Available online at www.sciencedirect.com
SCIENCE DIRECT®
Inorganica Chimica Acta 358 (2005) 1386–1392
Inorganica Chimica Acta
www.elsevier.com/locate/ica

Gold(I) alkynyl complexes derived from ethynylanilines: crystal structure of [Au(C≡C-4-$C_6H_4NH_2$){P(3-tolyl)$_3$}] a polymer in the solid state via NH···Au contacts ☆

Graeme Hogarth [a,*], Miguel M. Álvarez-Falcón [a,b]

[a] Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, UK
[b] Departamento de Química Inorgánica, Facultad de Quimica, Universidad de Murcia, Apartado 4021, Murcia 30071, Spain

Received 7 April 2004; accepted 30 June 2004

Dedicated to Professor Gordon Stone in recognition of his contributions to organometallic chemistry

Abstract

Reaction of [AuCl(SMe$_2$)] with *para*-ethynylaniline and *para*-ethynyl-*ortho*-toluidine affords oligomers, [Au(C≡C-4-$C_6H_3RNH_2$)]$_n$ (R = H, Me), which in turn react with tertiary phosphines or 2,5-dimethylphenylisocyanide to give monomeric adducts, [Au(C≡C-4-$C_6H_3RNH_2$)L]. One of these, [Au(C≡C-4-$C_6H_4NH_2$){P(3-tolyl)$_3$}], has been crystallographically characterised and is a polymer in the solid state, being held together via NH···Au contacts.

Keywords: Gold(I) complexes; Alkynyl complexes; Ethynylanilines; X-ray crystal structure

1. Introduction

There is continued interest in the chemistry of alkynyl gold(I) complexes primarily resulting from their physical properties, such as, luminescence [1–5], non-linear optical behavior [6–8] and liquid crystalline [9] properties. Further, the linearity of the M–C≡C moiety and the preference of gold(I) for linear two coordination, makes alkynyl gold(I) compounds attractive candidates for the design of rigid-rod molecules [10] or metal-containing linear-chain polymers with extended electronic conjugation along the backbone [8,11–13]. One way of building up extended chains containing these sub-units is to utilise alkynyl ligands with a second metal binding site. In this context, ethynylanilines are potentially useful building blocks towards the synthesis of multimetallic arrays [14], especially in which the binding sites are electronically conjugated and can potentially incorporate alternating high and low-valent metal centres.

Herein, we describe the synthesis of new alkynyl gold(I) complexes derived from 4-ethynylaniline and 2-methyl-4-ethynylaniline by using well-known and straightforward synthetic pathways such as the "acac method" [15] and depolymerization reactions [16–18]. In addition, the crystal structure of [Au(C≡C-4-$C_6H_4NH_2$){P(3-tolyl)$_3$}] is reported which shows that the molecules pack through N–H···Au contacts. As far as we know, this is the first time such contacts have been shown to play an important role in the molecular packing of gold complexes.

2. Results and discussion

The reactions between [AuCl(SMe$_2$)] and the corresponding ethynylanilines in the presence of triethylam-

☆ Dedicated to Professor Stone for his inspiring undergraduate lectures and kind support during my early career.

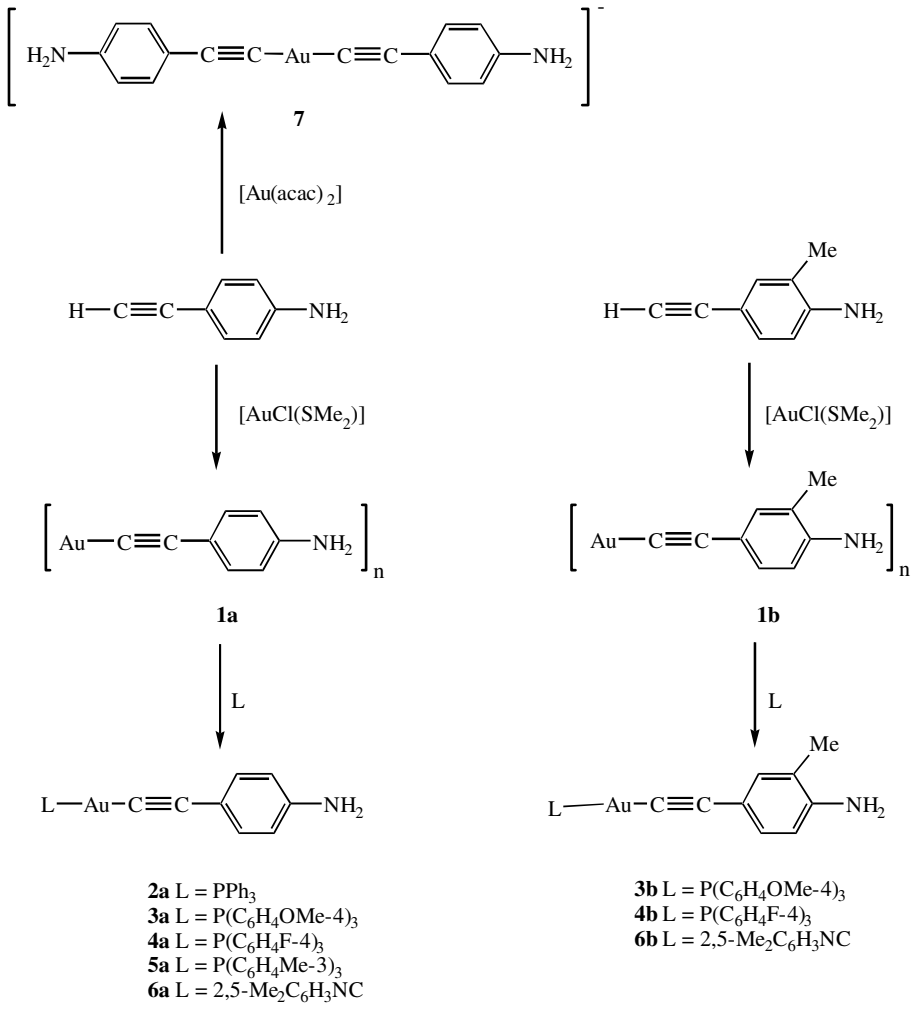
* Corresponding author. Tel.: +44 207 679 4603; fax: +44 207 380 7463.
E-mail addresses: g.hogarth@ucl.ac.uk (G. Hogarth), miguelaf@um.es (M.M. Álvarez-Falcón).

