

Use of phosphine gold acetylides $[(R_3P)AuC\equiv CR]$ to form phosphine gold derivatives of tetra-iron and penta-iron clusters

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Abstract

Five new gold acetylides, $[AuC\equiv CR]$, with hydroxyl or amino functions in the organic radical R have been prepared. From these, nine phosphine complexes $[(R_3P)AuC\equiv CR]$ with R = Ph or Cy were synthesised. Reactions between the phosphine gold acetylides $[(Ph_3P)AuC\equiv CC(Me)(OH)Et]$ or $[(Cy_3P)AuC\equiv CC(Me)(OH)Et]$ and the iron carbonyl cluster $[Et_4N][Fe_4N(CO)_{12}]$ gave both neutral $[(R_3P)AuFe_4N(CO)_{12}]$ and ionic compounds $[(R_3P)_2Au][Fe_4N(CO)_{12}]$. Reaction with the penta-iron cluster $[Et_4N][Fe_5N(CO)_{14}]$ afforded $[(R_3P)_2Au][Fe_5N(CO)_{14}]$, $[(R_3P)_2Au][Fe_4N(CO)_{12}]$ and $[(R_3P)AuFe_4N(CO)_{12}]$. The gold–iron clusters were characterised with spectroscopic methods (IR, NMR and Mössbauer) and in the case of $[(Cy_3P)AuFe_4N(CO)_{12}]$ a single-crystal X-ray analysis.

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1. Introduction

The most common precursor used to form gold-containing iron carbonyl clusters is $[(R_3P)AuCl]$ [1] and the clusters formed usually incorporate the $\{Ph_3PAu\}$ group. A notable feature in the structural chemistry of the gold-containing clusters which has been commented on by Hoffmann [2] and a number of other authors is the isolobal nature of the proton and $\{Ph_3PAu\}^+$ species which often leads to observed structural similarities in compounds which differ only in the replacement of a

proton by the $\{Ph_3PAu\}^+$ group. In the present work it was decided to synthesise some phosphine gold acetylides as alternative precursors for the formation of $\{R_3PAu\}$ -containing clusters. The present work initially describes the synthesis of new gold acetylides, $[AuC\equiv CR]$, with the R groups containing either a hydroxy or amino function. Phosphine derivatives of these compounds were synthesised and the reactions between two of the compounds, $[(R_3P)AuC\equiv CC(Me)(OH)Et]$ where R = Ph and Cy, with the tetra- and penta-iron carbonyl clusters $[Et_4N][Fe_4N(CO)_{12}]$ and $[Et_4N][Fe_5N(CO)_{14}]$ were investigated. The gold acetylides and their phosphine derivatives were characterised by elemental analyses, melting points and IR spectroscopy and the gold–iron clusters were also characterised with ¹³C NMR and Mössbauer spectroscopies. In the case of

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$[(\text{Cy}_3\text{P})\text{AuFe}_4\text{N}(\text{CO})_{12}]$ a single-crystal X-ray structure analysis was carried out.

2. Results and discussion

2.1. Synthesis of gold acetylides and their phosphine derivatives

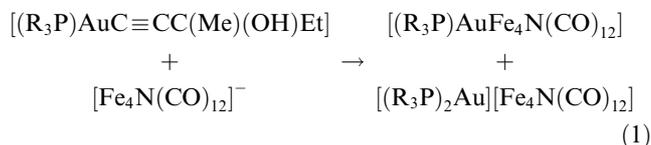
Two gold acetylides had been previously prepared, i.e. $[\text{AuC}\equiv\text{CC}(\text{Me})(\text{OH})\text{Et}]$ (**1**) and $[\text{AuC}\equiv\text{CC}(\text{Me})(\text{OH})\text{Ph}]$ (**2**) and their Ph_3P derivatives synthesised [3]. The synthetic method used to prepare five new compounds, i.e. $[\text{AuC}\equiv\text{CC}(\text{Me})_2\text{NH}_2]$ (**7**, 63%), $[\text{AuC}\equiv\text{C}-\text{C}(\text{Me})(\text{OH})\text{CH}_2\text{CH}(\text{Me})_2]$ (**5**, 75%), $[\text{AuC}\equiv\text{CC}(\text{H})(\text{OH})\text{Et}]$ (**3**, 92%), $[\text{AuC}\equiv\text{CC}(\text{H})(\text{OH})(\text{CH}_2)_4\text{Me}]$ (**4**, 80%) and $[\text{AuC}\equiv\text{CCH}_2\text{Optm}]$ (ptm = phthalimide, **6**, 26%) was based on a literature procedure [4].

Generally, phosphine derivatives of the parent gold acetylides were prepared from the reaction between a suspension of the gold acetylide in toluene and a solution of the ligand in toluene. After stirring the reaction mixture at room temperature for 5 min, it was filtered and the solvent removed under reduced pressure to afford samples of the product, $[\text{LAuC}\equiv\text{CR}]$.

2.2. Reactions between phosphine gold acetylides $[(\text{Ph}_3\text{P})\text{AuCCC}(\text{Me})(\text{OH})\text{Et}]$ (**8**) or $[(\text{Cy}_3\text{P})\text{AuCCC}(\text{Me})(\text{OH})\text{Et}]$ (**15**) and the iron carbonyl clusters $[\text{Et}_4\text{N}][\text{Fe}_4\text{N}(\text{CO})_{12}]$ (**19**) and $[\text{Et}_4\text{N}][\text{Fe}_5\text{N}(\text{CO})_{14}]$ (**20**)

