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$[Au_2Cl_2(fdpp)_3]$, a Structural Intermediate in the Assembly of Gold–Phosphine Chain Polymers

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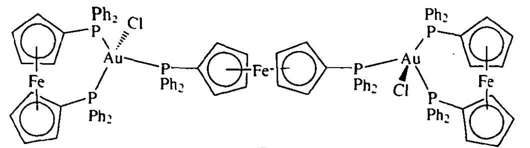
Abstract

The reaction of 1,1′-bis(diphenylphosphine)ferrocene, fdpp, with a twofold excess of $AuCl(SMe_2)$ in dichloromethane yields [μ-1,1′-bis(diphenylphosphine)ferrocene-κP:$\kappa P'$]bis{chloro[1,1′-bis(diphenylphosphine)ferrocence-P,P']gold}–dichloromethane (1/2), $[\{AuCl[Fe(C_{17}H_{14}P)_2]\}_2\{\mu\text{-}Fe(C_{17}H_{14}P)_2\}].2CH_2Cl_2$. The coordination at the Au atoms in the dimeric $[Au_2Cl_2(fdpp)_3]$ complex is distorted, involving three P—Au bonds and a long Au···Cl contact. The fdpp ligand adopts both chelating and bridging binding modes.

Comment

We have recently reported the synthesis and structural characterization of a gold-based coordination chain polymer incorporating 1,1′-bis(diphenylphosphine)ferrocene, fdpp (Houlton, Mingos, Murphy, Williams, Phang & Hor, 1993). The conformational flexibility of the ferrocenyl moiety gives rise to two pseudo-polymorphic forms of $[AuCl(\mu\text{-fdpp})]_n$, which differ principally in the torsion angle P1···X1···X2···P2 (where X1 and X2 represent the centroids of the C_5H_4 rings). Here we report a multimolecular complex which may be considered to be a structural intermediate in the formation of these polymeric gold-phosphine chains.

An X-ray structure determination revealed that the product from the reaction of a 2:1 ratio of $AuCl(SMe_2)$ and fdpp in dichloromethane did not have the anticipated 2:1 stoichiometry. In fact, the product is a multi-molecular species containing a complex ion with the structural formula $[Au_2Cl_2(fdpp)_3]$, (1). The 2:3 gold:ligand ratio of this complex highlights the documented fact that in Au^I chemistry the material isolated in the solid state is not necessarily the same as the predominant species observed in solution (Colburn, Hill, McAuliffe & Parish, 1979; McAuliffe, Parish & Randall, 1979; Parish, Parry & McAuliffe, 1981; Al-Sáady, McAuliffe, Moss, Parish & Fields, 1984; Al-Baker, Hill & McAuliffe, 1985).



(I)

In (1), the fdpp ligands adopt both bridging and chelating binding modes with the Fe atom of the central bridging ligand lying at a centre of symmetry. Au^I is in a distorted trigonal-pyramidal coordination environment, with two approximately equivalent Au—P bonds from the chelating ligand (≃2.40 Å), and a significantly shorter bond of 2.345 (3) Å to the bridging ligand. Au^I is displaced by ~0.3 Å out of the P_3 plane towards the Cl^- ion. The Au···Cl distance is very long [2.929 (3) Å, compared with 2.550 (3) Å in $\{AuCl(fdpp)\}_n$], suggesting considerable $Au^+\cdots Cl^-$ character. Comparable geometry has been reported for the orthorhombic form of $[Au(PPh_3)_3SCN]$, where the Au—P distances average 2.391 Å and the Au···S distance is 2.928 Å with the Au atom displaced 0.4 Å out of the plane of the three P atoms in the direction of the S atom (Muir, Muir, Arias, Jones & Sheldrick, 1984).

