# The First Metal Complexes Derived from 3,5-Diethynylpyridine. X-ray Crystal Structure of $[(AuPTo_3)_2\{\mu\text{-}(C{\equiv}C)_2Py\}]$ (Py = Pyridine-3,5-diyl; To = *p*-Tolyl)

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The reactions of 3,5-diethynylpyridine ($Py(C{\equiv}CH)_2$) with PPN[Au(acac)$_2$] (2.5:1; PPN = $Ph_3P{=}N{=}PPh_3$) or with [AuCl(SMe$_2$)] and NEt$_3$ (1:2:2) give respectively PPN[Au{C≡C(Py)-C≡CH}$_2$] (**1**) and $[Au_2\{\mu\text{-}(C{\equiv}C)_2Py\}]_n$ (**2**). Complex **2** reacts with monodentate ligands (1:2) or with 1,6-bis(diphenylphosphino)hexane (dpph, 1:1) to give neutral dinuclear complexes of the general formula $[(AuL)_2\{\mu\text{-}(C{\equiv}C)_2Py\}]$ (L = CN$^t$Bu (**3**), PMe$_3$ (**4**), PPh$_3$ (**5**), PTo$_3$ (To = C$_6$H$_4$Me-4) (**6**); Au$_2$L$_2$ = Au$_2$($\mu$-dpph) (**7**)). The reactions of **6** with the complexes [MCl] and TlTfO (1:1:1) (TfO = CF$_3$SO$_3$) give the cationic trinuclear complexes [M{Py(C≡CAuPTo$_3$)$_2$}]TfO (M = AuPTo$_3$ (**8**), *cis*-PtCl(PPh$_3$)$_2$ (**9**)). The crystal structure of complex **6** has been determined.

## Introduction

Metal complexes with bridging −C≡C(Ar)C≡C− spacers (Ar being an aromatic ring) have been shown to possess electrical conductivity, nonlinear optical, or liquid crystalline properties derived from the extended electronic conjugation they display.[1] The (arenediethynyl)gold(I) complexes reported so far include the Ar groups C$_6$H$_4$-1,3,[2] C$_6$H$_4$-1,4,[1] (C$_6$H$_3$Me-5)-1,3, (C$_6$H$_2$Me$_2$-2,5)-1,4,[3] (C$_6$HMe$_3$-2,4,6)-1,3, C$_6$Me$_4$-2,3,5,6,[2] and different fluorene-2,7-diyl[4] derivatives, many of which are luminescent. Among them only a few, described by Puddephatt[5] and by us,[2,6] are *m*-arenediethynyl derivatives; four of these derivatives have been characterized by X-ray diffraction methods, namely $[(AuL)_2\{(C{\equiv}C)_2Ar\text{-}1,3\}]$ (Ar = C$_6$H$_4$, C$_6$HMe$_3$-2,4,6, L = PPh$_3$; Ar = C$_6$H$_3$Me-5, L = PPh$_2$Me, P(OMe)$_3$). Apart from these, the crystal structures of only three other arenediethynyl complexes of any element (Ru,[7] Pt,[8] and Fe[9]) have been reported.

3,5-Diethynylpyridine has been used for the synthesis of some fully conjugated ligands containing pyridinediyndiyl subunits (Chart 1), from which some Re,[10] Ru,[11] and Pt[12−14] complexes have been obtained and shown to possess metallamacrocyclic structures and interesting physical properties. However, although it was first reported in 1978,[15] there is no previous report on any complex derived from 3,5-diethyndiylpyridine, which is rather surprising in view of the tempting possibilities this ligand offers as a potential building block for multimetallic complexes, including metallamacrocycles and polymers. Two platinum(II) complexes derived from the monoalkyne HC≡C(Py)C≡CSi$^i$Pr$_3$ have been reported.[14] On the basis of the related 2,5- or 2,6-diethynylpyridine a series of monomeric and polymeric organic compounds[16,17] as well as some $\sigma$-acetylide complexes of Ru, Os,[18] and Pt[17,19,20] and some $\pi$-complexes

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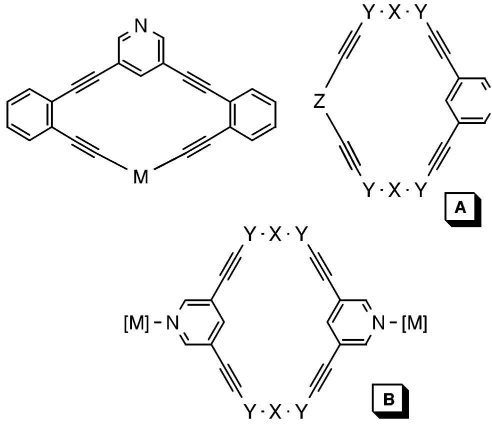
**Chart 1**[a]



[a] Legend: (**A**) $X = C{\equiv}C$, $Y = Ph_2C{=}C$, $-Z- = -[M]-$; (**B**) $X = C{\equiv}C$, $C{\equiv}CC{\equiv}C$, $Y = C_6H_4{-}1,3$ and $X = C{\equiv}CC{\equiv}C$, $Y = R_2C{=}C$ ($R = Me$, Ph).

of Co[21] have been described, which exhibit interesting optical and conductivity properties that in some cases are affected by quaternization of the pyridine nitrogen.[17] The crystal structure of a hexanuclear metallamacrocyclic complex of platinum containing $C_5H_3N(C{\equiv}C)_2$-2,6 ligands[20] represents the only example of a diethyndiylpyridine complex to be fully characterized.