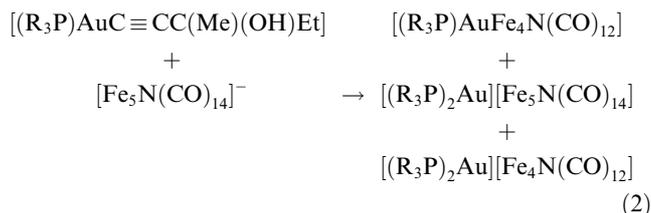
It was decided to investigate the use of two typical phosphine gold acetylides as reagents for the introduction of $\{(\text{R}_3\text{P})\text{Au}\}$ -units into transition element-based clusters. The clusters chosen were $[\text{Fe}_4\text{N}(\text{CO})_{12}]^-$ and $[\text{Fe}_5\text{N}(\text{CO})_{14}]^-$ [5]. The reactions were carried out at room temperature in dichloromethane solution. Six compounds were successfully characterised, namely $[(\text{R}_3\text{P})\text{AuFe}_4\text{N}(\text{CO})_{12}]$, R = Ph (**21**), Cy (**22**), $[(\text{R}_3\text{P})_2\text{Au}][\text{Fe}_4\text{N}(\text{CO})_{12}]$, R = Ph (**23**), Cy = (**24**) and $[(\text{R}_3\text{P})_2\text{Au}][\text{Fe}_5\text{N}(\text{CO})_{14}]$, R = Ph (**25**), Cy (**26**). In all cases the products were separated by preparative thin layer chromatography. They were characterised by C/H/N elemental analyses, infrared spectroscopy for compounds (**21**)–(**26**), ^{13}C NMR spectroscopy for compounds (**21**)–(**24**) and Mössbauer spectroscopy for (**21**)–(**23**), (**25**), (**26**). The structure of (**22**) was determined by a single crystal X-ray analysis.

Reaction of $[(\text{R}_3\text{P})\text{AuC}\equiv\text{CC}(\text{Me})(\text{OH})\text{Et}]$, R = Ph (**8**) or Cy (**15**) with $[\text{Et}_4\text{N}][\text{Fe}_4\text{N}(\text{CO})_{12}]$ (**19**) in dichloromethane at room temperature for between 30 min and 1 h resulted in the formation of the neutral complexes $[(\text{Ph}_3\text{P})\text{AuFe}_4\text{N}(\text{CO})_{12}]$ (**21**) or $[(\text{Cy}_3\text{P})\text{AuFe}_4\text{N}(\text{CO})_{12}]$ (**22**) and the cationic species $[(\text{Ph}_3\text{P})_2\text{Au}][\text{Fe}_4\text{N}(\text{CO})_{12}]$ (**23**) or $[(\text{Cy}_3\text{P})_2\text{Au}][\text{Fe}_4\text{N}(\text{CO})_{12}]$ (**24**), Eq. (1).

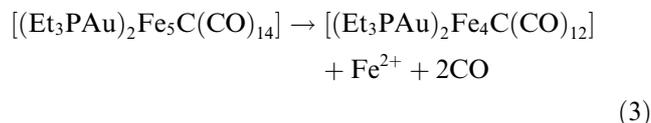


The neutral products were isolated by TLC in 100% hexane. Following this, elution with 80:20 CH_2Cl_2 :hexane afforded the cationic complexes. Both gold acetylide complexes (**8**) and (**15**) appeared to react in the same way with the major difference being that $[(\text{Cy}_3\text{P})\text{AuC}\equiv\text{CC}(\text{Me})(\text{OH})\text{Et}]$ (**15**) afforded 72% the neutral product (**22**) with only 9% of the cationic species (**24**) whereas the reaction of $[(\text{Ph}_3\text{P})\text{AuC}\equiv\text{CC}(\text{Me})(\text{OH})\text{Et}]$ (**8**) afforded approximately 62% of the neutral species (**21**) and 11% of the cationic product (**23**).

When a solution of the penta-iron cluster $[\text{Et}_4\text{N}][\text{Fe}_5\text{N}(\text{CO})_{14}]$ (**20**) in dichloromethane was reacted with $[(\text{Ph}_3\text{P})\text{AuC}\equiv\text{CC}(\text{Me})(\text{OH})\text{Et}]$ (**8**) at room temperature for 23 h, the cationic penta-iron complex $[(\text{Ph}_3\text{P})_2\text{Au}][\text{Fe}_5\text{N}(\text{CO})_{14}]$ (**25**, 32%) and the tetra-iron complexes $[(\text{Ph}_3\text{P})\text{AuFe}_4\text{N}(\text{CO})_{12}]$ (**21**, 46%) and $[(\text{Ph}_3\text{P})_2\text{Au}][\text{Fe}_4\text{N}(\text{CO})_{12}]$ (**23**, 10%) were isolated and characterised, Eq. (2), R = Ph.



Another product was isolated by TLC but it was too unstable to characterise fully. The CH_2Cl_2 solution IR spectrum of the unstable compound showed strong or very strong absorptions due to carbonyl groups at 2038 vs, 2024 s, 2012 vs and 2002 vs, while a ^{13}C NMR spectrum confirmed the presence of CO groups at 220.59, 218.28, 213.26 and 210.12 ppm. It may be postulated that the unstable product was $[(\text{Ph}_3\text{P})\text{AuFe}_5\text{N}(\text{CO})_{14}]$ (**27**), which spontaneously decomposed to give an Fe_4 species. The loss of an iron atom from an Fe_5 -system has previously been observed for a gold-iron cluster system with a Fe_5C framework, Eq. (3), [6]. This reaction occurred when a solution of $[(\text{Et}_3\text{PAu})_2\text{Fe}_5\text{C}(\text{CO})_{14}]$ was stirred at 4 °C for 100 h in air.



Some evidence for the loss of an iron atom from an Fe_5 -system in the present work is the observation that when $[\text{Et}_4\text{N}][\text{Fe}_5\text{N}(\text{CO})_{14}]$ (**20**) and $[(\text{Ph}_3\text{P})\text{AuC}\equiv\text{CC}(\text{Me})(\text{OH})\text{Et}]$ (**8**) were stirred in CH_2Cl_2 at room temperature, gas evolution was observed over 5–6 h as expected from Eq. (3).

When a solution of the penta-iron cluster, $[\text{Et}_4\text{N}][\text{Fe}_5\text{N}(\text{CO})_{14}]$ (**20**) in dichloromethane was reacted with $[(\text{Cy}_3\text{P})\text{AuC}\equiv\text{CC}(\text{Me})(\text{OH})\text{Et}]$ (**9**) at room temperature for 23 h, the cationic penta-iron complex $[(\text{Cy}_3\text{P})_2\text{Au}][\text{Fe}_5\text{N}(\text{CO})_{14}]$ (**26**, 20%) and the tetra-iron complexes $[(\text{Cy}_3\text{P})\text{AuFe}_4\text{N}(\text{CO})_{12}]$ (**22**, 50%) and $[(\text{Cy}_3\text{P})_2\text{Au}][\text{Fe}_4\text{N}(\text{CO})_{12}]$ (**24**, 5%) were isolated and characterised, Eq. (2), $\text{R} = \text{Cy}$.

