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Gold(I) phosphine-decorated 2,2′:6′,2″-terpyridine ligands

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Abstract

The synthesis and characterization of the ligands R_3PAu(**1**–H) (R = ^{n}Bu, Ph) and (**1**–H)Au(μ-dppe)Au(**1**–H) (**1** = HC≡CCH$_2$Otpy, tpy = 2,2′:6′,2″-terpyridine) are reported. The single crystal structures of $^n Bu_3PAu$(**1**–H) and (**1**–H)Au(μ-dppe)Au(**1**–H) have been determined, and weak hydrogen bonding rather than aurophilic interactions operate between the molecules in the solid state.

Keywords: Gold(I); 2,2′:6′,2″-Terpyridine; Phosphine; Alkyne; Ligand

1. Introduction

The use of terminal C≡CH groups to produce organometallic complexes through M–C σ-bond formation is well documented, with platinum(II) and gold(I) derivatives being especially important [1–4]. Current interest is these derivatives arises from possible applications in advanced materials based upon their luminescent [5–9] and nonlinear optical [3,10–13] properties. We have recently reported a family of platinum(II)-centred ditopic 2,2′:6′,2″-terpyridine (tpy) ligands which are synthesized by coupling 4′-(2-propyn-1-oxy)-2,2′:6′,2″-terpyridine (HC≡CCH$_2$Otpy (**1**)) with *trans*-[PtI$_2$(PR$_3$)$_2$] (R = Et, ^{n}Bu, Ph) [14,15] or 4′-(4,7,10-trioxadec-1-yn-10-yl)-2,2′:6′,2″-terpyridine with *trans*-[PtI$_2$(PEt$_3$)$_2$] [16]. Metal binding by the tpy domains leads to the formation of [n + n] metallomacrocyclic products with n = 2, 3 or 4 for M = Fe(II). Mixtures of these products convert in solution to the thermodynamically favoured $[Fe_2L_2]^{4+}$ [15]. We have now turned our attention to gold(I) alkynyl derivatives [17], and report here a series of new ligands in which tpy domains are linked to C≡CAuPR$_3$ (R = ^{n}Bu, Ph) or C≡CAu(μ-dppe)AuC≡C units (dppe = bis(diphenylphosphino)ethane). Previous examples of gold(I) σ-acetylide-functionalized polypyridine ligands have been based upon 1,10-phenanthroline [18–21].

2. Experimental

2.1. General procedures

Infrared spectra were recorded on a Shimadzu FTIR-8400S spectrophotometer with samples as solids using a Golden Gate ATR accessory. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer; the numbering scheme adopted for the ligands are shown in the reaction schemes. Chemical shifts for ^{1}H and ^{13}C NMR spectra are referenced with respect to residual solvent peaks and TMS = δ 0 ppm; ^{31}P NMR signals are referenced with respect to 85% aqueous H_3PO_4. MALDI-TOF mass spectra were recorded using a PerSeptive Biosystems Voyager mass spectrometer with α-cyano-4-hydroxycinnamic acid matrix. Electronic absorption spectra were recorded on a Varian-Cary 5000 spectrophotometer.

Compound **1** [22] $^n Bu_3PAuCl$ [23] and ClAu(μ-dppe)AuCl [24–26] were prepared by literature methods. Ph_3PAuCl was purchased from ChemPur.