0020-1693/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.ica.2004.06.068

ine afforded in high yields the neutral oligomers $[Au(C{\equiv}C\text{-}4\text{-}C_6H_3RNH_2)]_n$ **1a**–**b** as orange solids (Scheme 1). As a result of the tendency of many complexes of this type to explode on contact when pure [16–20], we did not attempt any further purification and due to their extreme insolubility in all common organic solvents, they could not be characterized by NMR techniques. Like related (alkynyl)gold(I) complexes [21], both **1a**–**b** showed a band at around 2000 cm^{-1} in the IR spectrum being attributed to the $\nu(C{\equiv}C)$ stretching mode, while elemental analysis were in agreement with the proposed formulation. We assume that **1a**–**b** adopt structures similar to other gold complexes of this type, whereby each gold atom is assumed to be simultaneously σ-coordinated to one alkynyl fragment and π-bonded to the carbon–carbon triple bond of an adjacent molecule [22–24], but cannot rule out the possibility of amine coordination.

One of the most widely used methods of preparing new (alkynyl)gold(I) compounds centres on the depolymerization reaction of neutral homoleptic alkynyl-gold(I) polymers, upon addition of good σ-donor ligands such as phosphines, isocyanides or halides. Such reactions have allowed the synthesis of a huge number of new neutral [18,25–28] and ionic [29–31] gold(I) alkynyl complexes. In this context, we reacted oligomeric **1a**–**b** with tertiary phosphines PR_3(R = Ph, C_6H_4Me-3, C_6H_4OMe-4, C_6H_4F-4) or 2,5-dimethylphenylisocyanide (XyNC) to obtain the corresponding mixed (alkynyl)gold(I) derivatives, $[LAu(C{\equiv}C\text{-}4\text{-}C_6H_3RNH_2)]$ **2a**–**6a**, **3b**, **4b** and **6b** (Scheme 1). All were carried out in dichloromethane, in which the oligomeric starting materials **1a**–**b** are completely insoluble. The addition of the appropriate ligand caused the immediate disappearance of the initial suspension, resulting in solutions from which the neutral derivatives were isolated in good to moderate yields (41–77%).

Characterisation was relatively straightforward. All show molecular ions in their FAB mass spectra, although for the phosphine complexes the spectra are dominated by signals corresponding to the $[AuPR_3]^+$ (100%) and $[Au(PR_3)_2]^+$ (90–50%) fragments, as has



Scheme 1.

previously been reported for other alkynyl(phosphine)gold(I) complexes [32]. All phosphine complexes also show a singlet resonance at around 40 ppm in the ^{31}P NMR spectra, being similar to that found for other alkynyl(phosphine)gold(I) complexes [33–37]. The ^{1}H NMR spectra of **2a**–**6a**, **3b**, **4b**, and **6b** show the signals expected for the ethynylanilines as well as the auxiliary phosphine and isocyanide ligands, and both their number and relative intensities are in agreement with the proposed structures (see Section 3). In all cases, no residual signals attributable to acetylenic hydrogens were observed, proving that in the syntheses of these complexes, the substitution of acetylenic hydrogens by the corresponding gold(I) fragments has been quantitative. The ^{13}C NMR spectra all show a singlet around 105 ppm, assignable to one of the carbons of the C≡CAu fragment, but in the absence of J_{CP} coupling constants we cannot unequivocally assign this resonance.

The crystal structure of **5a** has been carried out (Fig. 1). It shows the expected mononuclear complex in which the gold atom is coordinated to phosphine and alkynyl ligands in an approximately linear manner [C–Au–P 176.21(10)°]. The C≡C [1.198(4) Å], C–Au [1.990(3) Å] and AuP [2.2686(8) Å] bond distances are similar to those found in other alkynyl(phosphine) complexes [25,35,38–40].

Unlike the situation found for many other gold(I) complexes, intermolecular Au···Au contacts are not observed in **5a**. Rather intermolecular contacts N–H···Au are seen [$d_{H\cdots Au}$ = 3.114 Å, angle N–H···Au = 152.90°] that can be considered as hydrogen bonds (Fig. 2).