We have given different accounts on the "acac method"[22] which, on the basis of the ability of (acetylacetonato)gold(I) complexes of the types $[Au(acac)_2]^-$ and [Au(acac)L] to deprotonate substrates containing at least an acidic hydrogen atom, led to a variety of complexes, including alkynylgold(I) derivatives.[2,6,23−25] In this paper we report on the use of 3,5-diethynylpyridine to prepare a family of complexes of the types $[Au\{C{\equiv}C(Py)C{\equiv}CH\}_2]^-$, $[Au_2\{\mu\text{-}(C{\equiv}C)_2Py\}]_n$, $[(AuL)_2\{\mu\text{-}(C{\equiv}C)_2Py\}]$, and $[M\{Py(C{\equiv}CAuPTo_3)_2\}]^+$ (M = $AuPTo_3$, *cis*-$PtCl(PPh_3)_2$), which display all the potential coordination modes of the versatile 3,5-diethynylpyridine ligand.

## Experimental Section

IR spectroscopy, mass spectrometry (FAB$^{+/-}$), elemental analyses, conductance measurements in acetone, and melting point determinations were carried out as described elsewere.[26] The molar conductivity of the neutral complexes gave very low values (0−5 $\Omega^{-1}$ cm$^2$ mol$^{-1}$). The NMR spectra were measured on Bruker Avance 200, 300, and 400 MHz spectrometers. Chemical shifts are referred to TMS ($^1$H, $^{13}$C) or $H_3PO_4$ ($^{31}$P). Unless otherwise stated, the reactions were carried out at room temperature without any precautions to avoid oxygen or moisture. The syntheses of 3,5-diethynylpyridine,[13] $PPN[Au(acac)_2]$,[27] and $[AuCl(SMe_2)]$[28] were previously reported. $[AuCl(PTo_3)]$ and *cis*-$[PtCl_2(PPh_3)_2]$ were prepared by adding 1 or 2 equiv of the appropriate phosphine to $[AuCl(SMe_2)]$ and $[PtCl_2(NCPh)_2]$,[29] respectively. TlTfO (TfO = $CF_3SO_3$) was obtained by reacting in water $Tl_2CO_3$ and HTfO (1:2) after evaporation of the solvent and recrystallization of the residue from acetone and $Et_2O$. All other chemicals were obtained from commercial sources and used as received. The solvents were distilled before use.

**Synthesis of $PPN[Au\{C{\equiv}C(Py)C{\equiv}CH\}_2]$ (1).** A solution of $PPN[Au(acac)_2]$ (676 mg, 0.72 mmol) in acetone (15 mL) was slowly dropped over a solution of 3,5-diethynylpyridine (23 mg, 1.8 mmol) in the same solvent (10 mL). The mixture was stirred for 8 h and filtered through Celite and the solution concentrated to dryness. The residue was stirred with $Et_2O/CH_2Cl_2$ (14:1, 3 × 45 mL), and the colorless microcrystalline solid was filtered and dried under reduced pressure (ca. 1 mbar) for 1 h to give **1**·$H_2O$·$Et_2O$. Yield: 592 mg, 76%. Mp: 133 °C. Anal. Calcd for $C_{58}H_{50}AuN_3O_2P_2$: C, 64.50; H, 4.67; N, 3.89. Found: C, 64.49; H, 4.28; N, 3.93. IR (cm$^{-1}$): $\nu$(CH) 3294 (w), 3232 (w); $\nu$(C≡C) 2106 (s). $\Lambda_M$ ($\Omega^{-1}$ cm$^2$ mol$^{-1}$): 81. $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 8.51 (m, 2 H, py), 8.35 (m, 2 H, py), 8.23 (m, 2 H, py), 7.69−7.28 (m, 30 H, PPN), 3.5 (q, 4 H, $CH_2$, $Et_2O$, $^3J_{HH}$ = 7 Hz), 3.11 (s, 2 H, CH), 1.66 (s, 2 H, $H_2O$), 1.25 (t, 6 H, Me, $Et_2O$, $^3J_{HH}$ = 7 Hz). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): $\delta$ 21.1 (s, PPN). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta$ 152.6, 148.1, 141.5, 140.0, 133.8 (m, *p*-CH, PPN), 132.0 (m, *m*-CH, PPN), 129.6 (m, *o*-CH, PPN), 126.8 (m, *i*-C, PPN), 123.4, 117.9, 98.0 (C≡C), 80.6 (*C*≡CH), 79.7 (≡CH), 65.91 ($CH_2$, $Et_2O$), 15.20 (Me, $Et_2O$). MS-FAB$^-$ (*m*/*z*, %): 449 (M$^-$, 100%).

**Synthesis of $[Au_2\{(C{\equiv}C)_2Py\}]_n$ (2).** A mixture of 3,5-diethynylpyridine (198 mg, 1.6 mmol), $[AuCl(SMe_2)]$ (917 mg, 3.11 mmol), and $NEt_3$ (0.46 mL, 3.26 mmol) in $CH_2Cl_2$ (20 mL) was stirred for 0.5 h. The suspension was filtered and the solid washed successively with $CH_2Cl_2$ (4 × 10 mL) and $Et_2O$ (10 mL) and dried under vacuum (ca. 1 mbar) for 1 h to give **2** as a bright yellow powder. Its insolubility in all common solvents impeded measuring its NMR spectra or recrystallizing it to improve the elemental analysis (see Results and Discussion). Yield: 802 mg, 97%. Mp: 115 °C dec. Anal. Calcd for $C_9H_3Au_2N$: C, 20.83; H, 0.58; N, 2.70. Found: C, 22.15; H, 0.97; N, 3.06. IR (cm$^{-1}$): $\nu$(C≡C) 2114 (w).