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2.2. Compound 2

Compound **1** (0.219 g, 0.763 mmol), $^{n}Bu_3PAuCl$ (0.330 g, 0.759 mmol) and CuI (14.7 mg, 77.2 μmol) were added to Et_3N (10 ml). The reaction mixture was stirred at room temperature for 4 h. Solvent was then removed and the product was separated by column chromatography (alumina, CH_2Cl_2–acetone 99:1). There was a single fraction, from which **2** was isolated as a white oil (0.233 g, 0.340 mmol, 44.8%). Crystals of **2** could be obtained by slow evaporation of the crude reaction mixture. Compound **2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.65 (ddd, *J* 4.7, 1.8, 0.8 Hz, 2H, H^{A6}), 8.54 (dt, *J* 7.9, 0.9 Hz, 2H, H^{A3}), 8.04 (s, 2H, H^{B3}), 7.79 (dt, *J* 7.6, 2.0 Hz, 2H, H^{A4}), 7.26 (ddd, *J* 7.6, 5.1, 1.0 Hz, 2H, H^{A5}), 5.01 (s, 2H, OCH_2), 1.67 (m, 6H, PCH_2), 1.48 (m, 6H, PCH_2CH_2), 1.38 (sextet, *J* 7.6 Hz, 6H, CH_2CH_3), 0.87 (t, *J* 7.6 Hz, 9H, CH_3); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 166.4 (C^{B4}), 156.9 ($C^{B2/A2}$), 156.1 ($C^{B2/A2}$), 148.9 (C^{A6}), 136.5 (C^{A4}), 123.5 (C^{A5}), 121.2 (C^{A3}), 107.7 (C^{B3}), 96.6 ($C{\equiv}CAu$), 57.2 (OCH_2), 27.1 (s, CH_2CH_3), 25.4 (d, J_{PC} 33.0 Hz, PCH_2), 24.1 (d, J_{PC} 14.0 Hz, PCH_2CH_2), 13.5 (s, CH_3), signal for $C{\equiv}CAu$ not resolved; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ (ppm) 25.7. MALDI-MS *m*/*z* 686 $[M]^+$, 288 $[M-AuPBu_3]^+$. IR (ν, cm^{-1}) 2955 w, 2924 w, 2862 w, 2361 w, 2130 w, 1736 w, 1558 m, 1450 m, 1404 m, 1335 m, 1188 m, 1088 m, 1018 s, 879 w, 795 m, 741 m, 617 w, 563 w, 525 w. UV/Vis λ_{max}/nm 247, 277.

2.3. Compound 3

Compound **1** (0.0820 g, 0.285 mmol), Ph_3PAuCl (0.148 g, 0.299 mmol) and CuI (10.9 mg, 57.3 μmol) were added to Et_3N (12 ml) and CH_2Cl_2 (12 ml). The reaction mixture was stirred at room temperature for 2 h. The precipitate that formed was separated by filtration, and then solvent was then removed from the filtrate to give a yellow-green oil. Purification by column chromatography (alumina, CH_2Cl_2–acetone 99:1) gave one fraction yielding **3** as a white oil (0.145 g, 0.194 mmol, 68.1%). **2**: ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.67 (ddd, *J* 4.5, 2.0, 1.2 Hz, 2H, H^{A6}), 8.57 (dt, *J* 8.0, 1.2 Hz, 2H, H^{A3}), 8.09 (s, 2H, H^{B3}), 7.81 (dt, *J* 7.6, 1.6 Hz, 2H, H^{A4}), 7.47 (m, 9H, $H^{Ph3,4}$), 7.41 (m, 6H, H^{Ph2}), 7.28 (ddd, *J* 7.2, 4.8, 1.2 Hz, 2H, H^{A5}), 5.08 (s, 2H, OCH_2); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ (ppm) 166.5 (C^{B4}), 157.0 ($C^{B2/A2}$), 156.2 ($C^{B2/A2}$), 149.0 (C^{A6}), 136.6 (C^{A4}), 134.2 (d, J_{PC} 13.8 Hz, $C^{Ph2/3}$), 131.5 (s, C^{Ph4}), 129.9 (d, J_{PC} 140 Hz, $C{\equiv}CAu$), 129.5 (d, J_{PC} 55.0 Hz, C^{Ph1}), 129.1 (d, J_{PC} 11.3 Hz, $C^{Ph2/3}$), 123.6 (C^{A5}), 121.3(C^{A3}), 107.8 (C^{B3}), 96.8 (d, J_{PC} 26 Hz, $C{\equiv}CAu$), 57.2 (OCH_2); $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ (ppm) 38.8. MALDI-MS *m*/*z* 748 $[M]^+$, 289 $[M-Ph_3PAu]^+$ (base peak). IR (ν, cm^{-1}) 3066 w, 2963 w, 2921 w, 2863 w, 2350 w, 2130 w, 1581 s, 1563 s, 1469 m, 1436 m, 1406 m, 1345 m, 1334 m, 1186 m, 1101 m, 1020 s, 795 m, 745 m, 692 s. UV/Vis λ_{max}/nm (2.39×10^{-5} mol dm^{-3}, CH_2Cl_2) 249 (ε/dm^3 mol^{-1} cm^{-1} 106,000), 278 (72,700).