A recent paper by Schmidbaur [41] describes the head to tail packing through intermolecular aurophilic contacts in [$Me_3PAuC{\equiv}CAuPMe_3$] to give a zig-zag chain analogous to that found in **5a**. A search in the Cambridge Crystallographic Data Base for structures that contain these kind of N–H···Au interactions, the restrictions [42–45] applied being d(H···Au)″d_{vdW} + 0.4 Å and N–H···Au angle ⩾135°, revealed the existence of only twelve structures [46–56] in which such contacts are present. Seven [46,49,50,53,54,56] display intermolecular aurophilic contacts which have been previously reported to be the main packing forces in a wide variety of gold(I) compounds [57], whereas the other five [48,51,52,55] show classical hydrogen bonds of the type N–H···E (E = N, O, S). Nevertheless, the authors do not mention the existence of these N–H···Au contacts in any of the papers above mentioned. It is noteworthy that in **5a**, N–H···Au contacts are the only intermolecular contacts found so that they could be responsible for the zig-zag chain packing observed.

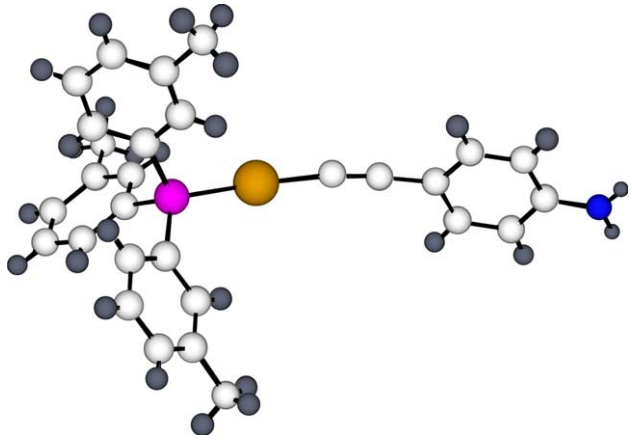


Fig. 1. Molecular structure of **5a** with selected bond lengths (Å) and angles (°); Au(1)–P(1) 2.2686(8), Au(1)–C(1) 1.990(3), C(1)–C(2) 1.198(4), P(1)–Au(1)–C(1) 176.21(10), Au(1)–C(1)–C(2) 166.9(3), C(1)–C(2)–C(3) 176.1(4).

Vicente et al. [15] have previously shown the synthetic versatility of the acetylacetonate (acac) gold(I) complexes as starting materials for the preparation of a wide variety of both organometallic and coordination gold compounds, including alkynyl derivatives [10,25,31,34,35,58,59]. The "acac method" is based on the ability of gold(I)acac derivatives to deprotonate substrates that contain an acidic hydrogen. The reactions occur with the formation of complexes in which the deprotonated ligands coordinate to the metal centre occupying the vacancy generated upon liberation of acetylacetone. This method has also allowed the synthesis of a range of homoleptic anionic (alkynyl)gold(I) derivatives of general formula PPN[Au(C≡CR)$_2$] (R = H, Bu^t, $SiMe_3$, CH_2Cl, CH_2Br, CH_2OH, C≡CH, *p*-$C_6H_4CCC_6H_5$) [34,35,60].

The reaction of PPN[Au(acac)$_2$] and 4-ethynylaniline (1:2) in degassed dichloromethane yielded the anionic complex, PPN[Au(C≡C-4-$C_6H_4NH_2$)$_2$] **7** in quantitative yield (Scheme 1). This was easily characterised on the basis of analytical and spectroscopic data. Notably, a molecular anion of 100% relative intensity was seen in the negative ion FAB mass spectrum and two doublets were seen in the aromatic region of the ^{1}H NMR spectrum.

In conclusion, we have shown that a range of gold(I) *para*-amino substituted arylacetylide complexes can be readily prepared in high yields from the corresponding ethynylanilines, and our future efforts will focus on the development of multimetallic arrays via functionalisation of the amino group.

3. Experimental

Technical grade solvents were purified by standard procedures. Unless otherwise stated, the reactions were carried out at room temperature without special precautions against moisture. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ solutions on a Bruker AMX400 spectrometer at room temperature. Chemical

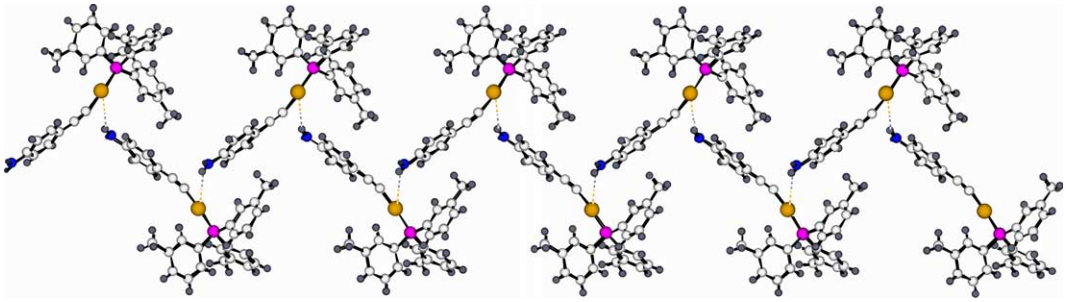


Fig. 2. Packing diagram for **5a** highlighting the intermolecular NH···Au interactions.

shifts are referenced to H_3PO_4 (^{31}P) or TMS (^1H and ^{13}C). The gold complexes [AuCl(SMe$_2$)] [61], PPN[Au(acac)$_2$] [62] and the organic ligands 4-ethynylaniline [63] and 2-methyl-4-ethynylaniline [64] were prepared as described in the literature.