**Synthesis of $[(AuL)_2\{\mu\text{-}(C{\equiv}C)_2Py\}]$ (L = $^t$BuNC (3), $PMe_3$ (4), $PPh_3$ (5), $PTo_3$ (6); $Au_2L_2 = Au_2(\mu\text{-dpph})$ (7)).** To a suspension of **2** (**3**, 286 mg, 0.55 mmol; **4**, 213 mg, 0.41 mmol; **5**, 120 mg, 0.23 mmol; **6**, 277 mg, 0.53 mmol; **7**, 243 mg, 0.47 mmol) in $CH_2Cl_2$ (**3**, 10 mL; **4** and **5**, 20 mL; **6**, 30 mL; **7**, 15 mL) was added the appropriate ligand (**3**, $^t$BuNC 0.25 mL, 2.2 mmol; **4**, $PMe_3$ 1 M in toluene, 2 mL, 2 mmol; **5**, $PPh_3$ 127 mg, 0.49 mmol; **6**, $PTo_3$ 325 mg, 1.07 mmol; **7**, dpph 213 mg, 0.47 mmol). The reaction mixture was stirred for 1 h at room temperature (**4**, under an $N_2$ atmosphere) or refluxed for 4 h (**7**) and filtered through Celite. The solvent was removed under vacuum to 1 mL (**4**) or 3 mL (**7**) or to dryness (**3**, **5**, **6**). When *n*-hexane (**3**, **4**, 10 mL) or $Et_2O$ (**5**, **7**, 20 mL) or a 1:1 mixture of both solvents (**6**, 20 mL) was added and the mixture was stirred for a few minutes, a suspension resulted, which was filtered. The solid was washed with the same solvent (2 × 5 mL) and air-dried to give a bright yellow (**3**·0.5$Et_2O$) or pale yellow (**4**, **5**·$H_2O$, **6**) or white (**7**·$H_2O$) powder.

**3**·0.5$Et_2O$: yield 276 mg, 73%. Mp: 140 °C. Anal. Calcd for $C_{21}H_{26}Au_2N_3O_{0.5}$: C, 34.92; H, 3.63; N, 5.82. Found: C, 34.80; H, 3.48; N, 6.35. IR (cm$^{-1}$): $\nu$(C≡N) 2230 (s); $\nu$(C≡C) 2120 (w). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 8.44 (d, 2 H, py, $^4J_{HH}$ = 2 Hz), 7.69 (t, 1 H, py, $^4J_{HH}$ = 2 Hz), 3.1 (q, 2 H, $CH_2$, $Et_2O$, $^3J_{HH}$ = 7 Hz), 1.57 (s, 18 H, $^t$Bu), 1.4 (t, 3 H, Me, $Et_2O$, $^3J_{HH}$ = 7 Hz). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta$ 150.3, 146.4 (CN), 141.6,

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126.6, 121.0, 99.2 (C≡C), 59.0 ($CH_2$, $Et_2O$), 58.6 (*C*$Me_3$), 29.6 (C*Me*$_3$), 8.9 (Me, $Et_2O$).

**4**: yield 191 mg, 69%. Mp: 293 °C dec. Anal. Calcd for $C_{15}H_{21}Au_2NP_2$: C, 26.84; H, 3.15; N, 2.09. Found: C, 26.88; H, 3.13; N, 2.08. IR ($cm^{-1}$): $\nu$(C≡C) 2098 (w). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 8.47 (d, 2 H, py, $^4J_{HH} = 2$ Hz), 7.73 (t, 1 H, py, $^4J_{HH} = 2$ Hz), 1.55 (d, 18 H, $PMe_3$, $^2J_{HP} = 10$ Hz). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): $\delta$ 1.36 (s).$^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta$ 150.5 (py), 141.5 (py), 121.2 (d, *C*CAu, $^3J_{CP} = 5$ Hz), 100.7 (d, CAu, $^2J_{CP} = 30$ Hz), 15.7 (d, $PMe_3$, $^1J_{CP} = 35$ Hz).

**5**·$H_2O$: yield 161 mg, 67%. Mp: 115 °C. Anal. Calcd for $C_{45}H_{35}NAu_2OP_2$: C, 50.91; H, 3.32; N, 1.32. Found: C, 50.79; H, 3.39; N, 1.27. IR ($cm^{-1}$): $\nu$(C≡C) 2112 (s). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.55 (d, 2 H, py, $^4J_{HH} = 2$ Hz), 7.83 (t, 1 H, py, $^4J_{HH} = 2$ Hz), 7.57−7.45 (m, 30 H, $PPh_3$), 1.66 (s, 2 H, $H_2O$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ 42.61 (s). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta$ 150.7 (py), 141.5 (py), 137.5 (py), 134.3 (d, *o*-CH, $PPh_3$, $^2J_{CP} = 14$ Hz), 131.6 (d, *p*-CH, $PPh_3$, $^4J_{CP} = 3$ Hz,), 129.6 (d, *i*-C, $PPh_3$, $^1J_{CP} = 56$ Hz), 129.2 (d, *m*-CH, $PPh_3$, $^3J_{CP} = 11$ Hz), 121.2 (d, *C*CAu, $^3J_{CP} = 3$ Hz), 100.2 (d, CAu, $^2J_{CP} = 27$ Hz).