2.4. Compound 4

Compound **1** (0.270 g, 0.941 mmol), ClAu(dppe)AuCl (0.405 g, 0.469 mmol) and CuI (9.4 mg, 49.4 μmol) were added to Et_3N (12 ml) and CH_2Cl_2 (12 ml). The reaction mixture was stirred at room temperature for 4 d. The crude product formed as a precipitate and was removed by filtration. It was purified by column chromatography (alumina, CH_2Cl_2–acetone 90:10). One fraction was eluted and from this, **4** was isolated as a white oil (0.253 g, 0.185 mmol, 39.4%). Crystalline 4 was obtained from a $CHCl_3$ solution left standing at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.63 (ddd, *J* 4.8, 1.8, 0.8 Hz, 4H, H^{A6}), 8.55 (dt, *J* 8.0, 0.8 Hz, 4H, H^{A3}), 8.06 (s, 4H, H^{B3}), 7.78 (dt, *J* 7.6, 1.8 Hz, 4H, H^{A4}), 7.56 (m, 8H, Ph), 7.7–7.3 (overlapping m, 12H, Ph), 7.25 (ddd, *J* 7.6, 4.8, 1.0 Hz, 4H, H^{A5}), 5.00 (s, 4H, OCH_2), 2.56 (br s, 4H, PCH_2); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 166.4 (C^{B4}), 157.0 ($C^{B2/A2}$), 156.1 ($C^{B2/A2}$), 149.0 (C^{A6}), 136.6 (C^{A4}), 134.9 (C^{Phipso}), 133.2 (t, J_{PC} 7 Hz, $C^{Ph2/3}$), 132.1 (C^{Ph4}), 129.5 (t, J_{PC} 5 Hz, $C^{Ph2/3}$), 123.7 (C^{A5}), 121.3 (C^{A3}), 107.7 (C^{B3}), 97.0 ($C{\equiv}CAu$), 57.1 (OCH_2), 23.7 (PCH_2), signal for $C{\equiv}CAu$ not resolved; $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ (ppm) 36.5. MALDI-MS *m*/*z* 1388 $[M+Na]^+$. IR (ν, cm^{-1}) 3055 w, 2924 m, 2854 m, 1697 w, 1558 s, 1435 s, 1404 s, 1335 s, 1258 m, 1188 s, 1103 m, 1018 s, 879 s, 795 m, 725 s, 687 s. UV/Vis λ_{max}/nm (4.62×10^{-5} mol dm^{-3}, CH_2Cl_2) 233 (ε/dm^3 mol^{-1} cm^{-1} 55,500), 253 sh (37,900), 277 (30,400).

2.5. Crystal structure determinations: general

Data were collected on an Enraf Nonius Kappa CCD instrument; data reduction, solution and refinement used the programmes COLLECT [27], SIR92 [28], DENZO/SCALEPACK [29] and CRYSTALS [30].

