collected by filtration. This, when combined with a second crop of product from the filtrate, gave a total yield of 2.15 g (87%). The identity of this product was checked against its reported spectroscopic data.

3.3. Synthesis of $[AuCl(dppf)]_x$ (1) and $[AuCl(\mu\text{-dppf})]_n$ (2)

Upon dropwise addition of a solution of $[Au_2Cl_2(\mu\text{-dppf})]$ (0.050 g, 0.05 mmol) in THF (10 ml) to a THF solution (5 ml) of dppf (0.027 g, 0.05 mmol) via a teflon transfer tube, an orange precipitate formed almost instantly. The resultant mixture was further stirred for 30 min and filtered. The precipitate was washed copiously with THF and dried *in vacuo* to give $[AuCl(dppf)]_x$ (**1**). Yield: 0.074 g (97%) (Found: C, 52.59; H, 3.95; Cl, 4.68; Fe, 6.07. Calcd. for $C_{34}H_{28}AuClFeP_2$:C, 51.90; H, 4.59; Cl, 4.51; Fe, 7.10%). MW 668 ($CHCl_3$) (Calcd. 787 for $x = 1$). $\delta_P(CDCl_3)$ 26.51 (s, br), 28.48 (s, br). Reversing the addition of dppf to the Au[I] complex gave the same complex.

Upon dissolution in $CDCl_3$, **1** slowly deposited orange yellow crystals of $[AuCl(\mu\text{-dppf})]_n$ (**2**), which could also be obtained by slow diffusion of hexane into a CH_2Cl_2 solution of **1**. The latter process gave a near quantitative yield of $[AuCl(\mu\text{-dppf})]_n \cdot nCH_2Cl_2$. Found: C, 48.17; H, 3.47; Au, 21.49; Cl, 12.79; Fe, 6.15; P, 6.83. Calcd. for $C_{35}H_{30}AuCl_3FeP_2$:C, 48.22; H, 3.47; Au, 22.59; Cl, 12.20; Fe, 6.41; P, 7.11%. The same complex could be obtained directly from $[AuCl(SMe_2)]$ (0.085 g, 0.29 mmol) in THF (10 ml) upon addition of CH_3CO_2Na (0.024 g, 0.29 mmol) in MeOH (5 ml), followed by dppf (0.160 g, 0.29 mmol) in THF (15 ml). Recrystallisation from MeOH gave an orange yellow product (50–55% yield) together with some black deposits which could be removed by a second recrystallisation from CH_2Cl_2/hexane. Complex **2** dissolves slowly in a mixture of $CDCl_3$ and CH_2Cl_2 to give $[AuCl(\mu\text{-dppf})]_2$, Y. [$\delta_P$ 29.21 (s, br)]. Single crystals of **2** suitable for X-ray study were grown by layering a hexane solution on a CH_2Cl_2 solution of the purified complex.

3.4. Synthesis of [Au_2(dppf-P,P')$_2$(μ-dppf)](NO_3)$_2$ · 2H_2O (3)

A solution of **1** (0.050 g) in CH_2Cl_2 (10 ml) was added dropwise with stirring to a solution of $AgNO_3$ (0.011 g, 0.06 mmol) in EtOH/H_2O (9:1) (2 ml) in a reaction flask shielded from direct light. The resultant suspension was stirred for 3 h to given an orange brown solution which was filtered and evaporated to dryness *in vacuo*. The oily residue thus obtained was extracted by CH_2Cl_2, filtered via a teflon tube into a MeOH solution (10 ml) of HCO_2Na (0.004 g, 0.06 mmol), and the mixture stirred for 16 h. The resultant red solution was stripped of its solvent and the residue extracted with minimal CH_2Cl_2. Excess formate was filtered off and the solution evaporated to dryness. The product was extracted into MeOH and precipitated by Et_2O to give a reddish brown solid. Yield: 0.031 g. Careful layering of Et_2O onto a MeOH sample solution gave a red non-crystalline solid presently unidentified and orange brown crystals of **3** (as dihydrate) suitable for X-ray diffraction. (Found: C, 52.87; H, 4.02; Au, 15.25; Fe, 6.93; N, 1.01; P, 8.24. Calcd. for $C_{102}H_{88}Au_2Fe_3N_2O_6P_6$: C, 55.26; H, 4.00; Au, 17.17; Fe, 7.56; N, 1.26; P, 8.38%). Repeated analysis of the purified sample consistently gave a low carbon content. A similar problem was experienced in some other Au-dppf complexes [14]. $\nu_{max}(NO_3^-)$ 1370s, 1330s cm^{-1}; $\delta(H_2O) \approx 1620$ (br) cm^{-1}. Assignment of the NMR spectrum is tentative because of the partially overlapping resonances from the several species present in solution. $\delta_P(CD_3OD)$ 38.82 [d, 4P; J(PP) 126 Hz], 38.31 [t, 2P; J(PP) 120 Hz], and other presently unidentified resonances at 41.98, 41.04, 40.29, 38.43 and 36.73 ppm.