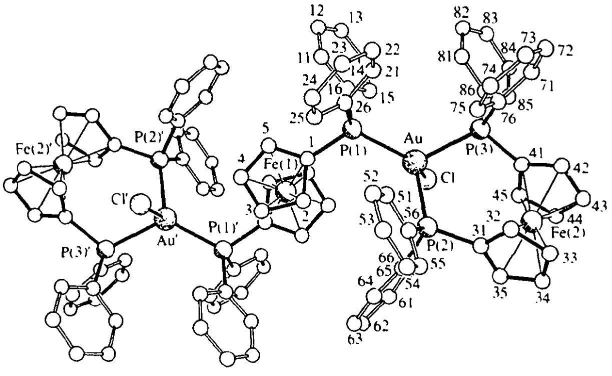


Fig. 1. Molecular structure of the complex $[Au_2Cl_2(fdpp)_3]$. H atoms and the solvent of crystallization (CH_2Cl_2) have been omitted for clarity. C atoms are indicated by numbers and primed atoms are related to the corresponding unprimed atoms by the centre of symmetry at Fe(1).

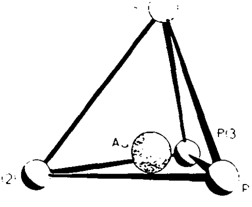


Fig. 2. The coordination sphere of Au, illustrating the trigonal-pyramidal coordination geometry.

Previously reported $AuClP_3$ structures (where P is a phosphine) have been described as displaying coordination geometries intermediate between idealized three- and fourfold (Jones, 1981, 1983). However, the Au···Cl distances in these structures are considerably shorter than in (1). For example, in $AuCl(PPh_3)_3$ the Au—P bond lengths are 2.395 (2), 2.404 (4) and 2.431 (2) Å, and the Au—Cl distance is 2.710 (2) Å (Jones, Sheldrick, Muir, Muir & Bird Pulgar, 1982). Similarly for $AuCl(DBP)_3$ (where DBP is 1-phenyldibenzophosphole), the Au—Cl distance is 2.735 (2) Å and the Au—P bond lengths lie within the range 2.359 (1)–2.382 (1) Å (Attar, Bearden, Alcock, Alyea & Nelson, 1990).

The effect of the close proximity of the Cl anion on the Au coordination geometry in (1) can be gauged by a comparison with the perchlorate salt of (1) in which the nearest perchlorate O atom is approximately 3.4 Å from the Au atom (Gimeno, Laguna, Sarroca & Jones, 1993). In the presence of this non-coordinating anion the Au atom is only about 0.1 Å out of the P_3 plane.

Structurally characterized examples of $[Au_2(P\text{-}P)_3]$ diphosphine complexes include the complexes for which $P\text{-}P$ is bis(dimethylphosphino)methane (Beusch, Prelati & Ludwig, 1986) and 2,6-bis(diphenylphosphino)pyridine (Shieh, Peng & Che, 1993). However, the bonding in these compounds differs from that in (1) in that the ligands act exclusively in a bridging manner. For (1), the distinct binding modes observed can be ascribed to the conformational flexibility of the ferrocenyl moiety.

A number of crystallographic studies of Au^I complexes with fdpp formed under a variety of conditions have now been reported; these include a study of $[Au_3Cl_3(fdpp^*)_2]$, where fdpp* is $[(\eta^5\text{-}C_5H_4PPh_2)Fe\{\eta^5\text{-}C_5H_3(PPh_2)CH(CH_3)N(CH_3)\text{-}CH_2CH_2N(CH_3)_2\}]$ (Togni, Pastor & Rihs, 1990). With the characterization of the coordination polymer $[AuCl(\mu\text{-fdpp})]_n$, both $[Au_3Cl_3(fdpp^*)_2]$ and (1) can be identified as structural intermediates in the formation of these polymeric gold–phosphine chains.

Experimental

Crystal data

$[Au_2Fe_3Cl_2(C_{17}H_{14}P)_6]\cdot 2CH_2Cl_2$
$M_r = 2297.8$
Orthorhombic
$Pbca$
$a = 19.142$ (8) Å
$b = 20.759$ (4) Å
$c = 23.645$ (10) Å
$V = 9395$ (6) Å^3
$Z = 4$
$D_x = 1.624$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 20 reflections
$\theta = 3\text{–}12°$
$\mu = 3.885$ mm^{-1}
$T = 293$ K
Rhomb
0.22 × 0.13 × 0.08 mm
Yellow

Data collection

Siemens $P4/PC$ diffractometer
ω scans
Absorption correction: empirical
$T_{\min} = 0.384$, $T_{\max} = 0.588$
8290 measured reflections
8287 independent reflections
4464 observed reflections [$F > 4.0\sigma(F)$]