2.6. Crystal data for 2

$C_{30}H_{39}AuN_3OP$, $M = 685.60$, triclinic, space group $P\bar{1}$, $a = 11.1882(2)$, $b = 11.3401(2)$, $c = 14.3037(2)$ Å, $\alpha = 92.6970(9)$, $\beta = 110.5440(7)$, $\gamma = 116.1495(8)°$, $U = 1480.86(5)$ $Å^3$, $Z = 2$, $D_{calc} = 1.537$ Mg m^{-3}, μ(Mo-Kα) = 5.047 mm^{-1}, $T = 173$ K, 8610 reflections collected. Refinement of 8555 reflections (325 parameters) with $I > 2.0\sigma I$) converged at final $R_1 = 0.0315$ (R_1 all data = 0.0498), $wR_2 = 0.0491$ (wR_2 all data = 0.0592), goodness-of-fit = 0.968.

2.7. Crystal data for 4 · 4CHCl3

$C_{66}H_{52}Au_2Cl_{12}N_6O_2P_2$, $M = 1842.49$, triclinic, space group $P\bar{1}$, $a = 8.7136(3)$, $b = 13.3106(4)$, $c = 15.9758(4)$ Å, $\alpha = 110.037(2)$, $\beta = 91.133(2)$, $\gamma = 95.801(2)°$, $U = 1728.92(9)$ $Å^3$, $Z = 1$, $D_{calc} = 1.770$ Mg m^{-3}, μ(Mo-Kα) = 4.797 mm^{-1}, $T = 173$ K, 7916 reflections collected. Refinement of 5094 reflections (442 parameters) with $I > 3.0\sigma$ *I*) converged at final $R_1 = 0.0325$ (R_1 all data = 0.0626),

$wR_2 = 0.0359$ (wR_2 all data = 0.0574), goodness-of-fit = 1.112.

3. Results and discussion

The reactions of alkyne **1** with $^{n}Bu_3PAuCl$ and Ph_3PAuCl were carried out using standard conditions [31] (Scheme 1). The yields of products **2** and **3** were affected by the choice of Et_3N or a mixture of Et_3N and CH_2Cl_2 as solvent. The MALDI mass spectra of **2** and **3** showed parent ions at m/z 686 and 748, respectively. Fragmentation by loss of the $AuPR_3$ unit was observed for both compounds. The $^{31}P\{^1H\}$ NMR spectrum of solutions of each of **2** and **3** exhibited one singlet (δ 25.7 ppm for **2**, δ 38.8 ppm for **3**). Both compounds were characterized by ^1H and ^{13}C NMR spectroscopies. In the ^1H NMR spectra, the signals assigned to the tpy protons of **2** and **3** were characteristic of a non-coordinated ligand, confirming that there had been no competition between alkyne and tpy domains for interaction with the gold(I) centre. The loss of the signal for the C≡CH proton in **1** was evidence for the formation of a C–Au bond. On going from **1** to **3**, the signals in the ^{13}C NMR spectrum assigned to the C≡C units shifted to higher frequency, from δ 77.6 and 76.3 ppm in **1** [22] to δ 129.9 and 96.8 ppm in **3**. Each of these signals was a doublet with coupling of the ^{31}P *trans* to the alkyne unit (J_{PC} 140 Hz, for C≡*C*Au and J_{PC} 26 Hz for *C*≡CAu). These chemical shifts and coupling constants are similar to data reported for other $RC{\equiv}CAuPR'_3$ species [32–36]. For compound **2**, the ^{13}C NMR signal for the *C*≡CAu carbon was observed at δ 96.6 ppm, but the resonance for the metal-bonded C atom could not be resolved. Single crystals of **2** suitable for X-ray crystallography were serendipitously grown by slow evaporation of the crude reaction mixture (CH_2Cl_2–Et_3N 1:1 solvent). Crystals of **2** (colourless plates) were separated from crystals of **1** (large blocks) by hand. The molecular structure of **2** is shown in Fig. 1 and selected bond parameters are listed in the caption. The tpy unit is in the *trans*,*trans*-conformation that is expected for a non-coordinated ligand. The terpy unit deviates slightly from planarity, with the angles between the least squares planes of the rings being 14.0(2)° (for rings containing N1 and N2) and 3.6(2)° (for rings containing N2 and N3). The fact that bond C8–O1 is shorter (1.367(4) Å) than O1–C16 (1.443(4) Å) is consistent with the O atom being sp^2 hybridized, and there being a degree of π-delocalization between the central pyridine ring and oxygen atom. The structural determination confirms the presence of a linear C–C≡C–Au–P unit. All other structural parameters are as expected. In the crystal lattice, molecules of **2** form dimeric motifs, supported by non-classical C–H···N hydrogen bonds (Fig. 2). Rows of dimers assemble along the *a*-axis, with weak C–H···π-alkyne interactions [37–42] operating between dimers (C15H151···C18 = 2.72 Å, C15H151···C17 = 3.00 Å). These rows are aligned so as to produce alternating domains of alkyl and tpy groups (Fig. 3). Interestingly, the weak C–H···N and C–H···π-alkyne interactions dictate the molecular packing, and there are no aurophilic [43,44] or π-stacking interactions.

