



Phosphine-gold(I) derivatives of 1,1'-bis(alkynyl)metallocenes: Molecular structures of $\text{Fc}'(\text{C}\equiv\text{CX})_2$ [$\text{X} = \text{Au}(\text{PPh}_3)$, SiMe_3] and $\text{Au}_4\{(\text{C}\equiv\text{C})_2\text{Fc}'\}_2(\text{PPh}_3)_2$ [$\text{Fc}' = \text{Fe}(\eta\text{-C}_5\text{H}_4\text{-})_2$]

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ABSTRACT

Desilylation of $\text{Fc}'(\text{C}\equiv\text{CSiMe}_3)_2$ [$\mathbf{1}$; $\text{Fc}' = \text{Fe}(\eta\text{-C}_5\text{H}_4\text{-})_2$] with LiMe or KOH/MeOH, followed by addition of $\text{AuCl}(\text{PR}_3)$, afforded $\text{Fc}'\{\text{C}\equiv\text{CAu}(\text{PR}_3)\}_2$ [$\text{R} = \text{Ph}$ $\mathbf{2a}$, tol $\mathbf{2b}$]; the Ru analogue of $\mathbf{2a}$ was also prepared. The XRD structures of $\mathbf{1}$ and $\mathbf{2a}$ are reported. In the presence of CuI, a similar reaction over 2 h afforded the Au_4 cluster $\text{Au}_4\{(\text{C}\equiv\text{C})_2\text{Fc}'\}_2(\text{PPh}_3)_2$ $\mathbf{3}$. The X-ray determined structure of $\mathbf{3}$ showed a planar centrosymmetric Au_4 rhomb, two opposed Au atoms being σ -bonded to the $\text{C}\equiv\text{C}$ group, while the other two Au atoms are each η^2 -bonded to the $\text{C}\equiv\text{C}$ group and a PPh_3 ligand.

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1. Introduction

1,1'-Bis(ethynyl)ferrocene, $\text{Fc}'(\text{C}\equiv\text{CH})_2$ [$\text{Fc}' = \text{Fe}(\eta\text{-C}_5\text{H}_4\text{-})_2$] is an unstable molecule, being readily oxidised or converted to cyclic ferrocenophanes in the presence of air, water or alcohols. However, the corresponding SiMe_3 $\mathbf{1}$ or SnMe_3 derivatives are stable [1]. While these properties have limited the application of this diyne as a ligand, the literature contains accounts of complexes derived from $\text{Co}_2(\text{CO})_8$ [1], $\text{Ru}_3(\text{CO})_{12}$ [2], $\text{Os}_3(\text{CO})_{12}$ [3], $\text{PtCl}_2\text{Ph}(\text{PR}_3)_2$ and related oligomeric materials [4]. The ruthenium–vinylidene complex $\{\text{Fc}'[\text{C}(\text{SiMe}_3)=\text{C}=\text{C}]\}_2\text{RuCl}_2(\text{PPr}^i_3)_2$ is also known [5]. In seeking to extend this chemistry, we have made phosphine-gold(I) derivatives of 1,1'-bis(ethynyl)-ferrocene and -ruthenocene and have found that formation of a related derivative containing an Au_4 cluster bridging two bis(ethynyl)ferrocene moieties may also occur. This work is described below.

