Aurated clusters derived from (μ_3-ketenylidene)-Fe$_3$ and -Fe$_2$Co clusters [*]

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Abstract

The ketenylidene bridged cluster (PPN)$_2$[Fe$_3$(CO)$_9$(μ_3-CCO)] (1) is converted by Ph$_3$PAuCl into (Ph$_3$PAu)$_2$Fe$_3$(CO)$_9$(μ_3-CCO) (3) containing the intact ketenylidene ligand. Allyl bromide and 1 yield (PPN)[Fe$_3$(CO)$_9$(μ_3-CO)(μ_3-CC$_3$H$_5$)] (4), as evidenced by a structure determination. Compound 4 and Ph$_3$PAuCl form the analogous neutral compound (Ph$_3$PAu)Fe$_3$(CO)$_9$(μ_3-CO)(μ_3-CC$_3$H$_5$) (5). Auration of the cobalt containing cluster (PPN)[Fe$_2$Co(CO)$_9$(μ_3-CCO)] (2) yields an unstable main product and the byproduct (Ph$_3$PAu)Fe$_3$Co(CO)$_{12}$(μ_5-C) (6) which has been characterized by a structure determination.

Keywords: Aurated clusters; Ketenylidene-Fe$_3$-cluster; Ketenylidene-Fe$_2$Co-cluster; X-ray structure; Iron; Cobalt

1. Introduction

The cluster-bound ketenylidene ligand CCO is a very attractive species in the context of the cluster-surface analogy as it combines unusual bonding situations of CO and also of a "bare" carbon atom. Accordingly, a significant body of knowledge has been accumulated on the chemistry of ketenylidene-bridged clusters, mainly by the group of Shriver [1–3]. A common feature of the investigated cluster compounds is that they are mostly anionic species, which imposes limitations both on the handling of reaction products and on the nature of possible reagents.
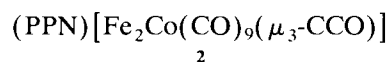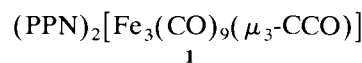
We therefore considered it desirable to obtain neutral cluster compounds with μ_3-ketenylidene ligands, especially since we had observed that such compounds may open an entry to the chemistry of the cluster-bound carbon atom [4]. The simplest method of "neutralization" of the anionc species, i.e. protonation, does not work for the first-row transition metal clusters as they undergo rearrangement reactions with loss of the ketenylidene ligand [2]. Auration with R$_3$PAu–X

reagents has, however, been established as a mild method to prepare stable AuM$_n$ clusters as derivatives of HM$_n$ clusters [5]. We therefore tried to obtain neutral AuFe and AuFeCo clusters with ketenylidene ligands by this method.

2. Results and discussion

2.1. Reactions

Starting materials for our investigations were the cluster compounds 1 and 2, which are readily available [6,7].

$$(PPN)_2[Fe_3(CO)_9(\mu_3\text{-CCO})]$$
$$\mathbf{1}$$

$$(PPN)[Fe_2Co(CO)_9(\mu_3\text{-CCO})]$$
$$\mathbf{2}$$

The reaction of 1 with Ph$_3$PAuCl proceeded as expected to form the neutral cluster compound 3 in good yields; 3 will be used for further studies of the ketenylidene ligand reactivity.

$$(Ph_3PAu)_2Fe_3(CO)_9(\mu_3\text{-CCO})$$
$$\mathbf{3}$$

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In order to exploit the functionality of **1** by means of neutral compounds, this starting cluster was first derivatized with a functional electrophile. For this purpose allyl bromide was chosen. It converts **1**, with loss of CO from the ketenylidene ligand, into the μ_3-alkylidyne bridged cluster **4**, as was previously observed for the reaction of **1** with methyl iodide [6]. Compound **4** in turn can be aurated with Ph_3PAuCl to yield the cluster **5**, which, although not a ketenylidene-bridged cluster, bears reactivity in the form of the μ_3-allylmethylidyne ligand.