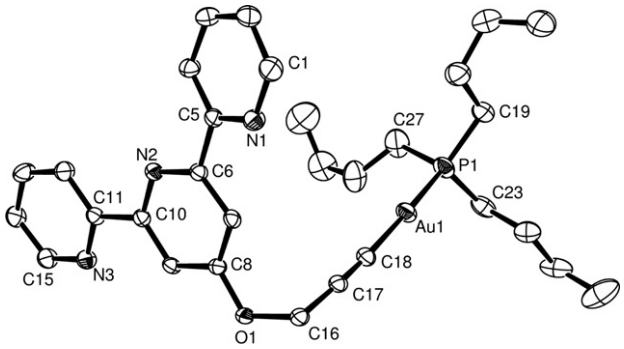
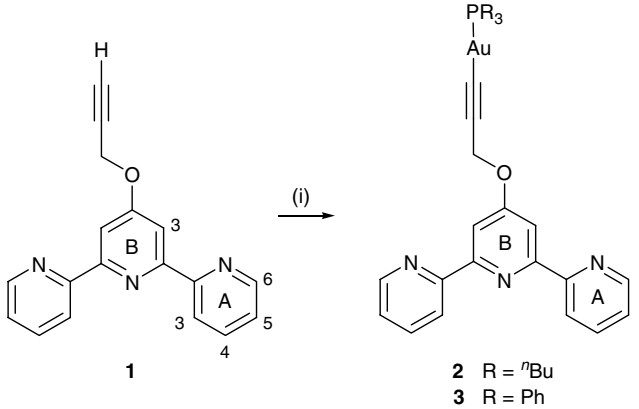


Fig. 1. The structure of **2** with displacement ellipsoids drawn at the 30% probability level; H atoms omitted for clarity. Selected bond lengths and angles: Au1–P1=2.279(1), Au1–C18 = 2.018(4), C17—C18 = 1.186(5), C16–C17 = 1.467(5), C16–O1 = 1.443(4), C8–O1 = 1.367(4), C5–C6 = 1.491(4), C10–C11 = 1.493(4) Å; P1–Au1–C18 = 175.1(1), Au1–C18–C17 = 175.3(3), C18–C17—C16 = 176.7(4), C17—C16–O1 = 111.5(3), C16–O1–C8 = 117.4(3)°.



Scheme 1. Reaction scheme for the formation of **2** and **3**: (i) R_3PAuCl, CuI in Et_3N (for **2**) or Et_3N/CH_2Cl_2 (for **3**). The ring labelling is used for NMR assignments.