2. Results and discussion

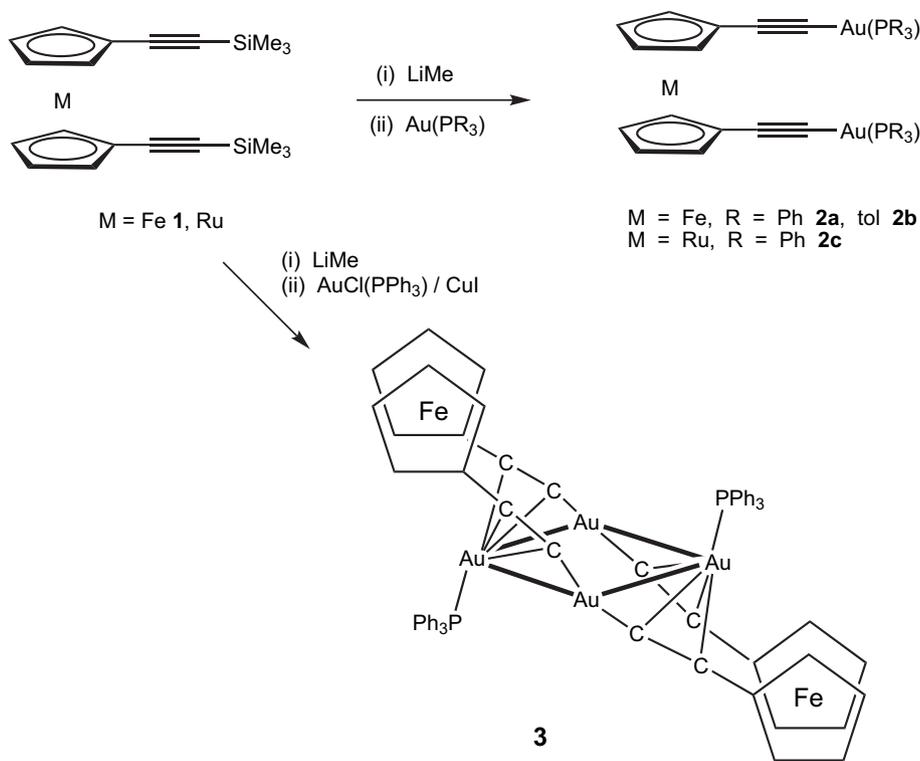
Desilylation of $\text{Mc}'(\text{C}\equiv\text{CSiMe}_3)_2$ [$\text{Mc}' = \text{M}(\eta\text{-C}_5\text{H}_4\text{-})_2$, $\text{M} = \text{Fe}$ $\mathbf{1}$, Ru] with LiMe followed by addition of two equivalents of $\text{AuCl}(\text{PR}_3)$

afforded the expected aurated products $\text{Mc}'\{\text{C}\equiv\text{CAu}(\text{PR}_3)\}_2$ ($\text{Mc}' = \text{Fc}'$, $\text{R} = \text{Ph}$ $\mathbf{2a}$ 75%, tol $\mathbf{2b}$ 70%; $\text{M} = \text{Rc}'$, $\text{R} = \text{Ph}$ $\mathbf{2c}$ 64%) as orange or light yellow solids, respectively (Scheme 1). These compounds were characterised by elemental analyses and from their mass spectra, which contained $[\text{M} + \text{H}]^+$ at m/z 1151, 1235 and 1197, respectively. Their IR spectra contain very weak $\nu(\text{C}\equiv\text{C})$ bands between 2102 and 2125 cm^{-1} , while the ^1H and ^{13}C NMR spectra contain resonances characteristic of the C_5H_4 and R groups respectively. We found only resonances for the C(sp) attached to the C_5 ring at δ 101.05 ($\mathbf{2a}$) and 99.85 ($\mathbf{2c}$). In the ^{31}P spectrum, the PPh_3 resonances occurred at δ 43.3, 41.6 and 42.85, respectively.

The molecular structures of $\text{Fc}'(\text{C}\equiv\text{CX})_2$ [$\text{X} = \text{SiMe}_3$ $\mathbf{1}$, $\text{Au}(\text{PPh}_3)$ $\mathbf{2a}$,] have been determined from single-crystal XRD studies. Fig. 1 contains plots of molecule $\mathbf{1}$ of the silane $\mathbf{1}$ (upper) and one centrosymmetric molecule of $\mathbf{2a}$ (lower), with significant bond parameters being presented in the caption. The central ferrocene-1,1'-diyl fragment of $\mathbf{2a}$ carries a $\text{C}\equiv\text{CAu}(\text{PPh}_3)$ substituent on each ring, disposed in a *trans* arrangement. The bond lengths fall in the expected ranges for Au–P, Au–C(sp) single and $\text{C}\equiv\text{C}$ triple bonds; average C–C bonds within the C_5 rings [1.42(1) Å] and Fe–C bonds to these rings [2.04(2) Å] do not deserve comment, with the exception of Fe–C(3) (bearing the alkynyl substituent) which is the longest separation at 2.065(11) Å. The P(1)–Au–C(1)–C(2)–C(3) sequence shows the usual small deviations from linearity [2.6, 7.4, 6.3°] probably induced by “crystal packing forces”. The common

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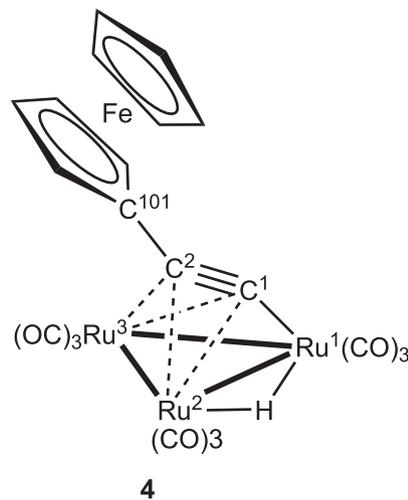
Scheme 1.

geometries of **1** and **2a** are closely similar, the former containing two molecules in the unit cell, each of which has independent $C_5H_4C\equiv CSiMe_3$ ligands on the central Fe atom.