$$(PPN)[Fe_3(CO)_9(\mu_3\text{-CO})(\mu_3\text{-CC}_3H_5)]$$
4

$$(Ph_3PAu)Fe_3(CO)_9(\mu_3\text{-CO})(\mu_3\text{-CC}_3H_5)$$
5

The starting cluster **2** proved to be more labile with respect to auration reactions. Treatment with Ph_3PAuCl converted it into a mixture of compounds of which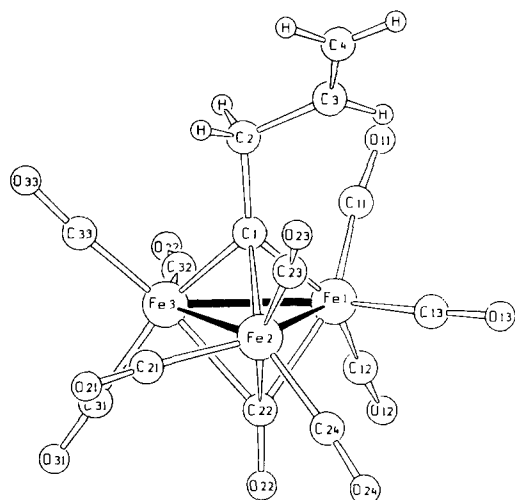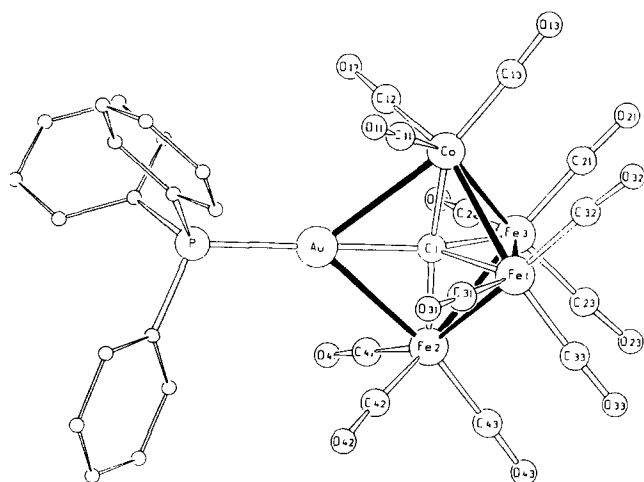 the main product may be the desired $(Ph_3PAu)Fe_2Co(CO)_9(\mu_3\text{-CCO})$, but it could not be identified owing to rapid decomposition. The second product, **6**, must have resulted from cluster fragmentation and recombination as it contains one more iron atom than **2** and has the Ph_3PAu unit attached to the carbon atom of the former ketenylidene ligand.

$$(Ph_3PAu)Fe_3Co(CO)_{12}(\mu_5\text{-C})$$
6

2.2. Spectra and constitutions

IR data for compounds **3–6** are given in Table 1. For **3** they are significantly different from those of $H_2M_3(CO)_9(\mu_3\text{-CCO})$ (M = Ru[8], Os[9]) to indicate a less symmetrical molecular structure. Accordingly, there are two ^{31}P NMR resonances at 56.7 and 33.2 ppm, revealing strikingly different environments of the two Ph_3PAu units. The ^{13}C NMR spectrum of **3** proves the presence of a μ_3-ketenylidene ligand with signals at 30.1 and 159.8 ppm for the α- and β-C atoms of CCO [1–3]. In the absence of a crystal structure determination, the heavy atom frameworks **3a** and **3b** which take into account the homophilicity of gold atoms [5] seem to be candidates for the correct molecular constitution of **3**.