**6**: yield 488 mg, 82%. Mp: 206 °C dec. Anal. Calcd for $C_{51}H_{45}Au_2NP_2$: C, 54.31; H, 4.02; N, 1.24. Found: C, 54.14; H, 4.30; N, 1.33. IR ($cm^{-1}$): $\nu$(C≡C) 2112 (w). $^1$H NMR (200 MHz, $CDCl_3$): $\delta$ 8.55 (d, 2 H, py, $^4J_{HH} = 2$ Hz), 7.82 (t, 1 H, py, $^4J_{HH} = 2$ Hz), 7.47−7.37 (m, 12 H, $PTo_3$), 7.25−7.21 (m, 12 H, $PTo_3$), 2.39 (s, 18 H, Me). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): $\delta$ 41.22 (s). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): $\delta$ 150.7, 141.9 (d, *p*-CH, $PTo_3$, $^4J_{CP} = 2$ Hz), 141.5, 134.1 (d, *o*-CH, $PTo_3$, $^2J_{CP} = 14$ Hz), 129.8 (d, *m*-CH, $PTo_3$, $^3J_{CP} = 12$ Hz), 126.6 (d, *i*-C, $PTo_3$, $^1J_{CP} = 58$ Hz), 121.2, 21.5 (d, Me, $^5J_{CP} = 1$ Hz).

**7**·$H_2O$: yield 226 mg, 49%. Mp: 131 °C dec. Anal. Calcd for $C_{39}H_{37}Au_2NOP_2$: C, 47.24; H, 3.76; N, 1.41. Found: C, 47.05; H, 3.41; N, 1.52. IR ($cm^{-1}$): $\nu$(C≡C) 2106 (w). $^1$H NMR (400 MHz, $CDCl_3$): $\delta$ 8.52 (d, 2 H, py, $^4J_{HH} = 2$ Hz), 7.79 (m, 1 H, py), 7.68−7.44 (m, 20 H, Ph), 2.37 (m, 4 H, $CH_2$), 1.66 (s, 2 H, $H_2O$), 1.59 (m, 4 H, $CH_2$), 1.43 (m, 4 H, $CH_2$). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ 37.35 (s). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$): $\delta$ 150.5, 141.5, 133.3 (d, *m*-CH, Ph, $^3J_{CP} = 8$ Hz), 131.6 (m, *p*-CH, Ph), 130.3 (d, *i*-C, Ph, $^1J_{CP} = 53$ Hz), 129.2 (d, *o*-CH, Ph, $^2J_{CP} = 15$ Hz), 121.2 (s, *C*CAu), 100.1 (s, CAu), 30.3 (d, $CH_2$, $^2J_{CP} = 15$ Hz), 27.8 (d, $CH_2$, $^1J_{CP} = 34$ Hz), 25.3 (d, $CH_2$, $^3J_{CP} = 3$ Hz). MS-FAB$^+$ (*m/z*, %): 974 ($M^+$, 6%), 651 ($Audpph^+$, 36%).

**Synthesis of [(AuPTo$_3$){Py(C≡CAuPTo$_3$)$_2$}]TfO (8).** A mixture of **6** (213 mg, 0.19 mmol), [AuClPTo$_3$] (107 mg, 0.20 mmol), and TlTfO (71 mg, 0.20 mmol) in dry THF (20 mL) was stirred under a nitrogen atmosphere for 0.5 h and then concentrated to dryness under reduced pressure. The residue was stirred with $CHCl_3$ (30 mL), and the suspension was filtered through Celite. The solution was concentrated to dryness, the residue stirred with *n*-pentane (2 × 20 mL), the suspension filtered, and the solid air-dried to give **8** as a microcrystalline bright yellow powder. Yield: 242 mg, 72%. Mp: 130 °C. Anal. Calcd for $C_{73}H_{66}Au_3F_3NO_3P_3S$: C, 49.31; H, 3.74; N, 0.79. Found: C, 49.53; H, 3.91; N, 0.66. IR ($cm^{-1}$): $\nu$(C≡C) 2114 (w). $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$): 105. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.49 (br, 2 H, py), 7.84 (t, 1 H, py, $^4J_{HH} = 1.8$ Hz), 7.41−7.22 (m, 36 H, Ar, $PTo_3$), 2.44 (s, 9 H, Me), 2.39 (s, 18 H, Me). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): $\delta$ 43.68 (s, CAuPTo$_3$), 36.85 (br s, NAuPTo$_3$). $^{13}C\{^1H\}$-APT NMR (100 MHz, $CDCl_3$): $\delta$ 150.5, 143.3 (p−C, $PTo_3$), 142.3 (*p*-C, $PTo_3$), 133.9 (d, *o*-CH, $PTo_3$, $^2J_{CP} = 14$ Hz), 133.7 (m, *o*-CH, NAuPTo$_3$), 130.5 (m, *m*-CH, NAuPTo$_3$), 129.9 (d, *m*-CH, $PTo_3$, $^3J_{CP} = 12$ Hz,), 125.7 (d, *i*-C, $PTo_3$, $^1J_{CP} = 61$ Hz), 124.2 (m, *i*-C, NAuPTo$_3$), 121.5, 21.5 (Me, $PTo_3$), 21.4 (Me, $PTo_3$). MS-FAB$^+$ (*m/z*, %): 1628 ($M^+$, 27%).