*3.1. Synthesis of [AuC≡CC$_6$H$_3$(R-2)NH$_2$ − 4]$_n$[R = H (**1a**), Me (**1b**)]*

To a solution of 2-R-4-ethynylaniline (R = H, 192 mg, 1.64 mmol; Me, 213 mg, 1.76 mmol) in CH_2Cl_2 (20 mL) were successively added NEt_3 (**1a**: 0.4; **1b**: 1 mL) and [AuCl(SMe$_2$)] (**1a**: 483 mg, 1.64 mmol; **1b**: 519 mg, 1.76 mmol). The reaction mixture was stirred for 0.5 (**1a**) or 1 (**1b**) h. In the case of R = H, the resulting suspension was filtered and the solid washed with CH_2Cl_2 (4 × 5 mL) and air dried to give **1a** as an orange powder. For R = Me, the resulting solution was concentrated under reduced pressure to ca. 10 mL and MeOH (10 mL) was added to precipitate a dark-orange powder which was filtered, washed with Et_2O (2 × 5 mL) and air dried to give **1b**.

*3.1.1. Compound **1a***

Yield: 456 mg, 89%. *Anal.* Calc. for C_8H_6AuN: C, 30.69; H, 1.93; N, 4.47. Found: C, 29.90; H, 2.40; N, 4.40%. IR (cm^{-1}): *ν*(NH), 3344(br), 3205(br); *ν*(C≡C), 1998(w).

*3.1.2. Compound **1b***

Yield: 412 mg, 72%. *Anal.* Calc. for $C_9H_8AuN \cdot CH_2Cl_2$: C, 28.98; H, 2.42; N, 3.38. Found: C, 28.12; H, 2.45; N, 3.57%. IR (cm^{-1}): *ν*(C≡C), 1988(w).

*3.2. Synthesis of [Au(C≡CC$_6$H$_3$(R-2)NH$_2$-4)(L)] [R = H, L = PPh$_3$ (**2a**), P(C$_6$H$_4$OMe-4)$_3$ (**3a**), P(C$_6$H$_4$F-4)$_3$ (**4a**), P(C$_6$H$_4$Me-3)$_3$ (**5a**), XylNC (**6a**); R = Me, L = P(C$_6$H$_4$OMe-4)$_3$ (**3b**), P(C$_6$H$_4$F-4)$_3$ (**4b**), XylNC (**6b**)]*

To a suspension of **1a** (**2a**: 166 mg, 0.53 mmol; **3a**: 290 mg, 0.92 mmol; **4a**: 273 mg, 0.87 mmol; **5a**: 150 mg, 0.48 mmol; **6a**: 230 mg, 0.78 mmol) or **1b** (**3b:** 313 mg, 0.96 mmol; **4b**: 188 mg, 0.6 mmol; **6b**: 196 mg, 0.62 mmol) in CH_2Cl_2 (15–25 mL) was added the appropriate ligand (**2a**: PPh_3, 209 mg, 0.8 mmol; **3a**: P(C$_6$H$_4$OMe-4)$_3$, 326 mg, 0.92 mmol; **4a**: P(C$_6$H$_4$F-4)$_3$, 276 mg, 0.87 mmol; **5a**: P(C$_6$H$_4$Me-3)$_3$, 146 mg, 0.48 mmol**;** **6a**: XylNC, 153 mg, 1.17 mmol; **3b**: P(C$_6$H$_4$OMe-4)$_3$, 337 mg, 0.96 mmol; **4b**: P(C$_6$H$_4$F-4)$_3$, 182 mg, 0.6 mmol; **6b**: XylNC, 94 mg, 0.7 mmol). The reaction mixture was stirred for 0.5 (**6b**) or 1 (**2a**, **4a**, **3b**, **4b**) or 1.5 (**3a**) or 2.5 (**6a**) or 3 (**5a**) h and filtered through anhydrous $MgSO_4$. The solution was concentrated under vacuum to 1 (**2a**, **6a**, **6b**) or 2 (**4a**, **3b**) mL or to dryness (**3a**, **5a**, **4b**) and Et_2O (**2a**, **3a**: 20 mL; **6b**: 10 mL) or *n*hexane (**4a**: 10 mL; **4b**: 20 mL) or a mixture of both (**5a**: 4:1, 25 mL; **6a**: 2:1, 15 mL; **3b**: 2:1, 30 mL) was added. After stirring for 15 min, the suspension was filtered and the solid was air dried to give a bright yellow (**2a**) or orange (**3a**, **6a**, **6b**) or pale yellow (**4a** · 2H_2O, **5a**) or brown (**3b**, **4b**) solid.

*3.2.1. Compound **2a***

Yield: 127 mg, 41%. *Anal.* Calc. for $C_{26}H_{21}AuNP$: C, 54.27; H, 3.68; N, 2.43. Found: C, 54.90; H, 3.90; N, 1.85%. IR (cm^{-1}): *ν*(NH), 3450(s), 3350(s); *ν*(C≡C), 2103(s). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.38–7.51 (m, 15 H, PPh_3), 7.31 (d, 2 H, Ar, $^3J_{HH}$ = 7 Hz), 6.54 (d, 2 H, Ar, $^3J_{HH}$ = 7 Hz), 3.66 (brs, 2 H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 145.3, 134.2 (d, *i*-PPh_3, $^1J_{CP}$ = 15 Hz), 133.6, 131.1 (m, m-+ *p*-PPh_3), 129.0 (d, *o*-PPh_3, $^2J_{CP}$ = 11 Hz), 114.6, 114.5, 104.8 (C≡C). ^{31}P NMR (162 MHz, $CDCl_3$): *δ* 39.9 (s, PPh_3). MS-FAB$^+$ (*m*/*z*, %) 575 (M$^+$, 23%).