3a   **3b**

Table 1
IR data (CH_2Cl_2, cm^{-1}) for the new compounds

3	2063vs, 2048w, 2001s, 1984s, 1937m
4	2048w, 1992vs, 1962vs, 1710w
5	2066m, 2049m, 2035vs, 2023vs, 2017vs, 2002s, 1965m, 1769w
6	2067m, 2007vs, 1932m

The IR data for **4**, indicating a μ_3-CO ligand, are in accord with the molecular structure (see below). For both **4** and **5** there is no evidence for ketenylidene ligands from the ^{13}C NMR spectra. The IR data for **5** again indicate a lower symmetry than that of **4**, but with a preservation of the μ_3-CO ligand. The ^{31}P NMR resonance of **5** at 56.2 ppm is in the normal range for Ph_3PAu units. The ^{1}H NMR signals of the allyl substituents in **4** and **5** are similar, showing badly resolved multiplets for each proton with that for the central CH at ca. 6.4 ppm and the other four clustered at 5.0–5.4 ppm. Deducing from the structure of **4** one therefore may write formulae **5a** and **5b** for the heavy atom framework of **5** which bear a similar relation as **3a** and **3b**.

5a   **5b**

The constitution of **6** is unusual and could not be deduced from the simple IR spectrum. Only the structure determination (see below) could reveal the nature of this rearrangement product containing five metal atoms linked to the carbide ligand resulting from the CCO group.

2.3. Structure determinations

Only one of the aurated products, **6**, yielded crystals for a structure determination. However, as **4** could be subjected to an X-ray analysis, some indirect evidence for the structure of **5** could be obtained. Details of the structure determinations are given in the Experimental section. Figs. 1 and 2 and Tables 2 and 3 summarize the results.

The anionic cluster **4** has a molecular shape which has been observed several times before. Similar metal triangles with two triply bridging carbon ligands have for instance been reported for $Fe_3(CO)_9(\mu_3\text{-CMe})(\mu_3\text{-COMe})$ [10] and $Fe_3(CO)_9(\mu_3\text{-CF})_2$ [11]. In **4** the $Fe_3(\mu_3\text{-C})_2$ skeleton is highly symmetrical, as evi-

denced by the Fe–Fe and Fe–C bond lengths and by the Fe–C1–C2 and Fe–C22–O22 angles. It is noteworthy that the Fe–C bonds for the μ_3-CO ligand are 0.1 Å longer than for the μ_3-C–allyl ligand. The C–C single and double bonds of the allyl group are clearly distinguished. A disorder problem amongst the iron atoms (see Experimental) is reflected in the apparent non-linearity of all Fe–C–O units.

The neutral cluster 6 is a new member of the growing class of carbide-centred metal clusters [12]. Among these the pentanuclear group is still relatively small, and trigonal-bipyramidal structures have been reported, e.g. for $[Os_5C(CO)_{15}I]^-$ [13] and Ru_5C $(CO)_{15}$-$(AuPPh_3)Cl$ [14]. An isoelectronic analogue of 6 is $(Ph_3PAu)HFe_4(CO)_{12}(\mu_5$-C), which also has a very similar structure [15] but which can be distinguished from 6 by means of its IR spectrum and unit cell. The M_5C cluster core of 6 is highly symmetrical, which means that iron and cobalt atoms cannot be distinguished. In the Fe_3Co butterfly arrangement the central Fe1–Fe3 bond is typically shorter than the other four equivalent bonds. The gold atom is only linked to Co and Fe2 while its distances to Fe1 (3.63 Å) and Fe3 (3.87 Å) are outside the bonding range. The central carbon atom has slightly shorter metal–carbon distances to the apical than to the equatorial metal atoms, which is again typical for such trigonal-bipyramidal arrangements.

3. Conclusion

The electrophiles allyl bromide and Ph_3PAuCl have been made to react with the anionic ketenylidene-bridged clusters 1 and 2. As with other reactions of this type, loss of CO from the ketenylidene ligand is a dominant feature. However, the formation of 3 in the desired manner has yielded a neutral Fe_3 cluster with a μ_3-CCO unit. The allylmethylidyne ligand in 4 and 5 permits new reactivity studies in the ligand sphere, and the unexpected formation of 6 is a reminder of the inherent lability of all these first-row transition metal clusters towards fragmentation and recombination.