**Synthesis of [{*cis*-PtCl(PPh$_3$)$_2$}{Py(C≡CAuPTo$_3$)$_2$}]TfO (9).** A mixture of **6** (230 mg, 0.2 mmol), *cis*-[PtCl$_2$(PPh$_3$)$_2$] (161 mg, 0.2 mmol), and TlTfO (72 mg, 0.2 mmol) in acetone (25 mL) was stirred for 1.25 h. The solvent was removed under vacuum, and the residue was stirred with $CHCl_3$ (20 mL). The resulting suspension was filtered through Celite, the solution concentrated to dryness, and the solid residue stirred with *n*-pentane (25 mL). The suspension was filtered and the solid dried under reduced pressure (ca. 1 mbar) for 1 h to give a microcrystalline pale yellow powder. Yield: 365 mg, 90%. Mp: 142 °C dec. Anal. Calcd for $C_{88}H_{75}Au_2ClF_3NO_3P_4PtS$: C, 52.02; H, 3.72; N, 0.69. Found: C, 52.08; H, 3.78; N, 0.89. IR ($cm^{-1}$): $\nu$(C≡C) 2114 (s); $\nu$(PtCl), 318(s). $\Lambda_M$ ($\Omega^{-1}$ $cm^2$ $mol^{-1}$): 146. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 8.17 (m, 2 H, py), 7.48−7.14 (m, 55 H, $PTo_3$ + $PPh_3$ + py), 2.42 (s, 18 H, Me). $^{31}P\{^1H\}$ NMR (121 MHz, $CDCl_3$): $\delta$ 40.22 (s, AuPTo$_3$), 16.67 (d, PtPPh$_3$, $^1J_{PPt} = 3655$ Hz, $^2J_{PP} = 18$ Hz), 4.74 (d, PtPPh$_3$, $^1J_{PPt} = 3240$ Hz, $^2J_{PP} = 18$ Hz). MS-FAB$^+$ (*m/z*, %): 1881 ($M^+$, 26%).

**Table 1. Crystal Data for Complex 6**

| | |
|---|---|
| formula | $C_{51}H_{45}Au_2NP_2$ |
| fw | 1127.75 |
| cryst size (mm) | 0.34 × 0.28 × 0.06 |
| cryst syst | monoclinic |
| space group | $P2_1/c$ |
| *a* (Å) | 9.9851(6) |
| *b* (Å) | 23.4212(19) |
| *c* (Å) | 19.0934(15) |
| α (deg) | 90 |
| $\beta$ (deg) | 91.270(6) |
| $\gamma$ (deg) | 90 |
| *V* (Å$^3$) | 4464.1(6) |
| *Z* | 4 |
| $\rho_{calcd}$ (Mg $m^{-3}$) | 1.678 |
| $\lambda$ (Å) | 0.710 73 |
| *T* (K) | 173(2) |
| *F*(000) | 2184 |
| $\mu$(Mo Kα) ($mm^{-1}$) | 6.671 |
| $\theta$ range (deg) | 3.05−25.00 |
| abs cor | $\psi$ scans |
| no. of rflns coll | 8437 |
| no. of indep rflns | 7835 |
| $R_{int}$ | 0.0407 |
| transmissn | 0.997 05/0.449 49 |
| no. of data/restraints/params | 7835/18/505 |
| R1 ($I > 2\sigma(I)$)[a] | 0.0403 |
| wR2 (all rflns)[b] | 0.0668 |

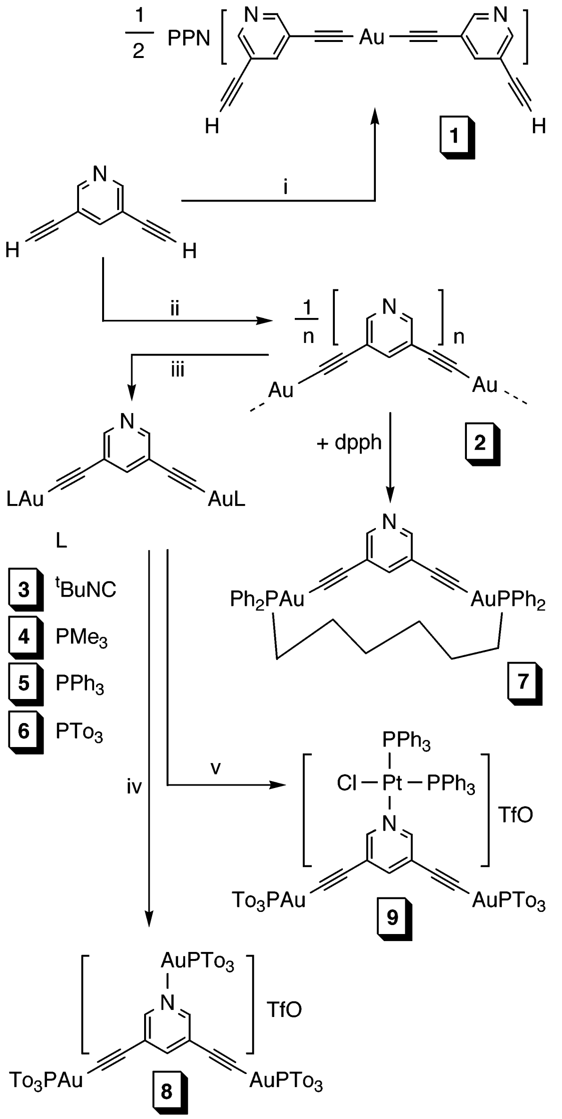
[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$ for reflections with $I > 2\sigma(I)$. [b] $wR2 = [\sum[w(F_o{}^2 - F_c{}^2)^2]/\sum[w(F_o{}^2)^2]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c{}^2 + F_o{}^2)/3$ and *a* and *b* are constants set by the program.