*3.2.2. Compound **3a***

Yield: 352 mg, 58%. *Anal.* Calc. for $C_{29}H_{27}AuNO_3P$: C, 52.34; H, 4.09; N, 2.11. Found: C, 52.48; H, 4.13; N, 1.67%. IR (cm^{-1}): *ν*(NH), 3459(s), 3345(s); *ν*(C≡C), 2104(s). ^1H NMR (400 MHz, $CDCl_3$): *δ* 7.47–7.42 (m, 6 H, PR_3), 7.33 (d, 2 H, Ar, $^3J_{HH}$ = 8 Hz), 6.95–6.93 (m, 6 H, PR_3), 6.56 (d, 2 H, Ar, $^3J_{HH}$ = 8 Hz), 3.83 (s, 9 H, MeO), 3.69 (brs, 2H, NH_2). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 162.0 (*p*-PR_3), 145.3, 135.6 (d, *o*-PR_3, $^2J_{CP}$ = 15 Hz), 133.5; 133.4, 121.4 (d, *i*-PR_3, $^1J_{CP}$ = 60

Hz), 114.6 (d, *m*-PR_3, $^3J_{CP}$ = 13 Hz), 114.5, 104.8 (C≡C), 55.3 (MeO). ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.4 (s, PR_3). MS-FAB$^+$ (*m*/*z*, %) 665 (M^+, 14%).

3.2.3. Compound **3b**

Yield: 350 mg, 54%. *Anal*. Calc. for $C_{30}H_{29}AuNO_3P$: C, 53.03; H, 4.30; N, 2.06. Found: C, 53.22; H, 4.66; N, 1.76%. IR (cm^{-1}): ν(NH), 3458(s), 3346(s); ν(C≡C), 2104(s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42–7.37 (m, 6 H, PR_3), 7.22 (d, 1 H, Ar, $^4J_{HH}$ = 2 Hz), 7.19 (dd, 1 H, Ar, $^3J_{HH}$ = 8 Hz, $^4J_{HH}$ = 2 Hz), 6.90–6.88 (m, 6 H, PR_3), 6.52 (d, 1 H, Ar, $^3J_{HH}$ = 8 Hz), 3.80 (s, 9 H, MeO), 3.61 (brs, 2 H, NH_2), 2.08 (s, 3 H, MeAr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.8 (*p*-PR_3), 143.6, 135.6 (d, *o*-PR_3, $^2J_{CP}$ = 16 Hz), 134.6, 131.2, 121.8 (d, *i*-PR_3, $^1J_{CP}$ = 60 Hz), 121.7, 114.6 (d, *m*-PR_3, $^3J_{CP}$ = 12 Hz), 114.6, 114.4, 55.4 (MeO), 17.2 (MeAr). ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm): 39.9 (s, PR_3). FAB$^+$ (*m*/*z*, %) 679 (M^+, 25%).

3.2.4. Compound **4a**

Yield: 421 mg, 77%. *Anal*. Calc. for $C_{26}H_{22}AuF_3NO_2P \cdot 2H_2O$: C, 46.93; H, 3.33; N, 2.11. Found: C, 47.47; H, 3.23; N, 2.25%. IR (cm^{-1}): ν(NH), 3432(s), 3325(s); ν(C≡C), 2109(s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54–7.46 (m, 6 H, PR_3), 7.29 (d, 2 H, Ar, $^3J_{HH}$ = 8 Hz), 7.18–7.13 (m, 6 H, PR_3), 6.55 (d, 2 H, Ar, $^3J_{HH}$ = 8 Hz), 3.69 (brs, NH_2, 2H), 1.66 (s, 4H, H_2O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9 (d, *p*-PR_3, $^1J_{CF}$ = 260 Hz), 136.3 (dd *o*-PR_3, $^3J_{CF}$ = 9 Hz, $^2J_{CP}$ = 16 Hz,), 133.6, 133.4, 125.3 (di-PR_3, $^1J_{CP}$ = 58 Hz,), 116.8 (dd *m*-PR_3, $^2J_{CF}$ = 21 Hz, $^3J_{CP}$ = 13 Hz,), 114.6, 114.1. ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.8 (s, PR_3). MS-FAB$^+$ (*m*/*z*, %) 629 (M^+, 25%).

3.2.5. Compound **4b**

Yield: 200 mg, 52%. *Anal*. Calc. for $C_{27}H_{20}AuF_3NP$: C, 50.41; H, 3.13; N, 2.18. Found: C, 50.70; H, 3.34; N, 2.12%. IR (cm^{-1}): ν(NH), 3450(s), 3356(s); ν(C≡C), 2109(s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.07 (s, 3H, MeAr), 3.63 (brs, 2H, NH_2), 6.52 (d, 1H, Ar, J_{HH} = 8Hz), 7.12–7.21 (m, 8 H, Ar + PR_3), 7.53–7.46 (m, 6 H, PR_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.9 (dd, *p*-PR_3, $^1J_{CF}$ = 253 Hz, $^4J_{CP}$ = 2 Hz), 143.9 (Ar), 136.3 (dd, *o*-PR_3, $^2J_{CP}$ = 16 Hz, $^3J_{CF}$ = 9 Hz), 134.6, 131.2, 125.2 (d, *i*-PR_3, $^1J_{CP}$ = 58 Hz), 121.7, 116.8 (dd, m-PR_3, $^2J_{CF}$ = 21 Hz, $^3J_{CP}$ = 12 Hz), 114.4, 114.0, 105.3 (C≡C), 17.2 (ArMe). ^{31}P NMR (162 MHz, $CDCl_3$): δ 41.6 (s, PR_3). FAB$^+$ (*m*/*z*, %) 643 (M^+, 35%).