4. Experimental details

The general experimental techniques were as described previously [16]. The starting clusters 1 [6] and 2 [7] were prepared according to published procedures.

4.1. Preparations

3. A 620 mg (0.40 mmol) amount of 1 and 400 mg (0.80 mmol) of Ph_3PAuCl were stirred in 30 ml of THF for 2 h. The solvent was removed in vacuo and the residue chromatographed with CH_2Cl_2/hexane (1:1)

Fig. 1. Molecular structure of the anion of 4.

Fig. 2. Molecular structure of 6.

Table 2
Selected bond lengths (Å) and angles (degrees) in 4

Fe1–Fe2	2.535(2)	C1–C2	1.52(1)
Fe1–Fe3	2.547(2)	C2–C3	1.50(1)
Fe2–Fe3	2.531(2)	C3–C4	1.31(1)
Fe1–C22	2.06(1)		
Fe2–C22	2.05(1)	Fe1–C1–C2	132.4(5)
Fe3–C22	2.17(1)	Fe2–C1–C2	130.6(5)
C22–O22	1.19(1)	Fe3–C1–C2	129.7(5)
Fe1–C1	1.967(5)	Fe1–C22–O22	136.5(5)
Fe2–C1	1.943(8)	Fe2–C22–O22	136.3(7)
Fe3–C1	1.905(7)	Fe3–C22–O22	133.7(6)

Table 3
Selected bond lengths (Å) in 6

Au–Co	287.3(1)	Au–P	226.7(1)
Au–Fe2	281.8(1)	Au–C1	206.9(3)
Co–Fe1	261.4(1)	Co–C1	184.7(5)
Co–Fe3	261.5(1)	Fe1–C1	194.6(3)
Fe1–Fe2	263.3(1)	Fe2–C1	184.5(5)
Fe1–Fe3	251.8(1)	Fe3–C1	193.5(3)
Fe2–Fe3	262.8(1)		

using a 20 × 2 cm i.d. silica gel column. After a trace of $Fe_3(CO)_{12}$, the second, purple fraction yielded 355 mg (63%) of **3**, black crystals, m.p. 210°C (decomp.). Anal. Found: C, 40.45; H, 2.12; Fe, 11.7. $C_{47}H_{30}Au_2Fe_3O_{10}P_2$ (1378.2) calc.: C, 40.96; H, 2.19; Fe, 12.16%.

4. Prepared similarity to **3** from 840 mg (0.55 mmol) of **1** and 13 mg (100 μl, 1.1 mmol) of allyl bromide. Workup as before and chromatography with CH_2Cl_2/ hexane (5 : 1) yielded from the second, red–brown fraction 290 mg (51%) of **4**, red–brown crystals, m.p. 104°C. Anal. Found: C, 57.69; H, 3.34; N, 1.35. $C_{50}H_{34}Fe_3NO_{10}P_2$ (1038.3) calc.: C, 57.84; H, 3.30; N, 1.35%.

5. A 50 mg (0.048 mmol) amount of **4** was dissolved in 20 ml of THF and 24 mg (0.048 mmol) of Ph_3PAuCl were added. After stirring for 2 h the solvent was removed in vacuo and the residue chromatographed with hexane using 20 × 2 cm i.d. silica gel column. After a trace of $Fe_3(CO)_{12}$, the second, dark-purple fraction yielded 22 mg (48%) of **5**, black crystals, m.p. 155°C (decomp.). Anal. Found: C, 40.37; H, 2.63; Fe, 17.0. $C_{32}H_{20}AuFe_3O_{10}P$ (960.0) calc.: C, 40.04; H, 2.10; Fe, 17.4%.