**X-ray Structure Determination for Complex 6.** The crystals were mounted in inert oil on a glass fiber and transferred to the diffractometer (Siemens P4 with LT2 low-temperature attachment). Crystal data and refinement details are presented in Table 1. The unit cell parameters were determined from a least-squares fit of 88 accurately centered reflections (14.1° < 2$\theta$ < 25.8°). The structure was solved by the heavy-atom method and refined anisotropically on $F^2$ (program SHELX-97, G. M. Sheldrick. University of Göttingen, Göttingen, Germany). The largest residual peak of 1.62 e was 1.13 Å from Au2. Hydrogen atoms were included using a riding model.

## Results and Discussion

**Synthesis.** The reaction of 3,5-diethynylpyridine with PPN[Au(acac)$_2$] to give the anionic complex PPN[Au{C≡C(Py)C≡CH}$_2$] (**1**), in which gold coordinates to two monoanionic HC≡C(Py)C≡C$^-$ (Py = pyridine-3,5-diyl) ligands, requires the use of an excess of the dialkyne over the stoichiometric 2:1 molar ratio (Scheme 1) in order to prevent the formation of insoluble oligomers of the type (PPN)$_n$[Au{(C≡C)$_2$Py}]$_n$. The complex [Au$_2${(C≡C)$_2$Py}]$_n$ (**2**) was obtained by reacting 3,5-diethynylpyridine with [AuCl(SMe$_2$)] and NEt$_3$

**Scheme 1**[a]



[a] Legend: (i) $+{}^{1}/_{2}$PPN[Au(acac)$_2$], −acacH; (ii) +2[AuCl(SMe$_2$)], +2NEt$_3$, −2SMe$_2$, −2[NHEt$_3$]Cl; (iii) +2L; (iv) +[AuCl(PTo$_3$)], +TlTfO, −TlCl; (v) +[PtCl$_2$(PPh$_3$)$_2$], +TlTfO, −TlCl.

(1:2:2) in dichloromethane upon replacement of both Cl and SMe$_2$ ligands from the coordination sphere of gold by the dialkynediyl ligand generated by deprotonation of the dialkyne with the amine. The insolubility of this complex in all common organic solvents suggests it to be a polymer in which gold would coordinate to the doubly deprotonated Py(C≡C)$_2$ ligand and is likely to complete its usual linear dicoordination with (C≡C)→Au interactions, as is assumed for related complexes. However, in the case of **2** it cannot be discarded that N→Au bonds also contribute to complete the dicoordination of gold. Complex **2** precipitates quantitatively in the reaction mixture, while SMe$_2$ and [NHEt$_3$]Cl remain soluble and are separated by filtration. The elemental analyses of **2** are compatible with the presence of a residual amount of NEt$_3$ that we suggest would be coordinated to the outer gold atoms in the polymer, since it is not removed after drying under reduced pressure for several hours. On the basis of the tendency of some analytically pure alkynylgold polymers to explode on contact,[5,30] we decided not to attempt any further purification of **2**, since it is a stable compound from which pure derivatives can be obtained.

Thus, complex **2** reacts with monodentate L ligands in a 1:2 molar ratio or with 1,6-bis(diphenylphosphino)hexane (1:1) to give neutral dinuclear complexes of the general formula [(AuL)$_2${$\mu$-(C≡C)$_2$Py}] (L = CN$^t$Bu (**3**), PMe$_3$, (**4**), PPh$_3$ (**5**), PTo$_3$ (**6**); Au$_2$L$_2$ = Au$_2$($\mu$-dpph) (**7**)). Addition of the appropriate ligand to suspensions of **2** in dichloromethane caused the immediate formation of solutions from which the neutral complexes were isolated in 50−80% yield upon concentration and addition of Et$_2$O or *n*-hexane.

The reaction of **6** and [AuCl(PTo$_3$)] (1:1) in the presence of TlTfO (TfO = CF$_3$SO$_3$) produces the immediate precipitation of TlCl. After filtration, a solution was obtained from which the trinuclear complex [(AuPTo$_3$){Py(C≡CAuPTo$_3$)$_2$}]TfO (**8**) was isolated in 72% yield, as the result of coordination of the pyridinic nitrogen present in the metalloligand complex **6** to the AuPTo$_3$ fragment generated in situ. The homologous reaction between **3** and [AuCl(SMe$_2$)] (1:1) did not produce the expected neutral trinuclear derivative. Instead, precipitation of the polymeric complex **2** took place and [AuCl(CN$^t$Bu)] was identified in the mother liquor. This result prompted us to attempt the synthesis of the pentanuclear complex [Au{Py(C≡CAuPTo$_3$)$_2$}$_2$]TfO by reacting **6** with [AuCl(SMe$_2$)] and TlTfO (2:1:1). However, precipitation of **2** took place again, and **8** was isolated from the mother liquor. An attempt to coordinate gold(III) to the nitrogen atom present in **6** by reacting it with [AuCl$_3$(PPh$_3$)] and TlTfO (1:1:1) gave a mixture of products that we could not separate.