On a few occasions, similar reactions between **1**, LiMe and AuCl(PPh₃), carried out in thf in the presence of CuI, afforded a different orange product, formulated as Au₄{Fc'(C≡C)₂}₂(PPh₃)₂ **3** from a single-crystal X-ray structure determination. A molecule of **3** is shown in Fig. 2, selected bond parameters being collected in the caption. The molecule contains two Fc'(C≡C)₂ moieties linked by an Au₄(PPh₃)₂ cluster. The central Au₄ cluster forms a centrosymmetric planar rhombus [Au(1)–Au(2, 2') 3.0029(6), 3.2956(6) Å], of which Au(1) is two-coordinate, being σ-bonded to two alkynyl groups [Au(1)–C(1,3') 1.984(10), 1.975(12) Å], while Au(2) is π-bonded to the two C≡C triple bonds [Au(2)–C(1,2) 2.208(9), 2.376(10) Å] and also carries a PPh₃ ligand [Au(2)–P 2.238(2) Å]. The ferrocene-1,1'-diyl nucleus serves to hold the C₂ groups apart, controlling the interaction with Au(2) [Au(2)⋯C(3,4) 2.986(10), 3.360(12) Å]. Au(1) is coplanar with C(1–4) [χ^2 891; δ (Au) 0.003(1) Å].

The C(1)–C(2), C(3)–C(4) separations are 1.236(14), 1.212(15) Å, slightly elongated from the normal C(sp)–C(sp) bond length and consistent with a small lowering of bond order as a result of π-bonding to the Au atoms. There is only a slight deviation from linearity along the C(201)–C(2)–C(1)–Au(1)–C(3') and C(401)–C(4)–C(3)–Au(1)–C(1') arrays [angles at individual atoms range between 170.3(1) and 176.2(4)°]. These parameters are similar to those found in the gold(I) alkynylcalix[4]crown-6 complex described by Yam and coworkers [6] [cf. values for Au(1)⋯Au(2) 3.1344(8), 3.2048(8) Å]. The central structure is also related to that found in Ag₂Au₂(C≡CPh)₄(PPh₃)₂, obtained from the reaction between Au(C≡CPh)(PPh₃) and {Ag(C≡CPh)}_n [7]. As is evident from the Figure, one of the phenyl rings projects over the central plane, with H⋯Au(1,1',2) distances 3.0₂, 3.2₃, 2.8₇ Å]. It is also of interest to compare the coordination of the alkynyl groups of **3**

with that in Ru₃(μ-H)(μ₃-CCFc)(CO)₉ **4** [8]. Of note in **4** is the considerably longer coordinated C≡C triple bond [1.30(1) Å in **4**, vs 1.236(14) Å in **3**] and the larger departure from linearity of the C(Fc)–C(2)–C(1)–Ru fragment, which has angles at C(1) and C(2) of 152.5(7) and 143.6(8)° [cf. 172.6(9) and 170.5(10)° in **3**]. These differences demonstrate the much greater back-bonding from the Ru₃ cluster to the alkynyl unit compared with that from the gold centres.

Ru₃(μ-H)(μ₃-CCFc)(CO)₉ **4**.

In conclusion, while the ferrocene-1,1'-bis(alkynyl) derivatives with SiMe₃ (**1**) or Au(PR₃) (**2**) substituents are stable [in contrast to Fc'(C≡CH)₂], loss of PPh₃ may occur during the preparation of **2a** in the presence of CuI (which acts as a PPh₃-abstractor) followed by dimerisation to give the Au₄ cluster **3**.