$\theta_{\max} = 25°$
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 24$
$l = 0 \rightarrow 28$
2 standard reflections monitored every 50 reflections intensity variation: 9% decay

Refinement

Refinement on F
$R = 0.0496$
$wR = 0.0438$
$S = 1.16$
4464 reflections
475 parameters
H atoms treated using a riding model with fixed, isotropic U's

$w = 1/[\sigma^2(F) + 0.0005F^2]$
$(\Delta/\sigma)_{\max} = 0.019$
$\Delta\rho_{\max} = 1.10$ e Å^{-3}
$\Delta\rho_{\min} = -0.90$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *SHELXTL/PC* (Sheldrick, 1992)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Au	0.0959 (1)	0.1650 (1)	0.1227 (1)	0.038 (1)
Fe(1)	0	0	0	0.033 (1)
Fe(2)	0.2799 (1)	0.2806 (1)	0.1391 (1)	0.050 (1)
Cl	0.0849 (2)	0.2274 (1)	0.0120 (1)	0.059 (1)
P(1)	−0.0035 (1)	0.0990 (1)	0.1208 (1)	0.034 (1)
P(2)	0.2129 (1)	0.1250 (1)	0.1277 (1)	0.040 (1)
P(3)	0.1025 (2)	0.2721 (1)	0.1611 (1)	0.039 (1)
C(1)	−0.0013 (5)	0.0232 (4)	0.0838 (4)	0.031 (3)
C(2)	0.0607 (6)	−0.0111 (5)	0.0702 (4)	0.044 (4)
C(3)	0.0396 (7)	−0.0723 (5)	0.0487 (4)	0.053 (5)
C(4)	−0.0324 (7)	−0.0767 (5)	0.0485 (4)	0.054 (5)
C(5)	−0.0577 (6)	−0.0184 (5)	0.0702 (4)	0.040 (4)
C(11)	−0.1495 (4)	0.1118 (3)	0.1246 (3)	0.059 (4)
C(12)	−0.2127	0.1407	0.1101	0.085 (6)
C(13)	−0.2134	0.1935	0.0736	0.089 (7)
C(14)	−0.1509	0.2173	0.0516	0.079 (6)
C(15)	−0.0877	0.1883	0.0661	0.066 (5)
C(16)	−0.0869	0.1356	0.1027	0.043 (4)
C(21)	−0.0296 (4)	0.1195 (3)	0.2345 (3)	0.049 (4)
C(22)	−0.0309	0.1033	0.2918	0.055 (5)
C(23)	−0.0181	0.0399	0.3086	0.062 (5)
C(24)	−0.0041	−0.0072	0.2681	0.052 (4)
C(25)	−0.0029	0.0089	0.2108	0.042 (4)
C(26)	−0.0157	0.0723	0.1940	0.031 (3)
C(31)	0.2834 (6)	0.1815 (5)	0.1410 (5)	0.051 (4)
C(32)	0.2978 (7)	0.2093 (5)	0.1955 (5)	0.060 (5)
C(33)	0.3592 (8)	0.2483 (6)	0.1904 (8)	0.078 (7)
C(34)	0.3789 (7)	0.2470 (6)	0.1330 (9)	0.088 (7)
C(35)	0.3325 (6)	0.2060 (5)	0.1020 (6)	0.069 (5)
C(41)	0.1811 (6)	0.3157 (5)	0.1413 (5)	0.048 (4)
C(42)	0.2245 (7)	0.3539 (5)	0.1758 (5)	0.057 (5)
C(43)	0.2800 (8)	0.3778 (5)	0.1425 (7)	0.076 (6)
C(44)	0.2687 (7)	0.3570 (6)	0.0852 (6)	0.069 (6)
C(45)	0.2075 (6)	0.3185 (5)	0.0840 (5)	0.050 (4)
C(51)	0.1711 (3)	0.0465 (4)	0.2159 (3)	0.059 (5)
C(52)	0.1808	0.0059	0.2623	0.077 (6)
C(53)	0.2479	−0.0146	0.2768	0.066 (5)
C(54)	0.3052	0.0055	0.2450	0.073 (6)
C(55)	0.2955	0.0461	0.1986	0.056 (5)
C(56)	0.2285	0.0666	0.1841	0.039 (4)