However, the reaction of **6** with [PtCl$_2$(PPh$_3$)$_2$] and TlTfO (1:1:1) caused the immediate precipitation of TlCl, and the cationic complex [{*cis*-PtCl(PPh$_3$)$_2$}{Py(C≡CAuPTo$_3$)$_2$}]TfO (**9**) (Scheme 1) was isolated from the solution. A small amount (ca. 7%) of the isomer containing the *trans*-PtCl(PPh$_3$)$_2$ fragment was evidenced by the $^{31}$P{$^1$H} NMR spectrum. Although **9** is stable in the solid state at low temperature, it decomposes after a few hours in solution to give [AuCl(PTo$_3$)] along with other unidentified species. In an attempt to prepare the new dicationic heteronuclear derivatives that would result from replacing both chloro ligands in [PtCl$_2$L$_2$] by two molecules of the metalloligand **6**, we reacted it with [PtCl$_2$(PPh$_3$)$_2$] and TlTfO (2.1:1:2). Unfortunately, after 5 h of stirring **9** was the only complex detected in the NMR of the reaction mixture, apart from the excess of **6**. An attempt to coordinate **6** to AgClO$_4$ (2:1) gave an insoluble species that we could not characterize.

We have also explored an alternative route to obtain heteronuclear complexes derived from 3,5-diethynylpyridine which would consist of coordinating first the pyridinic nitrogen to different metal centers with the purpose of replacing afterwards the acetylenic hydrogens by AuL fragments using the "acac method". However, the reactions of 3,5-diethynylpyridine with AgClO$_4$, AgTfO, [PdCl$_2$(dtbipy)] (dtbipy = 4,4′-di-*tert*-butyl-2,2′-bipyridine), and [PtCl(PPh$_3$)(dtbipy)]TfO led to mixtures of complexes or to insoluble products that we could not characterize.

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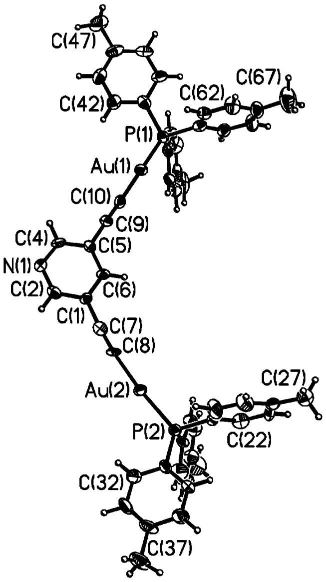

**Figure 1.** Ellipsoid representation of **6** (50% probability). Selected bond lengths (Å) and angles (deg): Au(1)−C(10) = 2.011(10), Au(1)−P(1) = 2.269(2), C(9)−C(10) = 1.188(11), C(10)−Au(1)−P(1) = 175.3(2), Au(2)−C(8) = 1.995(8), Au(2)−P(2) = 2.269(2), C(7)−C(8) = 1.183(11), C(8)−Au(2)−P(2) = 173.3(2).

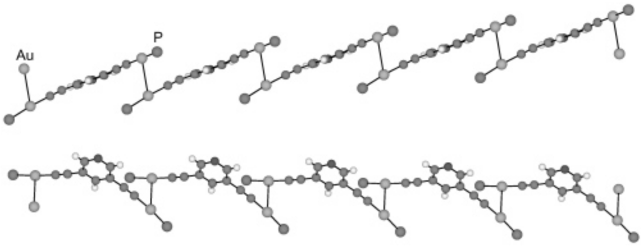

**Figure 2.** Two different views of the aurophilic contacts in **6** giving rise to infinite chains. The tolyl groups and the hydrogen atoms have been omitted. Selected bond lengths (Å) and angles (deg): Au(1)−Au(2)#1 = 3.2265(5), C(10)−Au(1)−Au(2)#1 = 76.6(2), P(1)−Au(1)−Au(2)#1 = 108.01(6), C(8)−Au(2)−Au(1)#2 = 76.1(2), P(2)−Au(2)−Au(1)#2 = 104.14(6).

**Crystal Structure of [(AuPTo$_3$)$_2${*μ*-(C≡C)$_2$Py}] (6).** The crystal structure of **6** (Figure 1, Table 1) shows a dinuclear complex in which two AuPTo$_3$ units are coordinated to the ethynyl fragments of the 3,5-pyridinediethyndiyl ligand, both gold atoms being in almost linear environments (C−Au−P = 175.3(2), 173.3(2)°). A search of the Cambridge Structural Data Base[31] reveals that the Au−C (2.011(10), 1.995(8) Å), Au−P (2.269(2) Å), and C≡C (1.183(11), 1.188(11) Å) bond distances found in **6** are similar to the mean values found for other alkynyl(phosphine)gold(I) dicoordinate complexes (Au−C = 2.004 Å, Au−P = 2.278 Å, C≡C = 1.195 Å). Additionally, the molecules of **6** are packed through intermolecular aurophilic contacts (Au···Au = 3.2265(5) Å) to give infinite chains (Figure 2). The molecules arrange in the chain so that the linear fragments C≡CAuPTo$_3$ of two vicinal molecules are almost perpendicular (dihedral angle PAu···AuP 89°). This type of "pseudopolymerization" in the solid state has been previously reported for other (alkynyl)gold(I) complexes.[5,32−34]

**NMR Spectra.** The heteroaromatic protons appear in the $^1$H NMR spectra of complexes **1**−**9** in the ranges 8.44−8.55 ppm (d) and 7.69−7.83 ppm (t), only very slightly shielded with respect to their homologues in the free 3,5-diethynylpyridine ligand (at 8.65 and 7.85 ppm, respectively). Additionally, the $^1$H NMR spectrum of **1** shows a singlet for the acetylenic protons at 3.11 ppm, slightly shifted to high field with respect to the free dialkyne (at 3.24 ppm), likely due to the anionic nature of **1**. The PTo$_3$ methyl protons in **8** give rise to two singlets. The singlet at 2.39 ppm corresponds to the C−AuPTo$_3$ fragments and is at higher field than that due to the N−AuPTo$_3$ moiety (at 2.44 ppm), in agreement with the greater electronegativity of nitrogen with respect to carbon.