3.2.6. Compound **5a**

Yield: 211 mg, 71%. *Anal*. Calc. for $C_{29}H_{27}AuNP$: C, 56.41; H, 4.41; N, 2.27. Found: C, 56.17; H, 4.55; N, 2.34%. IR (cm^{-1}): ν(NH), 3459(s), 3355(s); ν(C≡C), 2108(s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41 (m, 3H, PR_3), 7.31 (d, 2H, Ar, $^3J_{HH}$ = 9 Hz), 7.29–7.17 (m, 9 H, PR_3), 6.53 (d, 2H, Ar, $^3J_{HH}$ = 9 Hz), 3.67 (brs, NH_2, 2H), 2.31 (s, 9H, Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.3, 138.9 (d, PR_3, *J* = 12 Hz), 134.9 (d, PR_3, *J* = 16 Hz), 133.5, 132.2 (s, PR_3), 131.0 (d, PR_3, *J* = 12 Hz), 130.0 (d, *i*-PR_3, $^1J_{CP}$ = 55 Hz), 128.8 (d, PR_3, *J* = 12 Hz), 114.6, 114.4, 104.8 (C≡C), 21.4 (Me, PR_3). ^{31}P NMR (162 MHz, $CDCl_3$): δ 43.5 (s, PR_3). FAB$^+$ (*m*/*z*, %) 617 (M^+, 35%).

3.2.7. Compound **6a**

Yield 230 mg, 70%. *Anal*. Calc. for $C_{17}H_{15}AuN_2$: C, 45.96; H, 3.40; N, 6.31. Found: C, 45.86; H, 3.56; N, 6.13%. IR (cm^{-1}): ν(NH), 3452(s), 3352(s), ν(C≡N), 2194(s); ν(C≡C), 2110(s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31–7.25 (m, 3 H, Xyl + Ar), 7.13 (d, 2H, Xyl, $^3J_{HH}$ = 8 Hz), 6.53 (d, 2H, Ar, $^3J_{HH}$ = 9 Hz), 3.69 (brs, 2H, NH_2), 2.40 (s, 6 H, Me). ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.5, 136.1, 133.7, 130.7, 128.4, 124.4 (NCAu), 118.9, 114.5, 114.0, 104.7 (C≡C), 18.7 (Me). FAB$^+$ (*m*/*z*, %) 444 (M^+, 100%).

3.2.8. Compound **6b**

Yield: 150 mg, 55%. *Anal*. Calc. for $C_{18}H_{17}AuN_2$: C, 47.17; H, 3.74; N, 6.11. Found: C, 47.24; H, 3.79; N, 5.91%. IR (cm^{-1}): ν(NH), 3452(s), 3357(s); ν(C≡N), 2207; ν(C≡C), 2113(s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30–7.26 (m, 1H, Xyl), 7.16–7.11 (m, 4H, Ar + Xyl), 6.51 (d, 1 H, Ar, $^3J_{HH}$ = 8 Hz), 3.63 (s, 2H, NH_2), 2.39 (s, 6H, Me, Xyl), 2.06 (s, 3H, MeAr). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 136.0, 134.7, 131.4, 130.7, 128.3, 124.5 (NCAu), 121.6, 118.7, 114.4, 114.0, 105.0 (C≡C), 18.7 (Me, Xyl), 17.2 (MeAr). FAB$^+$ (*m*/*z*, %) 458 (M^+, 100%).

3.3. Synthesis of *PPN[Au(C≡CC$_6$H$_4$NH$_2$-4)$_2$]* (7)

To a solution of 4-ethynylaniline (284 mg, 2.4 mmol) in CH_2Cl_2 (30 mL) was added solid PPN[Au(acac)$_2$] (1.03 g, 1.1 mmol). After 6 h of stirring, the reaction mixture was filtered through anhydrous $MgSO_4$ and the solution was concentrated in vacuum to dryness. Et_2O (60 mL) was added, the resulting suspension stirred for 1.5 h, filtered, and the solid air dried to give **7** as a yellow powder. Yield: 1.04 g, 98%. *Anal*. Calc. for $C_{52}H_{42}AuN_3P_2$: C, 64.53; H, 4.37; N, 4.34. Found: C, 64.37; H, 4.33; N, 4.62%. IR (cm^{-1}): ν(NH), 3441(s), 3329(s); ν(C≡C), 2096(s). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.68–7.45 (m, 30 H, PPN), 7.12 (d, 4H, Ar, $^3J_{HH}$ = 7 Hz), 6.48 (d, 4H, Ar, $^3J_{HH}$ = 7 Hz), 3.61 (brs, 4H, NH_2). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 144.6, 134.1 (m, *p*-PPN), 133.1, 132.6–132.2 (m, *m*-PPN), 129.9–129.7 (m, *o*-PPN), 127.4 (dd, *i*-PPN, $^3J_{CP}$ = 2 Hz, $^1J_{CP}$ = 107 Hz), 118.0, 114.8, 114.3, 102.3 (C≡C). FAB$^-$ (*m*/*z*, %) 429 (M^-, 100%).