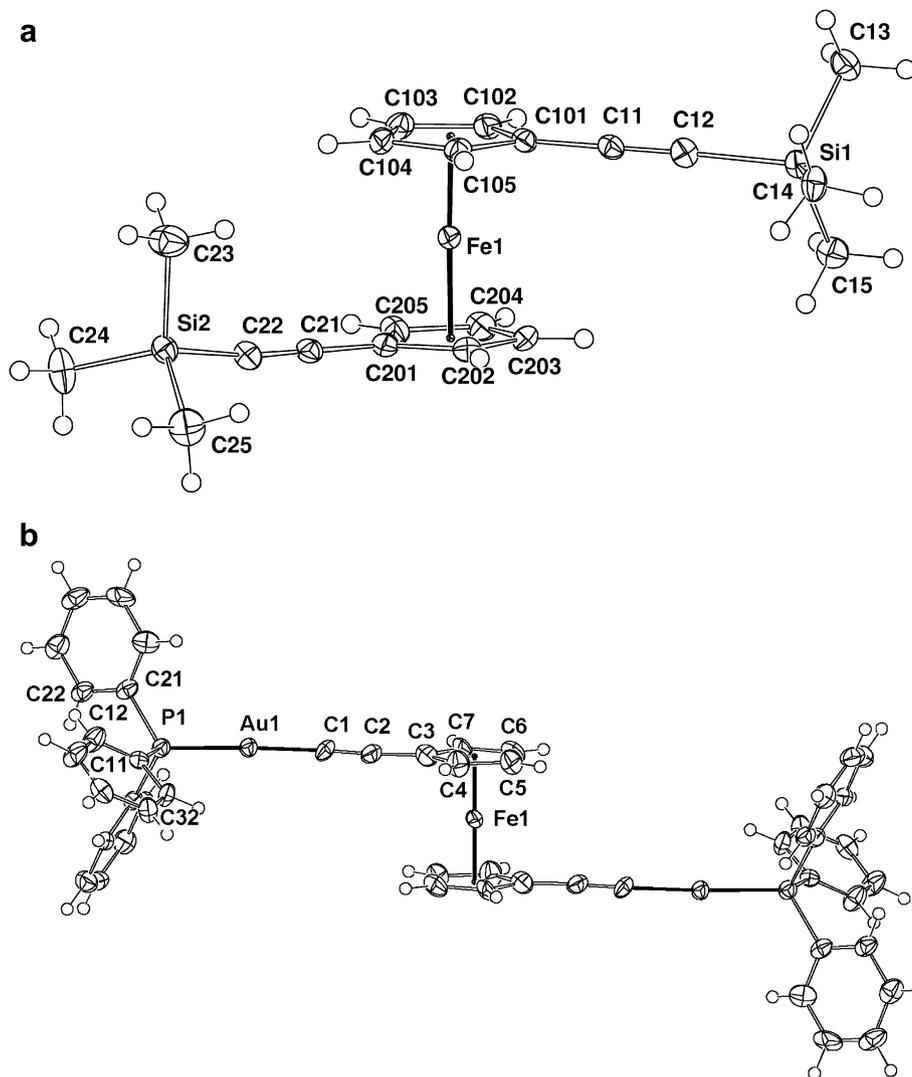


Fig. 1. Plots of (a) molecule 1 of $\text{Fc}'(\text{C}\equiv\text{CSiMe}_3)_2$ **1**. Selected bond parameters: distances (Å), mean values: $\text{C}(\text{cp})-\text{C}(\text{alkyne})$ 1.434(4), $\text{C}\equiv\text{C}-\text{Si}$ 1.204(2), $\text{C}(\text{alkyne})-\text{Si}$ 1.844(4); angles ($^\circ$) (ranges): $\text{C}(\text{cp})-\text{C}\equiv\text{C}$ 177.20(4), $\text{C}\equiv\text{C}-\text{Si}$ 168.63(3)–177.37(3); (b) a molecule of $\text{Fc}'\{\text{C}\equiv\text{CAu}(\text{PPh}_3)\}_2$ **2a**. Selected bond parameters: $\text{Au}-\text{P}(1)$ 2.269(3), $\text{Au}-\text{C}(1)$ 1.994(10), $\text{C}(1)-\text{C}(2)$ 1.20(1), $\text{C}(2)-\text{C}(3)$ 1.44(2) Å, $\text{P}(1)-\text{Au}-\text{C}(1)$ 177.4(3), $\text{Au}-\text{C}(1)-\text{C}(2)$ 172.9(10), $\text{C}(1)-\text{C}(2)-\text{C}(3)$ 173.7(13) $^\circ$.