The carbonyl infrared frequencies for the $[(\text{R}_3\text{P})\text{AuFe}_4\text{N}(\text{CO})_{12}]$ clusters (**21**) and (**22**) are almost identical to those previously reported by Gladfelter et al. for $[(\text{Ph}_3\text{P})\text{AuFe}_4\text{N}(\text{CO})_{12}]$ (**21**), [7]. They prepared (**21**) in 53% yield from $[\text{PPN}][\text{Fe}_4\text{N}(\text{CO})_{12}]$ and $[(\text{Ph}_3\text{P})\text{AuCl}]$ in the presence of $\text{Ti}[\text{PF}_6]$ in CH_2Cl_2 solution. The frequencies are similar to those reported for $[\text{HFe}_4\text{N}(\text{CO})_{12}]$ (**28**) [8] and there is no evidence of bridging carbonyl ligands in the infrared spectra of the neutral Fe_4N systems (**21**) and (**22**). The data obtained for the $[(\text{R}_3\text{P})_2\text{Au}][\text{Fe}_4\text{N}(\text{CO})_{12}]$ compounds (**23**) and (**24**) are very similar to those for the starting material $[\text{Et}_4\text{N}][\text{Fe}_4\text{N}(\text{CO})_{12}]$ (**19**) [9]. This can be taken as an indication that the overall structure of the anion has not been perturbed by the presence of the bis(phosphine)gold cations. In the solid state (KBr) spectra of the $[(\text{R}_3\text{P})_2\text{Au}][\text{Fe}_5\text{N}(\text{CO})_{14}]$ clusters (**25**) and (**26**), carbonyl absorptions at 1802 and 1800 cm^{-1} , respectively are due to the presence of bridging ligands. These are absent from the CH_2Cl_2 solution spectra. Other $[\text{X}][\text{Fe}_5\text{N}(\text{CO})_{14}]$ systems have bridging carbonyl absorptions in their solid state spectra at 1796, 1806 and 1808 cm^{-1} where $[\text{X}] = [\text{PPN}]$, $[\text{Et}_4\text{N}]$ and $[\text{Me}_4\text{N}]$, respectively and solid state isomers of the $[\text{Fe}_5\text{N}(\text{CO})_{14}]^-$ anion have been reported [10].

2.3. Crystal and molecular structure of $[(\text{Cy}_3\text{P})\text{AuFe}_4\text{N}(\text{CO})_{12}]$ (**22**)

An X-ray analysis of compound (**22**) was undertaken in order to determine details of its crystal and molecular structure. Dark green crystals of $[(\text{Cy}_3\text{P})\text{AuFe}_4\text{N}(\text{CO})_{12}]$ (**22**) were grown by slow diffusion of a layer of hexane into a CH_2Cl_2 solution of (**22**). The Fe_4 unit has the butterfly arrangement with the nitrogen atom co-ordinated to all four iron atoms and the gold atom bridging the hinge positions in the Fe_4 butterfly, Fig. 1. All carbonyl groups in (**22**) are terminal and each iron atom is bonded to three carbonyl ligands. Selected bond distances and angles are given in the figure legend. The gold phosphine unit in (**22**), bridges the $\text{Fe}(3)\text{--Fe}(4)$ interaction but is tipped slightly towards the $\text{Fe}(1)$ “wing-tip” site. This aspect of (**22**) is very similar to $[(\text{Et}_3\text{P})\text{AuFe}_4(\text{CO})_{13}]^-$ (**29**) [11] but in $[(\text{Ph}_3\text{PAu})(\mu\text{-H})\text{Fe}_4\text{C}(\text{CO})_{12}]$ (**30**) it is the hydride ligand which bridges the hinge $\text{Fe}\text{--Fe}$ bond while the gold atom interacts with both wing-tip iron sites and the carbide C atom [12].