The $^{31}$P{$^1$H} NMR spectrum of complex **1** shows a singlet at 21.1 ppm due to the PPN cation, while the spectra for the neutral complexes **3**−**7** display one singlet resonance (at 1.36 ppm (**4**, PMe$_3$) or in the range 36−44 ppm (**5**−**7**, PAr$_3$)) for the two equivalent phosphorus nuclei. In agreement with the $^1$H NMR, the $^{31}$P{$^1$H} NMR spectrum of **8** shows two singlet resonances with a 2:1 intensity ratio. The most intense one (at 43.68 ppm) corresponding to two C−AuP fragments is shifted to low field with respect to that due to the N−AuP fragment (at 36.85 ppm), despite nitrogen being more electronegative than carbon. This can be attributed to the greater trans influence of carbon-donor with respect to nitrogen-donor ligands. In fact, complexes with the AuPPh$_3$ fragment coordinated to the nitrogen atom of different substituted pyridines or to alkynyl groups show the $^{31}$P resonance at around 30 ppm[35] or in the range 42−56 ppm,[25,36] respectively. In the $^{31}$P{$^1$H} NMR spectrum of **9** the phosphine bonded to gold gives a singlet resonance (see Experimental Section), while those coordinated to platinum give two doublets with $^{195}$Pt satellites, corresponding to the isomer containing a *cis*-PtCl(PPh$_3$)$_2$ fragment. The spectrum of **9** shows a small singlet with $^{195}$Pt satellites at 14.86 ppm ($J_{\mathrm{PtP}}$ = 3677 Hz), compatible with the formation of a small amount (ca. 7%) of the isomer containing *trans*-PtCl(PPh$_3$)$_2$. Additionally, it shows a minor signal at 32.4 ppm (s) that grows with the acquisition time and is indicative of the formation of [AuClPTo$_3$] resulting from some decomposition process, which impeded us measuring its $^{13}$C NMR spectrum.

The $^{13}$C{$^1$H} NMR spectra of complexes **1** and **3**−**8** show the expected resonances (see Experimental Sec-

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tion). In those complexes containing C≡C−$AuPR_3$ fragments the α- and *β*-carbons of the C≡C subunits could be assigned when the $J_{CP}$ coupling constants were observed, on the basis of the admitted fact[23,34,37,38] that they are greater for the α-carbons. In all other cases, no assignment has been made, since controversial data can be found in the literature.[38]

NMR and analytical data prove that some complexes crystallize with $Et_2O$ (**3**·$0.5Et_2O$) or $H_2O$ (**5**·$H_2O$, **7**·$H_2O$).

**IR Spectra.** The infrared spectra of the ionic complexes show characteristic bands of the corresponding counterions (**1**, PPN;[6] **8, 9**, TfO).[39] All complexes show one medium to weak band in the range 2098−2114 $cm^{-1}$ assignable to the C≡C stretching mode.[40] This band was expected[32,41] to appear at lower wavenumber in the polymeric complex **2** due to the (C≡C)→Au bond component, and its position should also change with the electron density around the metal center. However, very similar or identical values are found for complexes **1**, **2**, **7**, and **8** (2106, 2114, 2106, and 2114 $cm^{-1}$, respectively), despite **1** being anionic, **2** polymeric, **7** neutral, and **8** cationic. In the spectrum of complex **1** two bands are observed (3294, 3232 $cm^{-1}$) for the ≡C−H stretching mode,[40] as observed in other alkynylgold complexes with two C≡CH moieties.[6] Additionally, complex **9** shows one *ν*(PtCl) band and **3**−**9** show the bands characteristic of the phosphine or isocyanide ligands they contain (see Experimental Section).

**FAB Mass Spectra.** The $FAB^-$ (**1**) or $FAB^+$ (**7**−**9**) mass spectra measured show in all cases the corresponding mass peak with relative intensity in the range of 6% (**7**) to 100% (**1**). The spectra of complexes **7**−**9** are dominated by the signals corresponding to the $[AuPR_3]^+$, $[Au(PR_3)_2]^+$, and $[PtCl(PR_3)_2]^+$ fragments.

## Conclusions

3,5-Diethynylpyridine has been used to prepare a family of mono- (**1**), di- (**2**−**7**), and trinuclear (**8**, **9**) homo- or heteronuclear complexes containing *σ* monoalkynyl (C≡C(Py)C≡CH, **1**) or *σ* dialkynyl (*μ*-C≡C(Py)C≡C, **2**−**7**) ligands. Furthermore, complex **6** is a metalloligand from which homo- (**8**) or heterotrinuclear (**9)** complexes can be obtained after coordination of a third metal center to the pyridinic nitrogen atom.

**Acknowledgment.** We thank the Ministerio de Ciencia y Tecnología, FEDER (BQU2001-0133), for financial support and Fundación Séneca (Comunidad Autónoma de la Región de Murcia, Spain) for a grant to M.M.A.F.

**Supporting Information Available:** A crystallographic file in CIF format for complex **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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