3. Experimental

3.1. General

All reactions were carried out under dry nitrogen, although normally no special precautions to exclude air were taken during subsequent work-up. Common solvents were dried, distilled under argon and degassed before use. Separations were carried out by preparative thin-layer chromatography on glass plates ($20 \times 20 \text{ cm}^2$) coated with silica gel (Merck, 0.5 mm thick).

3.2. Instruments

IR spectra: Bruker IFS28 FT-IR spectrometer. Nujol mull spectra were obtained from samples mounted between NaCl discs. NMR spectra: Varian 2000 instrument (^1H at 300.13 MHz, ^{13}C at 75.47 MHz, ^{31}P at 121.503 MHz). Samples were dissolved in C_6D_6 contained in 5 mm sample tubes. Chemical shifts are given in ppm relative to internal tetramethylsilane for ^1H and ^{13}C NMR spectra and external H_3PO_4 for ^{31}P NMR spectra.

Electrospray mass spectra (ES MS): Fisons Platform II spectrometer. Solutions in MeOH were injected via a 10 ml injection loop. Nitrogen was used as the drying and nebulising gas. Chemical aids to ionisation were used as required [9]. Elemental analyses were by CMAS, Belmont, Victoria, Australia, and Campbell Microanalytical Laboratory, University of Otago, Dunedin, New Zealand.

3.3. Reagents

$\text{AuCl}(\text{PR}_3)$ (R = Ph, tol) [10], $\text{Fc}'\text{-}1,1'\text{-(C}\equiv\text{CSiMe}_3)_2$ **1** [1] and $\text{Rc}'\text{-}1,1'\text{-(C}\equiv\text{CSiMe}_3)_2$ [11] were made by the cited procedures.

3.3.1. $\text{Fc}'\text{-}1,1'\text{-}\{\text{C}\equiv\text{CAu}(\text{PPh}_3)\}_2$ **2a**

LiMe (0.30 ml, 1.5 M in Et_2O , 0.45 mmol) was added to a solution of $\text{Fc}'\text{-}1,1'\text{-(C}\equiv\text{CSiMe}_3)_2$ (40 mg, 0.11 mmol) in dry thf (25 ml) and the mixture was stirred for 20 h at r.t. Solid $\text{AuCl}(\text{PPh}_3)$ (155 mg, 0.313 mmol) was then added and the mixture stirred for a further 10 min. After removal of solvent under vacuum, the residue was washed several times with Et_2O and then extracted into benzene.