4. X-ray data collection and solution

A single crystal of **5a** was mounted on a glass fibre and all geometric and intensity data were taken from this sample using a Bruker SMART APEX CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 293 ± 2 K. Data reduction was carried out with SAINT+ and absorption correction applied using the programme SADABS. The structure was solved by direct methods and developed by using alternating cycles of least-squares refinement and difference-Fourier synthesis. All non-hydrogen atoms were refined anisotropically. Hydrogens were generally placed in calculated positions (riding model). Structure solution used SHELXTL PLUS V6.10 program package. Crystallographic data for the structural analyses has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 233870.

Crystallographic data; yellow block, dimensions $0.15 \times 0.13 \times 0.12$ mm, monoclinic, space group $P21/n$, $a = 11.2208(7)$, $b = 13.9655(9)$, $c = 16.0613(10)$ (Å), $\beta = 97.945(1)$ (°), $V = 2492.7(3)$ (Å^3), $Z = 4$, $F(000) = 1208$, $D_{calc} = 1.645$ g cm^{-3}, $\mu = 5.982$ mm^{-1}, $T_{max}/T_{min} = 0.534/0.467$. 21 779 reflections were collected, 5975 unique [$R_{int} = 0.0251$] of which 4888 were observed [$I > 2.0\sigma(I)$]. At final convergence, $R_1 = 0.0275$, $wR_2 = 0.0634$ [$I > 2.0\sigma(I)$] and $R_1 = 0.0373$, $wR_2 = 0.0674$ (all data), for 292 parameters.

References

[1] H.-Y. Chao, W. Lu, Y. Li, M.C.W. Chan, C.M. Che, K.K. Cheung, N. Zhu, J. Am. Chem. Soc. 124 (2002) 14696.
[2] C.M. Che, H.Y. Chao, V.M. Miskowski, Y.Q. Li, K.K. Cheung, J. Am. Chem. Soc. 123 (2001) 4985.
[3] M. Bardaji, P.G. Jones, A. Laguna, J. Chem. Soc., Dalton Trans. (2002) 3624.
[4] V.W.W. Yam, K.K.-W. Lo, Chem. Soc. Rev. 28 (1999) 323.
[5] V.W.W. Yam, K.K.-W. Lo, K.M.C. Wong, J. Organomet. Chem. 578 (1999) 3.
[6] A.M. McDonagh, N.T. Lucas, M.P. Cifuentes, M.G. Humphrey, S. Houbrechts, A. Persoons, J. Organomet. Chem. 605 (2000) 193.
[7] S.K. Hurst, N.T. Lucas, M.P. Cifuentes, M.G. Humphrey, M. Samoc, B. Lutherdavies, I. Asselberghs, R. Vanboxel, A. Persoons, J. Organomet. Chem. 633 (2001) 114.
[8] S.K. Hurst, M.P. Cifuentes, A.M. McDonagh, M.G. Humphrey, M. Samoc, B. Lutherdavies, I. Asselberghs, A. Persoons, J. Organomet. Chem. 642 (2002) 259.
[9] P. Alejos, S. Coco, P. Espinet, New J. Chem. 19 (1995) 799.
[10] J. Vicente, M.T. Chicote, M.M. Alvarez-Falcon, M.A. Fox, D. Bautista, Organometallics 22 (2003) 4792.
[11] W.-Y. Wong, K.-H. Choi, G.-L. Lu, J.-X. Shi, P.-Y. Lai, S.-M. Chan, Z. Lin, Organometallics 20 (2001) 5446.
[12] M.J. Irwin, J.J. Vittal, R.J. Puddephatt, Organometallics 16 (1997) 3541.
[13] G.C. Jia, N.C. Payne, J.J. Vittal, R.J. Puddephatt, Organometallics 12 (1993) 4771.
[14] A.J. Deeming, G. Hogarth, M.-Y. Lee, M. Saha, S.P. Redmond, H. Phetmung, A.G. Orpen, Inorg. Chim. Acta 309 (2000) 109.
[15] J. Vicente, M.T. Chicote, Coord. Chem. Rev. 195 (1999) 1143.
[16] M.J. Irwin, L. Manojlovic-Muir, K.W. Muir, R.J. Puddephatt, D.S. Yufit, J. Chem. Soc., Chem. Commun. (1997) 219.
[17] M.J. Irwin, G. Jia, N.C. Payne, R.J. Puddephatt, Organometallics 15 (1996) 51.
[18] W.J. Hunks, M.A. MacDonald, M.C. Jennings, R.J. Puddephatt, Organometallics 19 (2000) 5063.
[19] M.A. MacDonald, R.J. Puddephatt, G.P.A. Yap, Organometallics 19 (2000) 2194.
[20] R.J. Puddephatt, J. Chem. Soc., Chem. Commun. (1998) 1055.
[21] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectrometric Identification of Organic Compounds, 4th ed. (1981) 110.
[22] G.E. Coates, C. Parkin, J. Chem. Soc. (1962) 3220.
[23] D.M.P. Mingos, J. Yau, S. Menzer, D.J. Williams, Angew. Chem., Int. Ed. 34 (1995) 1894.
[24] D.M.P. Mingos, R. Vilar, D. Rais, J. Organomet. Chem. 641 (2002) 126.
[25] J. Vicente, M.T. Chicote, M.M. Alvarez-Falcon, M.D. Abrisqueta, F.J. Hernandez, P.G. Jones, Inorg. Chim. Acta 347 (2003) 67.
[26] C.P. McArdle, J.J. Vittal, R.J. Puddephatt, Angew. Chem., Int. Ed. 39 (2000) 3819.
[27] C.P. McArdle, M.C. Jennings, J.J. Vittal, R.J. Puddephatt, Chem. Eur. J. 7 (2001) 3572.
[28] B.-C. Tzeng, W.-C. Lo, C.-M. Che, S.-M. Peng, J. Chem. Soc., Chem. Commun. (1996) 181.
[29] O.M. Abu-Salah, A.R. Al-Ohaly, Inorg. Chim. Acta 77 (1983) L159.
[30] C.-M. Che, H.-K. Yip, W.-C. Lo, S.-M. Peng, Polyhedron 13 (1994) 887.
[31] J. Vicente, M.T. Chicote, M.D. Abrisqueta, M.M. Alvarez-Falcon, J. Organomet. Chem. 663 (2002) 40.
[32] M.I. Bruce, M.J. Liddell, J. Organomet. Chem. 427 (1992) 263.
[33] F. Mohr, M.C. Jennings, R.J. Puddephatt, Eur. J. Inorg. Chem. (2003) 217.
[34] J. Vicente, M.T. Chicote, M.D. Abrisqueta, J. Chem. Soc., Dalton Trans. (1995) 497.
[35] J. Vicente, M.T. Chicote, M.D. Abrisqueta, P.G. Jones, Organometallics 16 (1997) 5628.
[36] S.K. Hurst, M.G. Humphrey, J.P. Morrall, M.P. Cifuentes, M. Samoc, B. Luther-Davies, G.A. Heath, A.C. Willis, J. Organomet. Chem. 670 (2003) 56.
[37] W.-Y. Wong, K.-Y. Ho, K.-H. Choi, J. Organomet. Chem. 670 (2003) 17.
[38] T.E. Müller, S.W.K. Choi, D.M.P. Mingos, D. Murphy, D.J. Williams, V.W.W. Yam, J. Organomet. Chem. 484 (1994) 209.
[39] I.R. Whittall, M.G. Humphrey, S. Houbrechts, A. Persoons, D.C.R. Hockless, Organometallics 15 (1996) 5738.
[40] J. Vicente, M.T. Chicote, M.D. Abrisqueta, M.C.R. Dearellano, P.G. Jones, M.G. Humphrey, M.P. Cifuentes, M. Samoc, B. Lutherdavies, Organometallics 19 (2000) 2968.
[41] R.Y. Liau, A. Schier, H. Schmidbaur, Organometallics 22 (2003) 3199.
[42] T. Steiner, G.R. Desiraju, Chem. Commun. (1998) 891.
[43] M. Mascal, Chem. Commun. (1998) 303.
[44] R. Taylor, O. Kennard, J. Am. Chem. Soc. 104 (1982) 5063.
[45] I. Dance, New J. Chem. 27 (2003) 22.
[46] P.G. Jones, S. Friedrichs, Chem. Commun. (1999) 1365.
[47] D. Koch, K. Sünkel, W. Beck, Z. Naturforsch. B 54 (1999) 96.
[48] B. Ahrens, S. Friedrichs, R. Herbst-Irmer, P.G. Jones, Eur. J. Inorg. Chem. (2000) 2017.
[49] D.B. Leznoff, B.-Y. Xue, R.J. Batchelor, F.W.B. Einstein, B.O. Patrick, Inorg. Chem. 40 (2001) 6026.