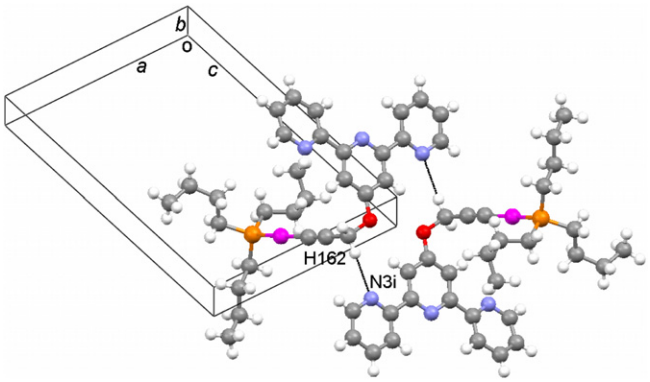


Fig. 2. Dimeric motif in the packing of **2**; symmetry code i = 2 − *x*, 2 − *y*, −*z*. C16H162···N3i=2.53, C16···N3i = 3.433(5) Å; C16–H162···N3i = 158.0°.

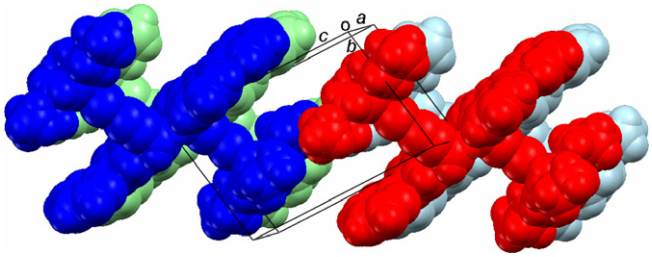
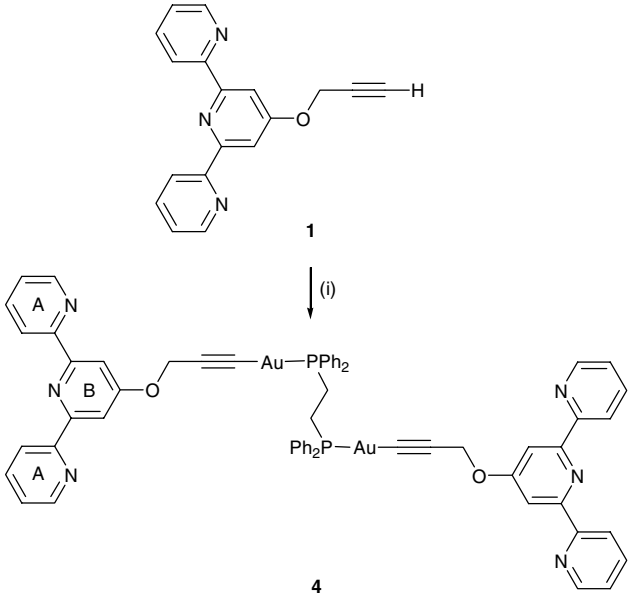


Fig. 3. Four dimers of **2** showing their assembly into rows along the *a*-axis, and the resulting domains of alkyl chains (centre of unit cell) and tpy groups.

Compounds **2** and **3** illustrate the success of the methodology of functionalizing a tpy metal-binding domain in the 4′-position with a gold(I) phosphine. However, in order to develop these systems further towards their use as building blocks in metallomacrocyclic or polymeric systems, it is necessary to incorporate a bridging bis(phosphine) ligand. For initial studies, we chose dppe. Ligand **1** reacts with ClAu(μ-dppe)AuCl in Et_3N/CH_2Cl_2 in the presence of CuI (Scheme 2) to yield **4** in moderate yield. In the MALDI mass spectrum, a peak at *m*/*z* 1388 was assigned to $[M + Na]^+$. The solution $^{31}P\{^1H\}$ NMR spectrum exhibited one signal (δ 36.5 ppm), consistent with the formation of a symmetrical product. The ^1H and $^{13}C\{^1H\}$ NMR spectra were also consistent with the presence of 2 equiv tpy units and a symmetrical dppe ligand. In **4**, the ^{13}C NMR signal for the $C{\equiv}CAu$ carbon was observed at δ 97.0 ppm, consistent with the chemical shifts observed for the analogous C centres in **2** and **3**. As in **2**, the signal for the gold-bonded C atom in **4** was not resolved.