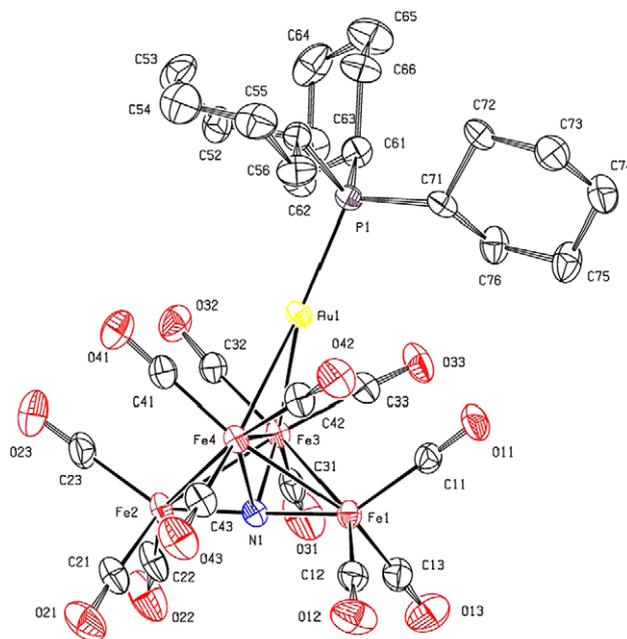


Fig. 1. ORTEP plot of the molecular structure of $[(\text{Cy}_3\text{P})\text{AuFe}_4\text{N}(\text{CO})_{12}]$ (**22**) showing the numbering scheme; ellipsoids are shown at the 30% probability level. Selected bond distances (Å) and angles ($^\circ$): $\text{Au}(1)\text{--Fe}(3)$ 2.7108(11), $\text{Au}(1)\text{--Fe}(4)$ 2.6876(13), $\text{Fe}(1)\text{--N}(1)$ 1.778(7), $\text{Fe}(2)\text{--N}(1)$ 1.773(7), $\text{Fe}(3)\text{--N}(1)$ 1.915(7), $\text{Fe}(4)\text{--N}(1)$ 1.918(6), $\text{Fe}(1)\text{--Fe}(3)$ 2.5886(16), $\text{Fe}(1)\text{--Fe}(4)$ 2.5835(17), $\text{Fe}(2)\text{--Fe}(3)$ 2.5969(17), $\text{Fe}(2)\text{--Fe}(4)$ 2.6137(16), $\text{Fe}(3)\text{--Fe}(4)$ 2.6242(15), $\text{Au}\text{--P}(1)$ 2.297(2); $\text{Fe}(1)\text{--N}(1)\text{--Fe}(2)$ 178.0(4), $\text{Fe}(3)\text{--Au}(1)\text{--Fe}(4)$ 58.17(3), $\text{Fe}(3)\text{--Au}(1)\text{--P}(1)$ 146.63(6), $\text{Fe}(4)\text{--Au}(1)\text{--P}(1)$ 154.95(6), $\text{Fe}(3)\text{--N}(1)\text{--Fe}(4)$ 86.4(3). $\text{Fe}\text{--C}$ distances range from 1.773(11) to 1.830(10) (mean 1.795 Å) and $\text{P}\text{--C}$ distances from 1.838(9) to 1.873(10) Å (mean 1.851 Å). Dimensions in CO and Cy groups are normal. Within the Fe_4N framework: mean $\text{Fe}_{\text{wing-tip}}\text{--N}\text{--Fe}_{\text{hinge}}$ 89.3 $^\circ$, mean $\text{Fe}_{\text{wing-tip}}\text{--Fe}_{\text{hinge}}\text{--N}$ 43.2 $^\circ$, mean $\text{Fe}_{\text{hinge}}\text{--Fe}_{\text{wing-tip}}\text{--N}$ 47.6 $^\circ$, mean $\text{Fe}\text{--C}\text{--O}$ 176.8 $^\circ$ and mean $\text{Au}\text{--P}\text{--C}$ 111.7 $^\circ$.

The $\text{Fe}(3)\text{--Au}(1)\text{--Fe}(4)$ angle in (**22**) is 58.17(3) $^\circ$ similar to the $\text{Fe}\text{--Au}\text{--Fe}$ angles in $[\text{Et}_4\text{N}][(\text{Ph}_3\text{PAu})\text{Fe}_2(\text{CO})_8]$ (**31**) at 58.6(1) $^\circ$ and in $[(\text{Et}_3\text{P})\text{AuFe}_4(\text{CO})_{13}]^-$ (**29**) at 59.57(4) $^\circ$ [11]. The $\text{Fe}\text{--Au}\text{--Fe}$ angle reported for (**30**) was much larger at 80.5(1) $^\circ$ but this is a result of the gold phosphine unit spanning the “wing-tip” iron atoms rather than the hinge position. The $\text{Fe}\text{--H}\text{--Fe}$ angle in (**29**) was 87(3) $^\circ$ [12].

The $\text{Fe}\text{--Fe}$ distances in $[(\text{Cy}_3\text{P})\text{AuFe}_4\text{N}(\text{CO})_{12}]$ range from 2.5835(17)–2.6242(15) Å, with the gold phosphine bridged $\text{Fe}(3)\text{--Fe}(4)$ hinge distance being the longest. In $[(\text{Ph}_3\text{PAu})(\mu\text{-H})\text{Fe}_4\text{C}(\text{CO})_{12}]$ (**30**) the hydride bridged $\text{Fe}\text{--Fe}$ hinge distance is 2.618(1) Å, while the other $\text{Fe}\text{--Fe}$ distances range from 2.626(1) to 2.644(1) Å (**29**). In (**29**) the $\text{Fe}\text{--Fe}$ distances range from 2.623(1) to 2.654(1) Å with the gold phosphine bridged distance being 2.649(2) Å [11]. The $\text{Fe}\text{--Au}$ distances in (**22**) are not unusual at 2.7108(11) and 2.6876(13) Å and compare with analogous distances of 2.666(1) Å in $[(\text{Et}_3\text{P})\text{AuFe}_4(\text{CO})_{13}]^-$ (**29**) [11]. The $\text{Fe}\text{--N}$ distances in

(22) are Fe(1)–N(1) 1.778(7), Fe(2)–N(1) 1.773(7) for bonds to the “wing-tip” iron atoms and Fe(3)–N(1) 1.915(7) and Fe(4)–N(1) 1.918(6) Å for the hinge iron atoms. The stronger interaction with the “wing-tip” sites is typical of the M_4N butterfly structures, e.g. in $[HFe_4N(CO)_{12}]$ (28) the $Fe_{\text{hinge}}-N$ distance is 1.92(2) Å and the $Fe_{\text{wing-tip}}-N$ distance is 1.77(1) Å [9].

2.4. Mössbauer spectra

2.4.1. $[(Ph_3P)AuFe_4N(CO)_{12}]$ (21) and $[(Cy_3P)AuFe_4N(CO)_{12}]$ (22)

In the solid state structure of $[(Cy_3P)AuFe_4N(CO)_{12}]$, Fig. 1, there appear to be three independent iron sites. The Au to Fe(1) distance was shorter than the Au to Fe(2) distance due to the displacement of the $\{Au(Cy_3P)\}$ group towards the Fe(1) atom, [i.e. $Fe(1) \neq Fe(2) \neq Fe(3) = Fe(4)$]. All Fe sites have only terminal carbonyl ligands. Thus, the Mössbauer spectrum could consist of three doublets if there are three independent sites, or, if the difference between Fe(1) and Fe(2) sites is not significant, two doublets. Moreover, if it is correct that the $\{(R_3P)Au\}^+$ group and the proton are isolobal species, it may be expected that compounds (21), (22) and $[HFe_4N(CO)_{12}]$ (28) will have similar Mössbauer spectra [10,13]. The spectra of (21) and (22), Fig. 2, and (28) all show closely similar spectra with two doublets due to two independent iron sites. This indicates that the difference between the Fe(1) and Fe(2) environment observed in the X-ray diffraction study of (22) was not detected by Mössbauer spectroscopy. For $[(Ph_3P)AuFe_4N(CO)_{12}]$ (21) the spectrum consists of four signals with only partial resolution of the two signals at positive velocity. The quadrupole splitting values (q) for the two iron sites are 0.90 and 0.65 $mm\ s^{-1}$, the associated isomer shift values (δ) are 0.09 and 0.46 $mm\ s^{-1}$. The spectrum shown by $[(Cy_3P)AuFe_4N(CO)_{12}]$ (22) is almost identical to that of (21), the only difference is that the signals at positive