3.5. Synthesis of [$Au_2(NO_3)_2$(dppf)], (4)

[Au_2Cl_2(μ-dppf)] (0.799 g, 0.78 mmol) in CH_2Cl_2 (45 ml) was added slowly to a MeOH solution (30 ml) of $AgNO_3$ (0.267 g, 1.57 mmol) and the mixture stirred for 2 h before it was filtered and the solvent removed. Sequential extractions by CH_2Cl_2 (to remove $AgNO_3$ and AgCl) and MeOH (to remove unreacted [Au_2Cl_2(μ-dppf)]) gave **4** which was precipitated and recrystallised from CH_2Cl_2/hexane. Yield: 0.676 g (80%). Found: C, 38.63; H, 2.85; Au, 36.65; Fe, 5.24; N,

TABLE 1. Crystallographic data and refinement details for [AuCl(μ-dppf)]$_n$ · nCH_2Cl_2 and [Au_2(dppf-P,P')$_2$(μ-dppf)](NO_3)$_2$ · 2H_2O

Molecular formula	[AuCl(μ-dppf)]$_n$ · nCH_2Cl_2	[Au_2(dppf-P,P')$_2$(μ-dppf)](NO_3)$_2$ · 2H_2O
FW	871.7 (n = 1)	2217.1
Colour and habit	Yellow prism	Yellow prism
Space group	$P2_1/c$(no. 14)	$C2/c$(no. 15)
a (Å)	11.058(7)	33.006(5)
b (Å)	24.154(9)	14.799(3)
c (Å)	13.122(4)	25.415(5)
β (deg)	108.94(4)	128.14(1)
U	3315(2)	9764(3)
Z	4	4
F(000)	1704	4400
D_c (g cm^{-3})	1.747	1.508
Standard reflections	(2,5,0), (0,10,0)	(0,0,2)(6,2,−6)
Intensity variation (%)	±1.5	±1.1
μ (cm^{-1})	52.10	35.83
Crystal size (mm)	0.038 × 0.34 × 0.22	0.28 × 0.30 × 0.36
Mean (μr)	0.78	1.52
Transmission factors	0.157–0.322	0.349–0.368
Scan rate (deg min^{-1})	3.0–15.6	3.08–29.3
Scan range	0.60° below Kα1 to 0.70° above Kα2	1.0° below Kα1 to 1.0° above Kα2
$2\theta_{max}$ (deg)	55	45
Unique data measured	8348	8594
Obs. data with $\|F_0\| > 6\sigma(\|F_0\|)$, n	5552	5681
No. of variables, p	379	283
R_F	0.037	0.049
R_G	0.038	0.067
S	1.43	1.18
Residual extrema in final difference map (eÅ^3)	+0.91 to −0.94	+1.40 to −0.80

* Details in common: crystal system monoclinic; ω scans; stationary counts for one-fifth of scan time at each end of scan range, h, k, ±l.