Crystals of $\mathbf{4} \cdot 4CHCl_3$ suitable for an X-ray diffraction study were grown from a $CHCl_3$ solution. The structure of **4** is shown in Fig. 4. The molecule is centrosymmetric, with



Scheme 2. Reaction scheme for the formation of **4**: (i) ClAu(dppe)AuCl, CuI in Et_3N/CH_2Cl_2. The ring labelling is used for NMR assignments.

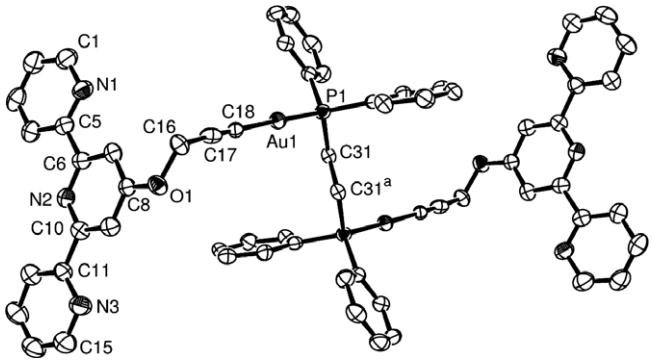


Fig. 4. The structure of **4** in $\mathbf{4} \cdot 4CHCl_3$ with displacement ellipsoids drawn at the 30% probability level; H atoms omitted for clarity. Selected bond lengths and angles: Au1–P1 = 2.275(1), Au1–C18 = 2.062(6), C17—C18 = 1.117(8), C16–C17 = 1.481(8), C16–O1 = 1.449(7), O1–C8 = 1.361(7) Å; P1–Au1–C18 = 178.8(2), Au1–C18–C17 = 177.6(5), C18–C17—C16 = 176.2(6), C17—C16–O1 = 112.3(5), C16–O1–C8 = 119.0(4)°.

the tpy groups adopting a *transoid* arrangement. As a result, there is no intramolecular Au···Au close contact. A search of the CSD [45] shows that in XAu(μ-dppe)AuX derivatives with relatively simple X substituents, a *transoid* arrangment of the Au(μ-dppe)Au unit is usually favoured [46–53], and the formation of an intramolecular Au···Au interaction appears not to drive the molecule towards adopting a *cisoid* arrangement. In several cases, intermolecular aurophilic interactions lead to the formation of polymeric chains [48,54,55]. The structure of ClAu(μ-dppe)AuCl is noteworthy. In both the unsolvated complex and ClAu(μ-dppe)AuCl · $0.4CH_2Cl_2$ [56,57], the Au(dppe)Au unit adopts a conformation between *cisoid* and *transoid*. Inspection of these structures using Mercury v. 1.4.2 [58] shows that in ClAu(μ-dppe)AuCl, intermolecular aurophilic interactions lead to the formation of cyclic dimers, while polymeric chains are present in ClAu(μ-dppe)AuCl · $0.4CH_2Cl_2$. In $\mathbf{4} \cdot 4CHCl_3$, one of the crystallographically independent solvate molecules is ordered, and the second is disordered over two sites (65:35%). The supramolecular interactions that dominate the packing of molecules of **4** are non-classical hydrogen bonds. The C–H···N and O···H–C interactions shown in Fig. 5a, along with those that are symmetry related to the latter, result in the assembly of hydrogen-bonded chains. Significantly, there are no intermolecular Au···Au or π-stacking interactions, and packing of the hydrogen-bonded chains (Fig. 5b) involves only very weak C–H···π-alkyne and C–H···π-aryl contacts along with hydrogen bonds between N2 and one $CHCl_3$ molecule (N2···H321C32 = 2.28 Å, N2···H321–C32 = 162°). Additional factors which may oppose the formation of Au···Au interactions are the steric demands of the substituents and the overall length of the molecule [59].