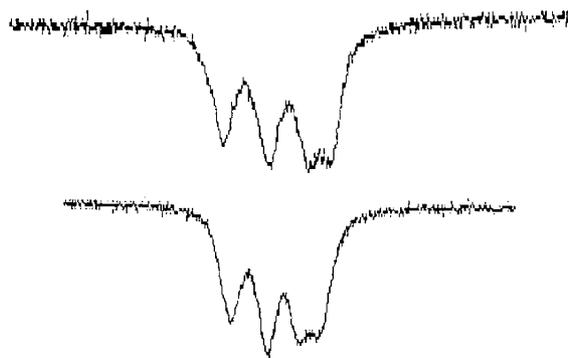


Fig. 2. Mössbauer spectra of (a) $[(Cy_3P)AuFe_4N(CO)_{12}]$ (22, above) and (b) $[(Ph_3P)AuFe_4N(CO)_{12}]$ (21, below).

velocity are slightly better resolved. The quadrupole splitting, q , and isomer shift δ , values assigned to the Fe_{hinge} site are 0.85 and 0.09 $mm\ s^{-1}$, and for the $Fe_{\text{wing-tip}}$ site the values are 0.62 and 0.43 $mm\ s^{-1}$. The quadrupole splitting values reported for $[HFe_4N(CO)_{12}]$ (28) are 1.01 and 0.87 $mm\ s^{-1}$, with corresponding isomer shift values of 0.15 and 0.42 $mm\ s^{-1}$, these are assigned as $Fe(CO)_3H_{br}$ and $Fe(CO)_3^t$, respectively [10,13]. Hence for (21) the signal at 0.90 $mm\ s^{-1}$ is assigned to the $Fe_{\text{hinge}}\{Fe(CO)_3(Ph_3PAu)_{br}\}$ site and the signal at 0.65 $mm\ s^{-1}$ is assigned to the $Fe_{\text{wing-tip}}$ site.

2.4.2. $[(Ph_3P)_2Au][Fe_4N(CO)_{12}]$ (23)

The core structure of the $[Fe_4N(CO)_{12}]^-$ anion most probably contains four iron atoms in a butterfly arrangement with two independent sites, Fe_{hinge} and $Fe_{\text{wing-tip}}$ similar to the neutral compounds (21) and (22). The Mössbauer spectrum of (23) shows three signals with the one signal at positive velocity approximately twice the intensity of the others. Based on previously published Mössbauer data of $[Fe_4N(CO)_{12}]^-$ compounds [10,13] the pair of signals in the spectrum of (23) with quadrupole splitting of 0.80 $mm\ s^{-1}$ and isomer shift of 0.18 $mm\ s^{-1}$ may be assigned to the Fe_{hinge} sites and those with quadrupole splitting of 0.58 $mm\ s^{-1}$ and isomer shift 0.33 $mm\ s^{-1}$ assigned to the wing-tip iron atoms. The values reported for $[Et_4N][Fe_4N(CO)_{12}]$ (19) are $q = 0.88$ and $\delta = 0.21\ mm\ s^{-1}$ and $q = 0.63$, $\delta = 0.34\ mm\ s^{-1}$, respectively, while the values reported for the isoelectronic species, $[Fe_4C(CO)_{12}]^{2-}$ are $q = 0.88$, $\delta = 0.22\ mm\ s^{-1}$ and $q = 0.62$, $\delta = 0.35\ mm\ s^{-1}$ for hinge and wing-tip iron sites, respectively.

2.4.3. $[(Ph_3P)_2Au][Fe_5N(CO)_{14}]$ (25) and $[(Cy_3P)_2Au][Fe_5N(CO)_{14}]$ (26)

If one assumes that the Fe_5N -compounds (25) and (26) both have core structures and the disposition of carbonyl ligands similar to $[Et_4N][Fe_5N(CO)_{14}]$ (20), then there should be three distinct iron sites. However, the Mössbauer spectra of (26) and (25), like that of (20), consist of one unresolved doublet and it is impossible to discern different sites and make detailed assignments, e.g. averaged values of $\delta = 0.59$ and $q = 0.30\ mm\ s^{-1}$ cover all sites in (25). Solid state isomers of $[Fe_5N(CO)_{14}]^-$ existing with different carbonyl ligand dispositions depending on the cation present $\{[PPN]^+, [Et_4N]^+ \text{ or } Cs^+\}$ have been reported and their Mössbauer spectra studied [10,13].

3. Conclusions

Five new gold acetylides, $[AuC\equiv CR]$, with hydroxyl or amino functions in the organic radical R and nine phosphine complexes of these gold acetylides $[(R_3P)AuC\equiv CR]$ where R = Ph or Cy were synthesised

and characterised. The phosphine gold acetylides were soluble in dichloromethane and proved to be effective reagents for the formation of $\{(R_3P)_nAu\}$ -containing clusters ($n = 1$ or 2). Reactions between two of the phosphine gold acetylides, $[(Ph_3P)AuC\equiv CC(Me)(OH)Et]$ and $[(Cy_3P)AuC\equiv CC(Me)(OH)Et]$, and the tetra-iron carbonyl cluster $[Et_4N][Fe_4N(CO)_{12}]$ afforded two compounds, namely $[(R_3P)AuFe_4N(CO)_{12}]$ and $[(R_3P)_2Au][Fe_4N(CO)_{12}]$. Reactions between the phosphine gold acetylides and $[Et_4N][Fe_5N(CO)_{14}]$ gave $[(R_3P)_2Au][Fe_5N(CO)_{14}]$ and both the tetra-iron complexes $[(R_3P)AuFe_4N(CO)_{12}]$ and $[(R_3P)_2Au][Fe_4N(CO)_{12}]$. The gold–iron clusters were characterised with spectroscopic methods (IR, NMR and Mössbauer) and in the case of $[(Cy_3P)AuFe_4N(CO)_{12}]$ a single-crystal X-ray analysis.