6. A 161 mg (0.16 mmol) amount of **2** and 77 mg (0.16 mmol) of Ph_3PAuCl in 10 ml THF were stirred for 1 h. The solvent was removed in vacuo and the residue was chromatographed with CH_2Cl_2/hexane (1 : 3) using a 20 × 2 cm i.d. silica gel column. From the first, brown fraction 30 mg of an unstable product (IR, in CH_2Cl_2 (cm^{-1}): 2101w, 2085w, 2078w, 2051vs, 2032vs, 2013s, 1965m, 1837m) were obtained. The sec-

Table 4
Crystallographic details

Parameter	4	6
Formula	$C_{50}H_{34}Fe_3NO_{10}P_2$	$C_{31}H_{15}AuCoFe_3O_{12}P$
Mol. wt.	1038.3	1033.9
Colour	Wine-red	Red
Crystallized from	CH_2Cl_2/pentane	Pentane
Crystal size (mm)	0.8×0.4×0.4	0.4×0.4×0.2
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	9.834(2)	11.095(2)
b (Å)	14.497(3)	12.797(3)
c (Å)	18.419(4)	13.721(3)
α (degrees)	66.98(3)	79.54(3)
β (degrees)	76.03(3)	81.49(3)
γ (degrees)	88.59(3)	64.73(3)
V (Å^3)	2338.1(8)	1727.0(6)
Z	2	2
$d_{calcd.}$ (g cm^{-3})	1.48	1.99
μ (cm^{-1})	10.8	67.1
2θ range (degrees)	4–50	4–50
hkl range	$\pm h \pm k +l$	$-h \pm k \pm l$
Reflections ($I \geq 4\sigma(I)$)	6609	5706
Variables	583	442
R index (unweighted)	0.079	0.025
Diff. electron density	+1.4	+0.8
Maxima (e Å^{-3})	-1.2	-0.9

Table 5
Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal coefficients (pm$^2 \times 10^{-1}$) for **4**