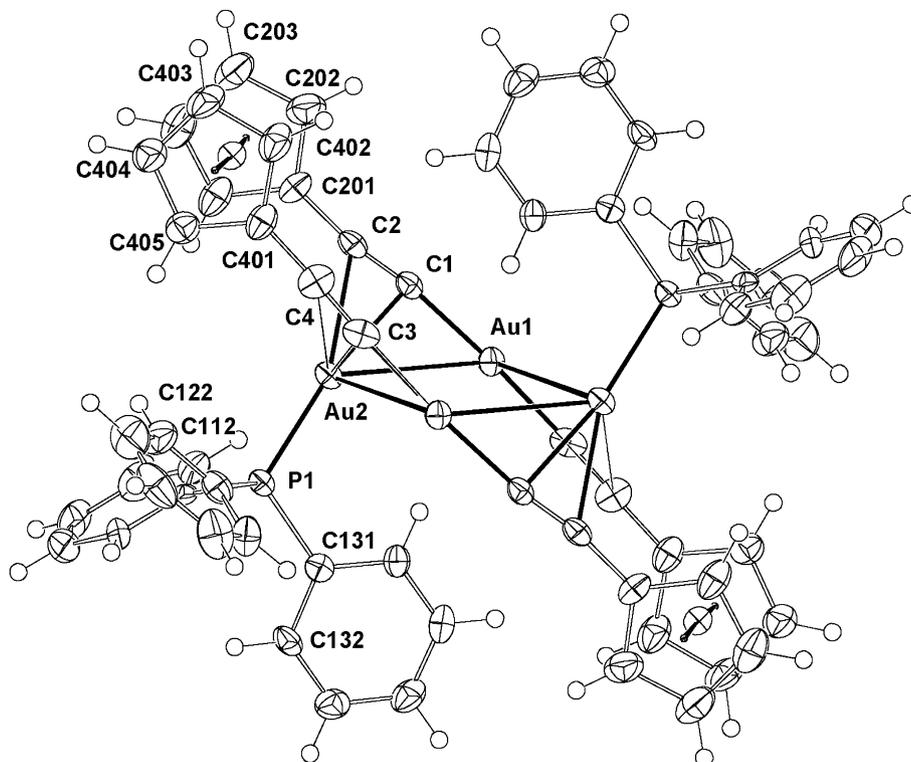


Fig. 2. Plot of a molecule of $[\text{Fc}'(\text{C}\equiv\text{C})_2\text{Au}_4(\text{PPh}_3)_2]$ **3**. Selected distances: $\text{Au}(1)\cdots\text{Au}(2,2')$ 3.0029(6), 3.2956(6), $\text{Au}(2)-\text{P}(1)$ 2.238(2), $\text{Au}(1)-\text{C}(1,3')$ 1.984(10), 1.975(12), $\text{Au}(2)-\text{C}(1)$ 2.208(9), $\text{Au}(2)-\text{C}(2)$ 2.376(10), $\text{C}(1)-\text{C}(2)$ 1.236(14), $\text{C}(3)-\text{C}(4)$ 1.212(15), $\text{C}(2)-\text{C}(201)$ 1.419(14), $\text{C}(4)-\text{C}(401)$ 1.419(15) Å. $\text{Au}(2)-\text{Au}(1)-\text{Au}(2')$ 107.31(1), $\text{Au}(1)-\text{Au}(2)-\text{Au}(1')$ 72.69(1), $\text{Au}(1')-\text{Au}(2)-\text{P}(1)$ 91.32(6), $\text{Au}(1)-\text{Au}(2)-\text{P}(1)$ 127.48(7), $\text{C}(1)-\text{Au}(1)-\text{C}(3')$ 176.2(4), $\text{Au}(1)-\text{C}(1)-\text{C}(2)$ 173.0(8), $\text{C}(1)-\text{C}(2)-\text{C}(201)$ 170.3(10) $^\circ$.

The filtered solution was reduced in volume and crystallisation was induced by addition of a small amount of hexane to give $\text{Fc}'\text{-}1,1'\text{-}\{\text{C}\equiv\text{CAu}(\text{PPh}_3)_2\}$ **2a** as an orange solid (95 mg, 75%). Anal. Found: C, 52.28; H, 3.35. Calcd ($\text{C}_{50}\text{H}_{38}\text{Au}_2\text{FeP}_2$): C, 52.20; H, 3.33; M, 1150. IR (nujol, cm^{-1}): 2101w, 2052w, 1914w [$\nu(\text{C}\equiv\text{C})$], 1603w, 1584w. ^1H NMR (C_6D_6): δ 4.28–4.29, 4.76–4.77 (2 \times m, 2 \times 4H, C_5H_4), 6.88–6.93, 6.99–7.04, 7.19–7.25 (3 \times m, 13 + 6 + 11H, Ph). ^{13}C NMR (C_6D_6): δ 70.57 (C_{ipso} of Fc), 72.19, 73.72 (C_5H_4), 101.05 (br, Fc– $\text{C}\equiv\text{C}$), 128.92, 129.50, 129.65, 130.54, 131.27, 131.66–131.67 (m), 134.73, 134.91 (Ph). ^{31}P NMR (C_6D_6): δ 43.3. HR-MS [found (calcd)]: $[\text{M} + \text{Na}]^+$ 1173.111 (1173.102); $[\text{M} + \text{H}]^+$ 1151.128 (1151.120).

3.3.2. $\text{Fc}'\text{-}1,1'\text{-}\{\text{C}\equiv\text{CAu}[\text{P}(\text{tol})_3]\}_2$ **2b**