2.53; P, 5.48. Calcd. for $C_{34}H_{28}Au_2FeN_2O_6P_2$: C, 38.08; H, 2.63; Au, 36.74; Fe, 5.21; N, 2.61; P, 5.78%. MW 1466 ($CHCl_3$) (Calcd. 1072). ν_{max} (NO_3) 1492s, 1380s, 1270s cm^{-1}. $\delta_H(CDCl_3)$ 7.53–7.46 [m, 20H, Ph], 4.74 [m, 4H, Cp] and 4.38 [m, 4H, Cp] ppm. $\delta_P(CDCl_3)$ 22.48 (s) ppm.

3.6. Synthesis of [Au_2(OBz-O)$_2$(μ-dppf)]

Complex **4** prepared *in situ* was dissolved in CH_2Cl_2 (50 ml) and added to a MeOH solution (50 ml) of $C_6H_5CO_2Na$ (0.226 g, 1.57 mmol). The orange mixture was stirred for 16 h after which the solvent was removed. Extraction with CH_2Cl_2 and precipitation with hexane gave [Au_2(OBz-*O*)$_2$(μ-dppf)]. Yield: 0.806 g (86%). Found: C, 48.34; H, 3.25; Au, 30.14; Fe, 4.53; P, 5.65. Calcd. for $C_{48}H_{38}Au_2FeO_4P_2$: C, 48.43; H, 3.22; Au, 33.09; Fe, 4.69; P, 5.20%. MW 1147 ($CHCl_3$) (Calcd. 1191). ν_{max}(OBz) 1609s (br), 1568s, 1329vs cm^{-1} (KBr). $\delta_H(CDCl_3)$ 8.16–8.05 [m, 4H, OBz], 7.71–7.29 [m, 26H, Ph + OBz], 4.89 [m, 4H, Cp] and 4.47 [quin, 4H, Cp] ppm. $\delta_P(CDCl_3)$ 22.75 (s) ppm.

3.7. X-ray crystallographic analysis

Single crystals of [AuCl(μ-dppf)]$_n$ · $n$$CH_2Cl_2$(**2**) and [$Au_2$(dppf-*P,P'*)$_2$($\mu$-dppf)]($NO_3$)$_2$ · 2H_2O(**3**) were grown from CH_2Cl_2/hexane and MeOH/Et_2O mixtures respectively at 25°C. Measurements were made on a Nicolet R3m/v diffractometer using graphite-monochromated Mo Kα radiation (λ 0.71073 Å). The determination of the crystal class, orientation matrix and cell dimensions was performed according to established procedures [35]. Crystal data, data collection parameters and the results of the analysis are listed in Table 1. All data processing was performed on a DEC Micro Vax-II computer with the SHELXTL-PLUS program package [36]. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated [37]. The raw data were processed with the learnt-profile procedure [38] and absorption corrections were applied by fitting a pseudo-ellipsoid to the ω-scan data of selected reflections over a range of two θ angles [39].

Both structures were solved with the Patterson superposition method. The positions of all hydrogen atoms were generated geometrically (C–H bonds fixed at 0.096 Å), assigned isotropic thermal parameters and allowed to ride on their respective parent C atoms. The non-hydrogen atoms of the solvent molecules have expected values for their thermal parameters and also occupy chemically reasonable positions in the unit cell. Table 2 summarises the bond lengths, angles and torsional angles and Table 3 lists the atomic coordinates

TABLE 2. Selected bond lengths (Å), angles (°) and torsional angles (°)

[AuCl(μ-dppf)$_n$ · nCH_2Cl_2			
Au(1)–P(2)	2.323(2)	Au(1)–P(1a)	2.293(2)
Au(1)–Cl(1)	2.709(2)	Fe(1)–C(1–5) (Ave)	2.043(6)
Fe(1)–C(6–10) (Ave)	2.048(6)	P(1)–C(1)	1.788(6)
P(2)–C(6)	1.799(6)		
P(2)–Au(1)–P(1a)	155.2(1)	P(2)–Au(1)–Cl(1)	91.2(1)
P(1a)–Au(1)–Cl(1)	113.6(1)	Au(1)–P(2)–C(6)	110.4(2)
Au(1b)–P(1)–C(1)	110.7(2)		
C(1)–Cp1–Cp2–C(6)	153.1		

Symmetry transformation: a (x, $1/2-y$, $1/2+z$); b (x, $1/2-y$, $-1/2+z$)
Cp1 is the centre of the ring composed of carbon atoms C(1)–C(5)
and Cp2 the centre of C(6)–C(10).