Atom	X	Y	Z	U_{eq}
P(1)	8777(2)	5674(1)	3349(1)	47(1)
C(111)	10596(6)	6002(4)	3217(3)	49(2)
C(112)	11102(7)	7015(5)	2826(4)	57(3)
C(113)	12484(7)	7288(5)	2719(4)	63(3)
C(114)	13386(7)	6567(5)	3006(4)	66(3)
C(115)	12904(7)	5572(6)	3385(4)	67(3)
C(116)	11515(6)	5279(4)	3489(4)	54(3)
C(121)	8468(5)	4340(4)	3891(3)	45(2)
C(122)	8204(8)	3744(5)	3501(4)	66(3)
C(123)	7988(9)	2710(5)	3918(5)	75(4)
C(124)	8048(8)	2265(5)	4723(5)	70(3)
C(125)	8285(7)	2855(5)	5115(4)	62(3)
C(126)	8496(6)	3882(5)	4709(4)	55(3)
C(131)	7770(6)	6224(4)	4006(4)	50(2)
C(132)	8361(8)	6723(5)	4371(4)	69(3)
C(133)	7510(10)	7123(7)	4878(6)	92(5)
C(134)	6087(10)	6996(7)	5041(6)	95(5)
C(135)	5477(9)	6489(7)	4698(7)	99(5)
C(136)	6313(7)	6092(6)	4188(5)	79(4)
N	8269(6)	5959(4)	2549(3)	63(2)
P(2)	8469(2)	6729(1)	1634(1)	50(1)
C(211)	9057(7)	7979(5)	1450(4)	58(3)
C(212)	10298(8)	8465(5)	881(5)	75(3)
C(213)	10736(11)	9406(7)	821(6)	100(5)
C(214)	9947(12)	9835(7)	1313(7)	105(6)
C(215)	8737(10)	9355(7)	1871(6)	90(2)
C(216)	8266(9)	8421(5)	1945(5)	74(4)
C(221)	9677(6)	6314(5)	950(4)	56(3)
C(222)	10583(8)	5589(6)	1245(5)	73(4)
C(223)	11538(8)	5282(7)	723(6)	93(5)
C(224)	11617(8)	5695(7)	-96(7)	92(5)
C(225)	10738(9)	6405(7)	-399(5)	85(4)
C(226)	9746(8)	6720(6)	117(4)	70(3)
C(231)	6816(6)	6781(4)	1378(3)	49(2)
C(232)	6022(7)	5881(5)	1623(4)	60(3)
C(233)	4750(7)	5888(6)	1413(4)	70(3)
C(234)	4279(7)	6786(6)	970(4)	66(3)
C(235)	5049(7)	7670(6)	732(4)	65(3)
C(236)	6316(7)	7680(5)	930(4)	59(3)
Fe(1)	4620(1)	2134(1)	1809(1)	53(1)
C(11)	5546(9)	2813(6)	2187(5)	81(4)
O(11)	6284(9)	3236(5)	2374(5)	136(5)
C(12)	4388(8)	3263(6)	988(5)	74(3)
O(12)	4302(7)	3957(4)	441(3)	105(3)
C(13)	6016(9)	1579(8)	1333(6)	102(6)
O(13)	6985(6)	1445(5)	958(5)	119(4)
C(22)	2853(7)	1633(5)	1617(4)	67(3)
O(22)	2301(5)	1854(4)	1070(3)	73(2)
Fe(2)	3528(2)	349(1)	2374(1)	53(1)
C(21)	1765(10)	-287(6)	2950(6)	93(4)
O(21)	838(6)	-840(5)	3275(4)	93(3)
C(23)	4549(8)	-586(5)	2836(5)	78(4)
O(23)	5008(8)	-1311(4)	3194(5)	123(4)
C(1)	4007(7)	1133(4)	2937(4)	57(3)
C(2)	4655(8)	831(6)	3660(4)	76(4)
C(3)	6192(9)	672(6)	3474(5)	82(4)
C(4)	6795(12)	-66(8)	3935(6)	113(6)
Fe(3)	2225(1)	1635(1)	2830(1)	53(1)
C(31)	525(9)	1704(8)	2571(5)	93(5)
O(31)	-507(7)	1857(8)	2392(5)	150(6)
C(32)	2491(12)	2913(7)	2707(7)	115(6)
O(32)	2375(11)	3624(6)	2767(6)	178(6)

Table 5

Atom	X	Y	Z	U_{eq}
C(33)	1568(8)	1058(6)	3892(4)	74(3)
O(33)	1217(8)	794(7)	4588(4)	130(4)
O(24)	4043(9)	−121(5)	903(4)	124(4)
C(24)	3892(10)	83(6)	1452(5)	87(4)
Fe(1B)	3963(4)	2405(3)	2093(2)	53(1)
Fe(3B)	1953(3)	1057(3)	2882(2)	53(1)
Fe(2B)	4210(4)	665(3)	2064(2)	53(1)

Table 6

Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal coefficients ($pm^2 \times 10^{-1}$) for **6**