On the basis of both FT-IR and Mössbauer spectra the solid state structures of $[(R_3P)AuFe_4N(CO)_{12}]$ and $[(R_3P)_2Au][Fe_4N(CO)_{12}]$ appeared to contain terminally bonded CO groups only as is also the case for the species $[HFe_4N(CO)_{12}]$. The single-crystal X-ray analysis of $[(Cy_3P)AuFe_4N(CO)_{12}]$ confirmed this but also showed an asymmetry in the bonding of the $\{(Cy_3P)Au\}$ -group to the Fe_4 -skeleton. This was not reflected in the Mössbauer spectrum. The reason for the asymmetric bonding is unclear. It seems unlikely that the H atom in $[HFe_4N(CO)_{12}]$ would adopt a similar arrangement. The asymmetric bonding of the $\{(Cy_3P)Au\}$ -group may be due to some weak solid-state interactions in the crystal rather than any difference in “isolobal” character of the gold atom compared to hydrogen.

The complex $[(R_3P)_2Au][Fe_5N(CO)_{14}]$ contained bridging and terminal CO groups as observed in previous $[Fe_5N(CO)_{14}]^-$ compounds. Neutral $[(R_3P)AuFe_5N(CO)_{14}]$ complexes could not be isolated during the present work.

4. Experimental

4.1. General methodology

All reactions and crystallisations were carried out under an inert nitrogen atmosphere but products were initially isolated and then manipulated in air. Preparative thin layer chromatography was carried out with Merck silica gel PF₂₅₄ on glass plates prepared in UCC. Elemental analyses, (C/H/N), were performed at the Micro-analytical Laboratory, University College, Cork. Infrared spectra were recorded either as KBr discs or in CH_2Cl_2 solution on a Perkin–Elmer Paragon FTIR spectrometer. ¹³C NMR spectra were recorded at 6.3 Tesla using a JEOL FT GSX-270 series spectrometer. Chemical shifts (δ) are expressed relative to internal $SiMe_4$ $\{(^1H)$ and $(^{13}C)\}$ standard. Single crystal X-ray analysis was performed using an Enraf-Nonius CAD-4

diffractometer. Accurate cell dimensions and crystal orientation matrix were determined by a least squares procedure from reflections obtained in the range $2 < \theta < 25^\circ$ using graphite monochromatised (Mo-K α) radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved via standard heavy-atom procedures using the NRCVAX suite of programs [14] and refined with full-matrix least-squares calculations using SHELXL-97-2 [15] in WinGX [16]. Plots and data validation checks were made with PLATON [17]. Full structural details in CIF format of $[(Cy_3P)AuFe_4N(CO)_{12}]$ (**22**) are available from the CCDC (reference number 263356).

Mössbauer spectra of the iron clusters were recorded at liquid nitrogen temperatures (80 K) using a commercial constant acceleration drive unit and transducer (Marwell Instruments) in conjunction with a Canberra System 40 multichannel analyser. The source was ⁵⁷Co in Rh and was of 20 mCi nominal strength. Data were referred to the spectrum of sodium nitroprusside as standard. Sampling times varied from 2–4 days.

The compounds $[Et_4N][Fe_4N(CO)_{12}]$ (**19**), $[Et_4N][Fe_5N(CO)_{14}]$ (**20**) were prepared according to literature methods [5]. The preparations of $[AuC\equiv CC(Me)(OH)Et]$ (**1**) and $[AuC\equiv CC(Me)(OH)Ph]$ (**2**) were as reported previously. The acetylenes and phosphine ligands were used as supplied by the Aldrich Chemical Co. Ltd. The gold reagent $H[AuCl_4] \cdot 2H_2O$ was supplied by Johnson Matthey.

4.2. Preparation of gold acetylides – general method

A solution of KBr (12.8 mmol) in water (40 ml) was added to a stirred solution of $H[AuCl_4] \cdot 2H_2O$ (1.68 mmol) in water (60 ml). After stirring for 2–3 min the resulting red solution of gold(III) was reduced to a colourless gold(I) solution by the dropwise addition of a freshly prepared aqueous solution of SO_2 . A solution of excess of the acetylene in acetone (2 mmol in 10 ml) was quickly added to the colourless solution and the mixture stirred for approximately 1 min. After this time the product was precipitated by the addition of a saturated aqueous solution of $K_2[CO_3]$. The solid product was isolated by filtration, washed with water and air-dried.

Compounds prepared by this method were $[AuC\equiv CC(Me)(OH)Et]$ (**1**), $[AuC\equiv CC(Me)(OH)Ph]$ (**2**), $[AuC\equiv CC(H)(OH)Et]$ (**3**), $[AuC\equiv CC(H)(OH)(CH_2)_4Me]$ (**4**), $[AuC\equiv CC(Me)(OH)CH_2CHMe_2]$ (**5**), $[AuC\equiv CCH_2Optm]$ (**6**, *ptm* = phthalimide) and $[AuC\equiv CC(Me)_2NH_2]$ (**7**). Analytical (%) and infrared spectral data $\{v_{max}(C\equiv C) \text{ cm}^{-1}\}$ for (**3**)–(**7**): (**3**) requires C, 21.4, H, 2.5; found C, 21.1, H, 2.5; 1982; (**4**) requires C, 29.8, H, 4.0; found C, 31.0, H, 4.3; 1978; (**5**) requires C, 29.8, H, 4.1; found C, 29.8, H, 4.15; 1972; (**6**) requires C, 32.3, H, 1.5, N, 3.5; found C,

31.6, H, 1.5, N, 2.9%: 2003; (7) requires C, 21.6, H, 2.9, N, 5.0; found C, 20.8, H, 2.45, N, 4.7%: 2119.