[Au_2(dppf-P,P')$_2$(μ-dppf)](NO_3)$_2$ · 2H_2O			
Au(1)–P(1)	2.335(3)	Au(1)–P(2)	2.395(3)
Au(1)–P(3)	2.383(3)	Fe(1)–Cp1	1.65(2)
Fe(2)–Cp2	1.63(2)	Fe(2)–Cp3	1.65(2)
P(1)–C(1)	1.81(1)	P(2)–C(18)	1.796(9)
P(3)–C(35)	1.79(1)	N(1)–O(1–3)	1.24(3)
P(1)–Au(1)–P(2)	123.7(1)	P(1)–Au(1)–P(3)	126.7(1)
P(2)–Au(1)–P(3)	109.2(1)	Au(1)–P(1)–C(1)	116.0(4)
Au(1)–P(2)–C(18)	112.1(3)	Au(1)–P(3)–C(35)	114.7(4)
O(1)–N(1)–O(2)	115.5(28)	O(1)–N(1)–O(3)	126.7(19)
O(2)–N(1)–O(3)	112.6(20)		
C(18)–Cp2–Cp3–C(35)	−39.6		

Symmetry transformation: a ($-x$, $-y$, $-z$)
Cp1 is the centre of the ring composed of carbon atoms C(1)–C(5),
Cp2 the centre of C(18)–C(22), Cp3 the centre of C(35)–C(39), respectively.

TABLE 3. Atomic co-ordinates of $[AuCl(\mu\text{-dppf})]_n \cdot nCH_2Cl_2$ ($\times 10^5$ for Au, Fe. P and Cl atoms; $\times 10^4$ for C atoms) and $[Au_2(\text{dppf-}P,P')_2(\mu\text{-dppf})](NO_3)_2 \cdot 2H_2O$ ($\times 10^5$ for Au and Fe; $\times 10^4$ for other atoms)