C(61)	0.2622 (4)	0.0225 (3)	0.0598 (3)	0.060 (5)
C(62)	0.2749	−0.0068	0.0077	0.091 (7)
C(63)	0.2633	0.0273	−0.0423	0.080 (6)
C(64)	0.2389	0.0905	−0.0402	0.071 (6)
C(65)	0.2262	0.1198	0.0119	0.065 (5)
C(66)	0.2378	0.0858	0.0619	0.042 (4)
C(71)	0.0916 (4)	0.3336 (3)	0.2666 (3)	0.069 (5)
C(72)	0.0919	0.3349	0.3256	0.090 (6)
C(73)	0.1052	0.2786	0.3560	0.086 (6)
C(74)	0.1181	0.2210	0.3274	0.071 (6)
C(75)	0.1178	0.2197	0.2684	0.054 (4)
C(76)	0.1045	0.2760	0.2380	0.051 (4)
C(81)	−0.0342 (5)	0.3099 (4)	0.1625 (3)	0.072 (6)
C(82)	−0.0915	0.3482	0.1485	0.109 (8)
C(83)	−0.0825	0.4026	0.1146	0.093 (7)
C(84)	−0.0161	0.4187	0.0948	0.087 (6)
C(85)	0.0412	0.3804	0.1088	0.060 (5)
C(86)	0.0322	0.3260	0.1426	0.047 (4)
C(100)	0.5092 (7)	0.1373 (7)	0.0465 (5)	0.083 (6)
Cl(1)	0.4363 (2)	0.0895 (2)	0.0457 (2)	0.087 (2)
Cl(2)	0.5865 (2)	0.0923 (2)	0.0550 (2)	0.115 (2)

Table 2. *Selected geometric parameters* (Å, °)

Au—P(1)	2.345 (3)	Au—Cl	2.929 (3)
Au—P(2)	2.391 (3)	Au···Fe(1)	4.850 (5)
Au—P(3)	2.405 (3)	Au···Fe(2)	4.280 (5)
P(1)—Au—Cl	100.5 (1)	P(2)—Au—Cl	105.3 (1)
P(1)—Au—P(2)	124.0 (1)	P(2)—Au—P(3)	104.6 (1)
P(1)—Au—P(3)	126.2 (1)	P(3)—Au—Cl	86.1 (1)

The structure was determined by direct methods using *SHELXTL-Plus* (Sheldrick, 1992) and refined using anisotropic displacement parameters for all non-H atoms and rigid-group constraints for the phenyl rings.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and bond distances and angles involving non-H atoms have been deposited with the IUCr (Reference: MU1114). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Disodium μ-(Ethylenediaminetetraacetato-*N*,*O*,*O*′:*N*′,*O*″,*O*‴)-di-μ-oxo-bis[oxomolybdate(V)](*Mo*—*Mo*) Tetrahydrate

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Abstract

In the title compound, $2Na[Mo_2O_4(C_{10}H_{12}N_2O_8)].4H_2O$, the hexadentate ethylenediaminetetraacetate (edta) ligand coordinates to each Mo atom through two carboxylate O atoms and an N atom while two bridging O atoms and a terminal O atom complete the coordination sphere around each Mo centre.

Comment

The $[Mo_2O_4(edta)]^{2}$ anion, (I), consists of two Mo atoms each coordinated in a distorted octahedral environment by five O atoms and an N atom. The hexadentate ethylenediaminetetraacetate (edta) ligand coordinates to each Mo atom through two carboxylate O atoms and an N atom. The Mo═O(carboxylate) distances are within the expected range for O atoms σ-bonded to Mo and are similar to those found in the structure $Cs_2[Mo^V(\mu\text{-}S)_2(\mu\text{-}edta)O_2]^{2}$ (Spivack & Dori, 1973). They are also comparable to the value of 2.12 A found in $Ba[Mo_2O_4(C_2O_4)_2(H_2O)_2]$ (Cotton & Morehouse, 1965). The

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