Atom	X	Y	Z	U_{eq}
Au	2101(1)	926(1)	2782(1)	39(1)
P	3888(1)	−819(1)	2776(1)	39(1)
C(111)	5428(4)	−688(3)	2269(3)	43(1)
C(112)	5449(5)	19(4)	1390(3)	65(2)
C(113)	6612(6)	130(5)	1001(4)	80(3)
C(114)	7761(5)	−453(5)	1475(4)	75(3)
C(115)	7745(5)	−1155(5)	2355(4)	75(3)
C(116)	6600(4)	−1286(4)	2749(3)	60(2)
C(121)	3694(4)	−1773(3)	2054(3)	48(2)
C(122)	2494(5)	−1878(5)	2183(4)	74(3)
C(123)	2294(7)	−2614(6)	1649(5)	99(4)
C(124)	3306(9)	−3219(5)	987(5)	96(4)
C(125)	4471(7)	−3092(5)	841(4)	90(3)
C(126)	4697(5)	−2386(4)	1370(3)	65(2)
C(131)	4223(4)	−1637(3)	4012(3)	42(1)
C(132)	4782(4)	−2837(4)	4150(3)	57(2)
C(133)	5094(5)	−3429(4)	5084(3)	70(2)
C(134)	4841(5)	−2830(4)	5881(3)	62(2)
C(135)	4275(5)	−1659(5)	5749(3)	69(2)
C(136)	3967(4)	−1039(4)	4819(3)	57(2)
Co(1)	1504(1)	3255(1)	3114(1)	46(1)
C(11)	3064(4)	2853(4)	2400(3)	61(2)
O(11)	4041(4)	2648(4)	1914(3)	97(2)
C(12)	2008(5)	2453(4)	4310(3)	59(2)
O(12)	2286(4)	1953(3)	5065(2)	85(2)
C(13)	1572(5)	4581(4)	3362(3)	64(2)
O(13)	1650(5)	5368(3)	3548(3)	100(3)
Fe(3)	−1038(1)	3683(1)	3375(1)	41(1)
C(21)	−1136(5)	4963(4)	3777(3)	68(2)
O(21)	−1313(5)	5802(3)	4068(3)	101(2)
C(22)	−1188(5)	2873(4)	4567(3)	67(2)
O(22)	−1274(5)	2357(4)	5305(3)	113(3)
C(23)	−2726(4)	4325(4)	3046(3)	53(2)
O(23)	−3804(3)	4784(3)	2855(3)	77(2)
Fe(1)	22(1)	3814(1)	1628(1)	37(1)
C(31)	1326(5)	3155(4)	696(3)	55(2)
O(31)	2150(4)	2728(4)	126(3)	84(2)
C(32)	108(5)	5186(4)	1589(3)	56(2)
O(32)	102(5)	6080(3)	1516(3)	85(2)
C(33)	−1407(4)	4326(4)	932(3)	52(2)
O(33)	−2287(4)	4710(3)	452(3)	79(2)
Fe(2)	−584(1)	2023(1)	2308(1)	40(1)
C(41)	−719(4)	905(4)	3248(3)	56(2)
O(41)	−793(4)	189(3)	3844(3)	89(2)
C(42)	194(4)	1143(4)	1330(3)	57(2)
O(42)	627(4)	593(4)	704(3)	91(2)
C(43)	−2244(4)	2491(4)	1905(3)	54(2)
O(43)	−3265(3)	2766(3)	1645(3)	77(2)
C(1)	528(3)	2557(3)	2731(2)	37(1)

ond, red fraction yielded 10 mg (6%) of **6**, red crystals, m.p. 225°C (decomp.). Anal. Found: C, 37.52; H, 2.04; Fe, 15.8. $C_{31}H_{15}AuCoFe_3O_{12}P$ (1033.9) calc.: C, 36.01; H, 1.46; Fe, 16.2%.

4.2. Structure determinations [17]

The crystallographic details are listed in Table 4. The data were obtained with a Nonius CAD 4 diffractometer using Mo $K\alpha$ radiation and the $\omega/2\theta$ technique. The structures were solved with Patterson techniques and refined anisotropically for all non-hydrogen atoms. All calculations were done with the SHELX program system [18]. Absorption corrections were based on psi-scans. Phenyl rings were treated as rigid bodies, and all hydrogen atoms were included with a common isotropic temperature factor and a fixed C–H distance of 0.96 Å. The structure of **4** did not refine well despite attempts to handle disorder problems by inclusion of a second set of iron atoms with a weight of 25%. Tables 5 and 6 list the atomic coordinates. The drawings were produced with the SCHAKAL program [19].

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[17] Further details of the structure determination may be obtained upon request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-76344 Eggenstein-Leopolshafen, refering to the depository numbers CSD 380022 (for 4) and CSD 380023 (for 6) and citing the authors and this paper.

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