A solution of KOH (100 mg in 5 ml MeOH, 2.78 mmol) was added to a stirred suspension of $\text{AuCl}[\text{P}(\text{tol})_3]$ (217 mg, 0.40 mmol) and $\text{Fc}'(\text{C}\equiv\text{CSiMe}_3)_2$ (70 mg, 0.19 mmol) in dry MeOH (20 ml) and the mixture was stirred for 1 h in an ice-bath. The resulting orange precipitate was collected and washed with cold MeOH to give $\text{Fc}'\text{-}1,1'\text{-}\{\text{C}\equiv\text{CAu}[\text{P}(\text{tol})_3]\}_2$ **2b** (163 mg, 70%) as an orange powder. Anal. Calcd ($\text{C}_{56}\text{H}_{50}\text{Au}_2\text{FeP}_2$): C, 54.47; H, 4.08; M, 1234. Found: C, 52.52; H, 3.97. IR (Nujol, cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2101w, 2025w, 1914w; 1597s, 1563w. ^1H NMR (C_6D_6): δ 1.93 (s, 18H, Me), 4.31–4.33 (m, 4H, C_5H_4), 4.79–4.81 (m, 4H, C_5H_4), 6.78–6.82 (m, 12H, C_6H_4), 7.27–7.38 (m, 12H, C_6H_4). ^{31}P NMR: δ 41.6. ES-MS/ m/z : 1235, $[\text{M} + \text{H}]^+$. HR-MS [found (calcd)]: $[\text{M} + \text{Na}]^+$ 1257.196 (1257.196); $[\text{M} + \text{H}]^+$ 1235.215 (1235.214).

3.3.3. $\text{Rc}'\text{-}1,1'\text{-}\{\text{C}\equiv\text{CAu}(\text{PPh}_3)_2\}$ **2c**

Similarly, LiMe (0.30 ml, 1.5 M in Et_2O , 0.45 mmol) was added to a solution of $\text{Rc}'\text{-}1,1'\text{-}\{\text{C}\equiv\text{CSiMe}_3\}_2$ (46 mg, 0.11 mmol) in dry thf (20 ml) and the mixture was stirred for 20 h at r.t. Solid $\text{AuCl}(\text{PPh}_3)$ (157 mg, 0.317 mmol) was then added and the mixture stirred for a further 10 min. After removal of solvent under vacuum, the

residue was washed several times with Et_2O and then dissolved in benzene. The filtered solution was evaporated to give $\text{Rc}'\text{-}1,1'\text{-}\{\text{C}\equiv\text{CAu}(\text{PPh}_3)_2\}$ **2c** as a light yellow solid (82 mg, 64%). Anal. Calcd ($\text{C}_{50}\text{H}_{38}\text{Au}_2\text{Ru.C}_6\text{H}_6$): C, 52.80; H, 3.48; M, 1196. Found: C, 52.40; H, 3.54. IR (nujol, cm^{-1}): 2125w [$\nu(\text{C}\equiv\text{C})$], 1584w. ^1H NMR (C_6D_6): δ 4.58–4.59, 5.20–5.21 (2 \times m, 2 \times 4H, C_5H_4), 6.88–6.94, 7.00–7.04, 7.17–7.24 (3 \times m, 13 + 6 + 11H, Ph). ^{13}C NMR (C_6D_6): δ 73.27, 75.96 (C_5H_4), 73.98 (C_{ipso}), 99.85 (br, $\text{Rc}-\text{C}\equiv\text{C}$), 128.92, 129.44–129.59, 130.53, 131.25, 131.60, 134.72–134.90 (Ph). ^{31}P NMR (C_6D_6): δ 42.9. HR-MS [found (calcd)]: $[\text{M} + \text{Au}]^+$ 1393.050 (1393.050); $[\text{M} + \text{H}]^+$ 1197.090 (1197.090); $[\text{Au}(\text{PPh}_3)_2]^+$ 721.154 (721.148).

3.3.4. $\text{Au}_4\{(\text{C}\equiv\text{C})_2\text{Fc}'\}_2(\text{PPh}_3)_2$ **3**