4.3. Preparation of phosphine derivatives of gold acetylides – general method

To a suspension of gold acetylide (0.28 mmol) in toluene (25 ml) was added an equimolar solution of the required phosphine (0.28 mmol) in toluene (5 ml). After stirring for 5–10 min, all of the acetylide had dissolved to yield a colourless solution. The solution was filtered and the solvent removed under reduced pressure (50 °C) to yield a colourless solid. The product was purified by recrystallisation from toluene/heptane solution. Analytical (%), melting point, yield and infrared spectral data $\{v_{\max}(\text{C}=\text{C}) \text{ cm}^{-1}\}$ for (8)–(18): are as follows: [(Ph₃P)AuC≡CC(Me)(OH)Et] (8) requires C, 51.8, H, 4.3; found C, 51.0, H, 4.7: 162–164, 79, 2134(w); (Ph₃P)AuC≡C–C(Me)(OH)Ph (9), requires C, 55.6, H, 4.0; found C, 55.9, H, 4.0: 168–170, 80, 2110(w); [(Ph₃P)AuC≡CC(H)(OH)Et] (10), requires C, 51.15, H, 4.2; found C, 50.9, H, 4.1: 99–101, 81, 2128(w); [(Ph₃P)Au–C≡CC(H)(OH)(CH₂)₄Me] (11), requires C, 53.4, H, 4.8; found C, 53.3, H, 4.8: 150–152, 75, 2127(m); [(Ph₃P)AuC≡CC(Me)(OH)CH₂–CH(Me)₂] (12), requires C, 53.4, H, 4.8; found C, 53.8, H, 5.0: 129–131, 92, 2124(w); [(Ph₃P)AuC≡CCH₂Optm] (13), requires C, 52.8, H, 3.2, N, 2.2; found C, 53.6, H, 3.5, N, 2.2: 170–172, 74, 2142(m); [(Ph₃P)AuC≡CC–(Me)₂NH₂] (14), requires C, 51.0, H, 4.3, N, 2.6; found C, 51.6, H, 4.3, N, 2.8: 114–116, 57, 2100(w); (Cy₃-P)AuC≡C–C(Me)(OH)Et] (15), requires C, 50.1, H, 7.4; found C, 50.4, H, 7.4: 196–198, 75, 2120(m); [(Cy₃-P)AuC≡C–C(H)(OH)Et] (16), requires C, 49.3, H, 7.2; found C, 49.75, H, 7.6: 125–128, 80, 2116(w); [(Cy₃-P)AuC≡CC(H)(OH)(CH₂)₄Me] (17), requires C, 51.8, H, 7.7; found C, 52.5, H, 8.0: 113–116, 65, 2122(w); [(Cy₃-P)AuC≡CC(Me)(OH)CH₂–CH(Me)₂] (18), requires C, 51.8, H, 7.7; found C, 52.3, H, 7.9: 112–114, 78, 1998(w).

4.4. Reactions between phosphine gold acetylides [(Ph₃P)AuCCC(Me)(OH)Et] (8) or [(Cy₃P)AuCCC(Me)(OH)Et] (15) and the iron carbonyl clusters [Et₄N][Fe₄N(CO)₁₂] (19) and [Et₄N][Fe₅N(CO)₁₄] (20)

4.4.1. Reaction of [Et₄N][Fe₄N(CO)₁₂] (19) with [(Ph₃P)AuC≡CC(Me)(OH)Et] (8)

To a brown–green solution of [Et₄N][Fe₄N(CO)₁₂] (19) (0.055 g, 0.078 mmol) in CH₂Cl₂ (30 ml) was added a solution of [(Ph₃P)AuC≡CC(Me)(OH)Et] (8) (0.039 g, 0.070 mmol) in CH₂Cl₂ (10 ml) and the reaction mixture was stirred for 30 min. The mixture was concentrated under reduced pressure (25 °C) and subjected to p.l.c. initially in cyclohexane to yield [(Ph₃P)AuFe₄N(CO)₁₂] (21) (0.045 g, 62.2%) and then

in CH₂Cl₂:hexane, (80:20), to yield [(Ph₃P)₂Au][Fe₄N(CO)₁₂] (23) (0.018 g, 11.0%). C₃₀H₁₅PAuFe₄NO₁₂ (21) requires C, 36.0, H, 1.5, N, 1.4; found C, 35.4, H, 1.8, N, 1.00%. C₄₈H₃₀P₂AuFe₄NO₁₂ (23) requires C, 44.5, H, 2.3, N, 1.1; found C, 44.6, H, 2.4, N, 1.1%. IR data cm⁻¹ (CH₂Cl₂ solution) [(Ph₃P)AuFe₄N(CO)₁₂] (21) 2078 m, 2039 vs, 2025 vs, 2003 s, 1991 w, 1959 w, 1942 vw; [(Ph₃P)₂Au][Fe₄N(CO)₁₂] (23) 2015 s, 1987 vs, 1966 m, 1929 w. ¹³C NMR data [(Ph₃P)AuFe₄N(CO)₁₂] (21), 213.2, 210.1 ppm (carbonyl groups), 135.0–130.2 ppm (phenyl groups); [(Ph₃P)₂Au][Fe₄N(CO)₁₂] (23), 216.5, 213.6 ppm (carbonyl groups), 134.6–130.4 ppm (phenyl groups).