Atom	x	y	z	Atom	x	y	z
$[AuCl(\mu\text{-dppf})_n \cdot nCH_2Cl_2$							
Au(1)	14794(2)	24058(1)	38542(2)	C(17)	4522(5)	3103(2)	-643(5)
Fe(1)	19289(7)	35836(3)	15849(7)	C(18)	5490(6)	2921(3)	248(6)
P(1)	29549(14)	32893(6)	-5586(13)	C(19)	6659(7)	2752(3)	149(7)
P(2)	7779(14)	33184(6)	36479(13)	C(20)	6842(7)	2767(3)	-852(7)
Cl(1)	-8752(15)	20397(7)	26743(14)	C(21)	5878(7)	2948(3)	-1732(7)
C(1)	3261(5)	3423(2)	843(5)	C(22)	4717(6)	3123(3)	-1647(5)
C(2)	3270(5)	3002(3)	1630(5)	C(23)	1863(6)	3818(3)	4510(5)
C(3)	3565(6)	3256(3)	2645(6)	C(24)	3133(7)	3665(3)	5089(6)
C(4)	3716(5)	3836(3)	2530(5)	C(25)	3975(8)	4047(4)	5676(7)
C(5)	3518(5)	3936(3)	1412(5)	C(26)	3607(10)	4585(4)	5739(8)
C(6)	545(5)	3553(2)	2296(5)	C(27)	2351(10)	4739(3)	5206(8)
C(7)	679(5)	4107(3)	1939(5)	C(28)	1486(7)	4368(3)	4596(6)
C(8)	420(6)	4086(3)	807(5)	C(29)	-734(5)	3460(2)	3870(5)
C(9)	139(5)	3534(3)	453(5)	C(30)	-799(6)	3493(3)	4913(5)
C(10)	200(5)	3198(3)	1364(4)	C(31)	-1927(7)	3604(3)	5086(6)
C(11)	2612(5)	3961(2)	-1215(5)	C(32)	-3019(7)	3677(3)	4226(6)
C(12)	1376(6)	4076(3)	-1864(6)	C(33)	-2992(6)	3646(3)	3186(6)
C(13)	1095(8)	4595(3)	-2353(7)	C(34)	-1863(6)	3531(3)	2992(5)
C(14)	2018(9)	4982(3)	-2193(8)	Cl(2)	7259(3)	396(1)	2115(2)
C(15)	3242(8)	4876(3)	-1559(7)	Cl(3)	7252(3)	498(1)	4339(3)
C(16)	3554(7)	4359(3)	-1069(6)	C(35)	7595(13)	773(4)	3260(9)
$[Au_2(\text{dppf-}P,P')_2(\mu\text{-dppf})](NO_3)_2 \cdot 2H_2O$							
Au(1)	12117(1)	20930(3)	3942(2)	C(27)	1602	4093	77
Fe(1)	0	0	0	C(28)	1840	4174	758
P(1)	318(1)	2125(2)	-214(1)	C(29)	1192(3)	4460(5)	1276(3)
C(1)	-6(4)	1047(7)	-516(5)	C(30)	991	4835	1575
C(2)	-521(4)	832(9)	-762(7)	C(31)	1176	4555	2212
C(3)	-610(6)	-74(10)	-991(7)	C(32)	1561	3900	2550
C(4)	-169(6)	-412	-895(8)	C(33)	1762	3525	2251
C(5)	205(5)	287(7)	-603(6)	C(34)	1577	3804	1614
C(6)	-240(3)	2366(3)	-1608(3)	C(35)	2360(3)	1317(6)	728(5)
C(7)	-415	2878	-2173	C(36)	2808(4)	813(7)	1214(5)
C(8)	-266	3799	-2104	C(37)	3247(4)	1309(8)	1445(5)
C(9)	59	4169	-1469	C(38)	3098(4)	2140(8)	1103(5)
C(10)	234	3657	-904	C(39)	2544(4)	2155(7)	667(5)
C(11)	85	2756	-973	C(40)	1846(3)	-165(5)	1198(4)
C(12)	-467(3)	3042(5)	-313(3)	C(41)	1878	-1019	1453
C(13)	-692	3431	-50	C(42)	1780	-1789	1073
C(14)	-421	3464	641	C(43)	1650	-1704	439
C(15)	76	3109	1069	C(44)	1619	-849	184
C(16)	301	2720	806	C(45)	1717	-80	563
C(17)	30	2687	115	C(46)	980(2)	1092(5)	-1116(3)
Fe(2)	28104(5)	20113(10)	16194(7)	C(47)	795	893	-1767
P(2)	1778(1)	3247(2)	1169(1)	C(48)	1118	483	-1876
P(3)	1693(1)	1046(2)	265(1)	C(49)	1625	271	-1336
C(18)	2416(4)	2825(7)	1801(5)	C(50)	1809	470	-685
C(19)	2911(4)	3211(8)	2061(5)	C(51)	1487	880	-575
C(20)	3281(5)	2605(10)	2521(6)	N(1)	1574(6)	1521(14)	2538(10)
C(21)	3056(5)	1849(9)	2572(6)	O(1)	1125(6)	1611(14)	2344(10)
C(22)	2517(4)	1982(7)	2120(5)	O(2)	1922(8)	1813(17)	3117(10)
C(23)	2092(3)	4974(5)	1095(3)	O(3)	1730(7)	939(14)	2362(10)
C(24)	2106	5692	751	O(1W)	558(11)	4078(19)	3025(14)
C(25)	1868	5611	70	O(2W)	2045(13)	2429(26)	4371(18)
C(26)	1616	4811	-266				

of 2 and 3. The phenyl rings were treated as rigid groups, and accordingly only the standard deviations of one atom of each ring are given.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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