The isolation of compounds **2**–**4** illustrates the viability of attaching a gold(I) phosphine unit to an alkynyl-functionalized tpy to produce either a gold(I)-decorated monotopic ligand or a gold(I) phosphine bridged ditopic ligand. We now plan to undertake investigations of the coordination behaviour of these ligands.

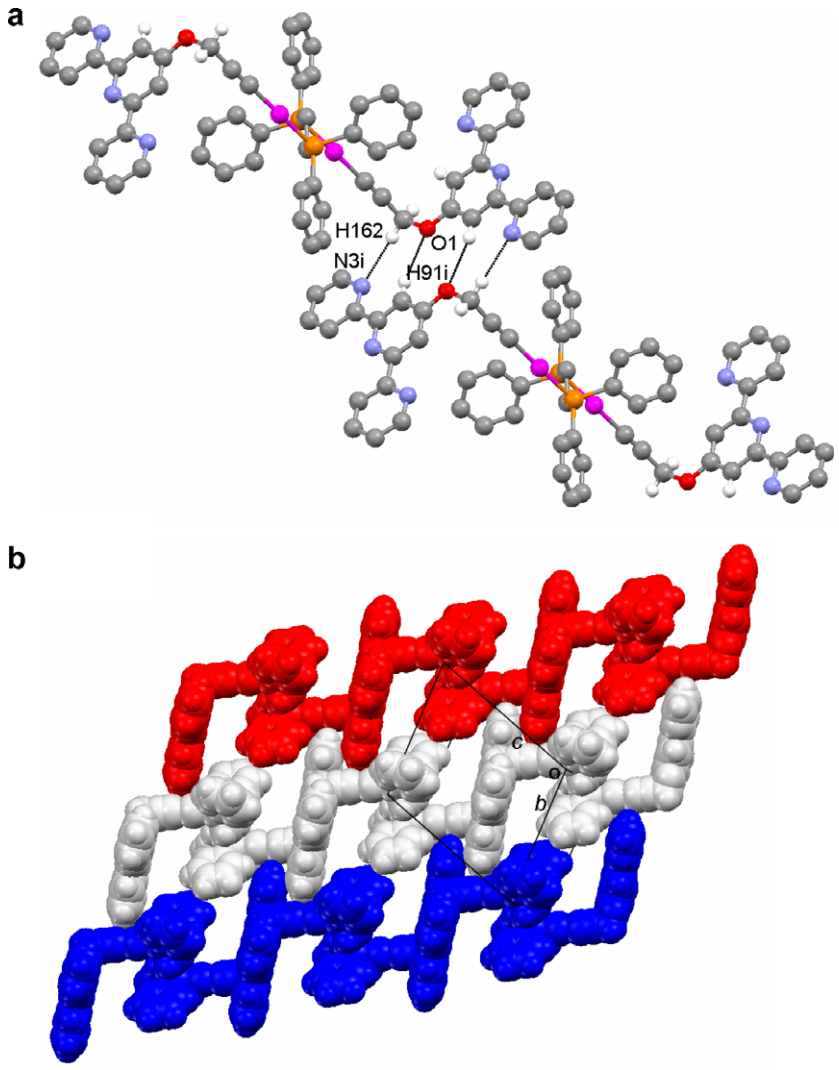


Fig. 5. (a) Non-classical hydrogen bonding interactions between molecules of **4**; symmetry code i = 1 − *x*, −1 − *y*, 1 − *z*. C16H162···N3i = 2.54, C16···N3i = 3.445(8) Å, C16–H162···N3i = 158°, O1···H91iC9i = 2.64, O1···C9i = 3.569(8) Å, O1···H91i–C9i = 162°. Hydrogen atoms other than those of the CH and CH_2 groups involved in hydrogen bonding are omitted for clarity. (b) Packing of hydrogen-bonded chains of **4**.

Acknowledgements

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Appendix A. Supplementary material

CCDC 648054 and 648054 contains the supplementary crystallographic data for **2** and **4**. These data can be obtained free of charge via www: http://www.ccdc.cam.ac.uk), or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.08.034.

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