4.4.2. Reaction of [Et₄N][Fe₅N(CO)₁₄] (20) with [(Ph₃P)AuC≡CC(Me)(OH)Et] (8)

To a brown–green solution of [Et₄N][Fe₅N(CO)₁₄] (20) (0.095 g, 0.12 mmol) in CH₂Cl₂ (50 ml) was added [(Ph₃P)AuC≡CC(Me)(OH)Et] (8) (0.064 g, 0.115 mmol). The reaction mixture was stirred for 23 h and the solvent removed under reduced pressure (25 °C). The residue was purified using p.l.c. with initially 100% hexane to yield a dark green compound identified as [(Ph₃P)AuFe₄N(CO)₁₂] (21) (0.054 g, 45.5%). Two further brown–green products were isolated by elution in CH₂Cl₂:cyclohexane (70:30). These two compounds were identified as [(Ph₃P)₂Au][Fe₅N(CO)₁₄] (25), (0.052 g, 32.1%) and [(Ph₃P)₂Au][Fe₄N(CO)₁₂] (23), (0.015 g, 10.1%). C₃₀H₁₅PAuFe₄NO₁₂ (21) requires C, 36.0, H, 1.5, N, 1.4; found C, 35.2, H, 1.4, N, 1.5%. C₅₀H₃₀P₂AuFe₅NO₁₄ requires (25) C, 42.7, H, 2.15, N, 1.0; found C, 42.7, H, 2.2, N, 1.0%. C₄₈H₃₀P₂AuFe₄NO₁₂ (23) requires C, 44.5, H, 2.3, N, 1.1; found C, 44.6, H, 2.5, N, 1.2%. A fourth product was also isolated but was very unstable and was only characterised by IR spectroscopy. IR data cm⁻¹ (CH₂Cl₂ solution) [(Ph₃P)₂Au][Fe₅N(CO)₁₄] (25), 2059 w, 2011 s, 2000 vs, 1989 s, 1965 w, 1941 w.

4.4.3. Reaction of [Et₄N][Fe₄N(CO)₁₂] (19) with [(Cy₃P)AuC≡CC(Me)(OH)Et] (15)

To a brown–green solution of [Et₄N][Fe₄N(CO)₁₂] (19) (0.023 g, 0.03 mmol) in CH₂Cl₂ (15 ml) was added a solution of [(Cy₃P)AuC≡CC(Me)(OH)Et] (15) (0.019 g, 0.033 mmol) in CH₂Cl₂ (10 ml). The reaction mixture was stirred for 60 min at room temperature, whereupon it was concentrated under reduced pressure (25 °C) and subjected to p.l.c. initially in hexane 100% and then in CH₂Cl₂:cyclohexane (40:60) to yield two products, [(Cy₃P)AuFe₄N(CO)₁₂] (22), (0.025 g, 72.0%), and [(Cy₃-P)₂Au][Fe₄N(CO)₁₂] (24), (0.004 g, 9.1%). C₃₀H₃₃PAuFe₄NO₁₂(22) requires C, 34.3, H, 3.2, N, 1.3; found C, 35.5, H, 3.5, N, 1.8. C₄₈H₆₆P₂AuFe₄NO₁₂ (24) requires C, 43.3, H, 5.0, N, 1.1; found C, 43.7, H, 4.9, N, 0.85%. IR data cm⁻¹ (CH₂Cl₂ solution) [(Cy₃P)AuFe₄N(CO)₁₂] (22) 2077 m, 2060 w, 2038 vs, 2023 vs, 2002 s, 1990 m,

1956 w, 1936 w; [(Cy₃P)₂Au][Fe₄N(CO)₁₂] (**24**) 2035 w, 2014 w, 2000 s, 1989 s, 1966 w. ¹³C NMR data [(Cy₃P)Au-Fe₄N(CO)₁₂] (**22**), 214.3, 210.9 ppm (carbonyl groups), 26.0–35.3 ppm (aliphatic groups); [(Cy₃P)₂Au][Fe₄N(CO)₁₂] (**24**), 216.7, 213.5 ppm (carbonyl groups), 26.3–36.0 ppm (aliphatic groups).

4.4.4. X-ray analysis of [(Cy₃P)AuFe₄N(CO)₁₂] (**22**)

Crystals of (**22**) suitable for X-ray diffraction were grown from dichloromethane/hexane solution. *Crystal data*: C₃₀H₃₃AuFe₄NO₁₂P, *M* = 1050.91, triclinic, *P* $\bar{1}$, *a* = 8.8806(19) Å, *b* = 12.5470(19) Å, *c* = 17.048(3) Å, α = 103.249(13), β = 97.860(16), γ = 92.601(18)°, *Z* = 2, *D*_x = 1.911 mg m⁻³, *F*(0 0 0) = 1028, μ = 5.657 mm⁻¹, λ (Mo-K α) = 0.71073 Å, Total number of reflections = 7924, *R*_F = 0.0604 based on 5914 data with [*F*² > 2 σ (*F*²)], *R*_w = *R*[*wR*(*F*²)] = 0.1644 for 7924 data.

4.4.5. Reaction of [Et₄N][Fe₅N(CO)₁₄] (**20**) with [(Cy₃P)AuC≡CC(Me)(OH)Et] (**15**)

To a brown–green solution of [Et₄N][Fe₅N(CO)₁₄] (**20**) (0.032 g, 0.04 mmol) in CH₂Cl₂ (20 ml) was added a solution of [(Cy₃P)AuC≡CC(Me)(OH)Et] (**15**) (0.024 g, 0.042 mmol) in CH₂Cl₂ (10 ml). The reaction mixture was stirred at room temperature for 23 h after which time it was concentrated under reduced pressure (25 °C) and subjected to p.l.c in hexane to yield [(Cy₃P)AuFe₄N(CO)₁₂] (**22**), (0.022 g, 49.8%). Re-elution in (CH₂Cl₂:cyclohexane, 70:30), yielded two further products identified as [(Cy₃P)₂Au][Fe₅N(CO)₁₄] (**26**), (0.012 g, 19.8%) and [(Cy₃P)₂Au][Fe₄N(CO)₁₂] (**24**), (0.003 g, 5.4%). C₃₀H₃₃PAuFe₄NO₁₂ (**22**) requires C, 36.0, H, 1.5, N, 1.4; found C, 36.1, H, 1.45, N, 1.05%. C₅₀H₆₆P₂AuFe₅NO₁₄ (**26**) requires C, 41.6, H, 4.6, N, 1.0; found C, 41.9, H, 4.45, N, 1.0%. C₄₈H₆₆P₂AuFe₄NO₁₂ (**24**) requires C, 43.3, H, 5.0, N, 1.0; found C, 44.1, H, 4.95, N, 1.0%. IR data cm⁻¹ (CH₂Cl₂ solution) [(Cy₃P)₂Au][Fe₅N(CO)₁₄] (**26**) 2035 w, 2014 w, 2000 s, 1989 s, 1966 w.

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