LiMe (0.30 ml, 1.5 M in Et_2O , 0.45 mmol) was added to a solution of $\text{Fc}'\text{-}1,1'\text{-}\{\text{C}\equiv\text{CSiMe}_3\}_2$ (40 mg, 0.11 mmol) in dry thf (10 ml) and the mixture was stirred for 20 h at r.t. A solution of $\text{AuCl}(\text{PPh}_3)$ (153 mg, 0.309 mmol) and CuI (7 mg, 0.037 mmol) in thf (20 ml) was added and the mixture was stirred for 2 h. After removal of solvent, the residue was extracted into C_6H_6 and purified by chromatography (neutral alumina, benzene). The orange band was collected and crystallised (Et_2O /hexane) to give $\text{Au}_4\{(\text{C}\equiv\text{C})_2\text{Fc}'\}_2(\text{PPh}_3)_2$ **3** as an orange solid (55 mg, 56%). Calcd ($\text{C}_{64}\text{H}_{46}\text{Au}_4\text{Fe}_2\text{P}_2$): C, 43.27; H, 2.61; M, 1776. Found: C, 46.19; H, 3.00 [satisfactory analyses could not be obtained]. IR (nujol, cm^{-1}): 2125w [$\nu(\text{C}\equiv\text{C})$], 1653w (br), 1100s. ^1H NMR (C_6D_6): δ 4.31–4.33, 4.79–4.81 (2 \times m, 2 \times 8H, C_5H_4), 6.78–6.82, 7.27–7.38 (2 \times m, 15 + 15H, Ph). ^{31}P NMR (C_6D_6): δ 48.1. EI-MS (MeCN, m/z): 857, $[\text{M} - 2\text{Au}(\text{PPh}_3)]^+$; 721, $[\text{Au}(\text{PPh}_3)_2]^+$; 575, $[\text{M} - 2\text{Au}]^{2+}$. X-ray quality crystals were obtained from benzene/ MeOH .

This compound was not formed in the reaction of $\text{Fc}'\text{-}\{\text{C}\equiv\text{CAu}(\text{PPh}_3)_2\}$ with CuI in Et_2O as a potential PPh_3 -abstraction agent. Further attempts to obtain the Au_4 cluster resulted in the formation

Table 1
Crystal data and refinement details.

	1	2a	3
Formula	C ₂₀ H ₂₆ FeSi ₂	C ₅₀ H ₃₈ Au ₂ FeP ₂	C ₆₄ H ₄₆ Au ₄ Fe ₂ P ₂
MW	378.44	1150.5	1776.5
Crystal	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>
<i>a</i> /Å	9.192(2)	6.960(5)	14.242(2)
<i>b</i> /Å	14.196(3)	20.895(5)	12.156(1)
<i>c</i> /Å	16.845(3)	14.365(5)	15.550(2)
α /°	70.92(2)	90	90
β /°	89.49(1)	94.731(5)	109.436(3)
γ /°	82.87(2)	90	90
<i>V</i> /Å ³	2060.1	2082.0	2539
ρ_c /g cm ⁻³	1.220	1.835	2.324
<i>Z</i>	4	2	2
$2\theta_{\max}$ /°	69	62	60
μ /mm ⁻¹	0.85	7.5	12.2
<i>T</i> _{min} / <i>T</i> _{max}	0.81	0.84	0.47
Crystal/mm ³	0.31 × 0.30 × 0.08	0.16 × 0.15 × 0.02	0.11 × 0.09 × 0.04
<i>N</i> _{tot}	40 612	21 453	39 203
<i>N</i> (<i>R</i> _{int})	16 459 (0.032)	6105 (0.110)	7366 (0.084)
<i>N</i> _o	9795	4248	4974
<i>R</i> 1 (<i>I</i> > 2σ(<i>I</i>))	0.038	0.063	0.052
<i>wR</i> 2 (all data)	0.098	0.17	0.15
<i>T</i> /K	100	100	150

of an insoluble polymeric material either as described above, or by treating the bis compound with CuI, as already described for the Ag₂Au₂ cluster [7].

3.4. Structure determinations

Diffraction data were measured using a CCD area-detector instrument using monochromatic Mo-*K*α radiation, λ = 0.71073 Å. *N*_{tot} reflections were merged to *N* unique (*R*_{int} cited) after multi-scan absorption correction (proprietary software), *N*_o with *I* > 2σ(*I*); all data were used in the full matrix least squares refinements on *F*². Anisotropic displacement parameter forms were refined for the non-hydrogen atoms, hydrogen atom treatment following a riding model. Residuals at convergence *R*1, *wR*2 are given. Neutral atom complex scattering factors were used; computation used the

SHELXL 97 program [12]. Pertinent results are given in Table 1 and the Figures (which show non-hydrogen atoms with 50% probability amplitude displacement ellipsoids and hydrogen atoms with arbitrary radii of 0.1 Å) and in the captions thereto.

Acknowledgements

We thank Professor Brian Nicholson (University of Waikato, Hamilton, New Zealand) for providing the mass spectra and the ARC for support of this work.

Appendix. Supplementary material

Full details of the structure determinations (except structure factors) have been deposited with the Cambridge Crystallographic Data Centre as CCDC 769762 (**1**), 765 979 (**2a**), 735 019 (**3**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or [www: http://www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk)).

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