[50] S. Friedrichs, P.G. Jones, Acta Crystallogr. Sect. C 55 (1999) 1625.
[51] O.E. Piro, E.E. Castellano, R.C.V. Piatti, A.E. Bolzán, A.J. Arvia, Acta Crystallogr., Sect. C 58 (2002) m252.
[52] I.K. Chu, I.P.Y. Shek, K.W.M. Siu, W.-T. Wong, J.-L. Zuo, T.-C. Lau, New J. Chem. 24 (2000) 765.
[53] P.G. Jones, B. Ahrens, New J. Chem. (1998) 1041.
[54] G.C. Jia, R.J. Puddephatt, J.J. Vittal, Polyhedron 11 (1992) 2009.
[55] J.D.E.T. Wilton-Ely, A. Schier, N.W. Mitzel, S. Nogai, H. Schmidbaur, J. Organomet. Chem. 643 (2002) 313.
[56] E. Colacio, F. Lloret, R. Kivekäs, J. Suarez-Varela, M.R. Sundberg, R. Uggla, Inorg. Chem. 42 (2003) 560.
[57] H. Schmidbaur, Chem. Soc. Rev. 24 (1995) 391.
[58] J. Vicente, M.T. Chicote, M.D. Abrisqueta, M.M. Alvarez-Falcon, M.C. RamirezdeArellano, P.G. Jones, Organometallics 22 (2003) 4327.
[59] J. Vicente, M.T. Chicote, M.D. Abrisqueta, P.G. Jones, Organometallics 19 (2000) 2629.
[60] M.I. Bruce, B.C. Hall, B.W. Skelton, M.E. Smith, A.H. White, J. Chem. Soc., Dalton Trans. (2002) 995.
[61] A. Tamaki, J.K. Kochi, J. Organomet. Chem. 64 (1974) 411.
[62] J. Vicente, M.T. Chicote, Inorg. Synth. 32 (1998) 172.
[63] A.P. Melissaris, M.H. Litt, J. Org. Chem. 59 (1994) 5818.
[64] G.C. Jia, R.J. Puddephatt, J.J. Vittal, N.C. Payne, Organometallics 12 (1993) 263.