Platinum(II) and Mixed Platinum(II)/Gold(I) σ-Alkynyl Complexes. The First Anionic σ-Alkynyl Metal Polymers

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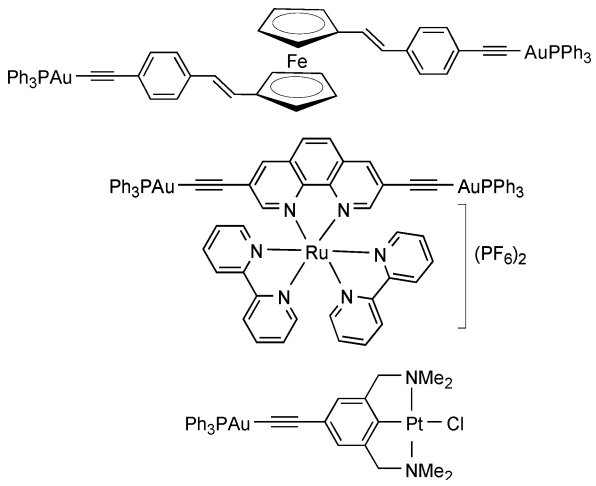
The alkynes $C_6Me_4(C{\equiv}CH)_2$-1,4, $C_6Me_4(C{\equiv}CH)_2$-1,2, and $C_6Me_3(C{\equiv}CH)_3$-1,3,5 react with *cis*-$[PtCl_2(PAr_3)_2]$ and $NHEt_2$ and a catalytic amount of CuI to give complexes *trans*-$[Pt(C{\equiv}CC_6Me_4C{\equiv}CH\text{-}4)_2(PAr_3)_2]$ [Ar = Ph (**1a**), C_6H_4Me-4 (To) (**1b**)], *trans*-$[Pt(C{\equiv}CC_6Me_4C{\equiv}CH\text{-}2)_2(PAr_3)_2]$ [Ar = Ph (**2a**), To (**2b**)], and *trans*-$[Pt\{C{\equiv}CC_6Me_3(C{\equiv}CH)_2\text{-}3,5\}_2(PAr_3)_2]$ [Ar = Ph (**3a**), To (**3b**)], respectively. The reactions of $[Au(acac)PAr_3]$ (acac = acetylacetonato) with complex **1a** or **1b** (2:1) or with **3b** (4:1) give the neutral mixed $Pt^{II}Au^{I}_2$ or $Pt^{II}Au^{I}_4$ σ-alkynyl complexes *trans*-$[Pt(C{\equiv}CC_6Me_4C{\equiv}CAuPAr_3\text{-}4)_2(PAr_3)_2]$ [Ar = Ph (**4a**), To (**4b**)] or *trans*-$[Pt\{C{\equiv}CC_6Me_3(C{\equiv}CAuPTo_3)_2\text{-}3,5\}_2(PTo_3)_2]$ (**5b**), respectively. Additionally, the replacement of the triarylphosphine ligands present in **1a**, **2a**, **4b**, or **5b** with various trialkylphosphines produces the homologous derivatives with PMe_3 (**1c**, **2c**, **4c**, **5c**), PEt_3 (**1d**), or $P(^nBu)_3$ (**1e**), respectively. PPN$[Au(acac)_2]$ reacts with complex **1a**, **1c**, or **1e** (1:1) to give $(PPN)_n$-$[trans\text{-}Pt\{(C{\equiv}CC_6Me_4C{\equiv}C\text{-}4)_2Au\}(PR_3)_2]_n$ [R = Ph (**6a**), Me (**6c**), ^nBu (**6e**)], while its reaction with **3b** (2:1) produces $(PPN)_{2n}[trans\text{-}Pt\{C{\equiv}CC_6Me_3(C{\equiv}C)_2\text{-}3,5Au_2(PTo_3)_2]_n$ (**7**). Complexes **6a**, **6c**, **6e**, and **7** are the first anionic σ-alkynyl metal polymers described so far. The crystal structures of **1a**·$CHCl_3$, **2b**·$2CHCl_3$, and **4b**·$5CH_2Cl_2$ have been determined. Each complex displays crystallographic inversion symmetry.

Introduction

Most of the heteronuclear (alkynyl)gold(I) complexes described in the literature are clusters containing Cu, Ag, Fe, or Ir,[1] and those structurally characterized by X-ray crystallography show, apart from metal−metal bonds, interactions between the π-electron density of the AuC≡C group and the other metal center. These bonding interactions are also present in most of the few noncluster heteronuclear (alkynyl)gold(I) complexes containing Cu, Ag, Mo, W, or Pt.[2−4] Additionally, some heteronuclear alkynylgold(I) complexes of the type [Au(C≡C−X)L] have been reported,[2,5−7] X being an organometallic fragment in which the second metal is not coordinated to the C≡C moiety (Chart 1). Most such complexes were obtained from organometallic complexes bearing C≡CH units and chlorogold(I) complexes in basic conditions.[5−7] Some of them display NLO[5] or

Chart 1



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luminescent properties,[7] or their electrical properties have been studied with the purpose of designing molecular wires.[7]

Among the great variety of heteropolynuclear σ-alkynyl complexes of any metal described in the literature,[8−13] we have found only two $Pt^{II}Au^{I}$ derivatives, which contain 1,4-butadiyndiyl[4,14] fragments and were characterized only by elemental analyses and NMR. We have just preliminarily reported the synthesis and crystal structure of the σ-alkynyl $Pt^{II}_2Au^{I}$ triangle PPN[Au{Pt(PMe_3)$_2$}$_2${μ-C_6Me_4(C≡C)$_2$-1,2}$_3$] starting from complex **2c**.[15] In general, polymers based on −C≡C− units and transition metals alternating along the polymeric backbone have been found to be of outstanding interest.[16,17] Most such σ-alkynyl polymers are homonuclear species, with metals of groups 8,[18] 9,[10,11,19] and 10,[10,20,21] although some heteronuclear[22] d^6/d^8 (Fe/Pd, Fe/Ni, and Ru/Pd) derivatives are also known. The overwhelming majority of these polymers present a linear rigid-rod structure and are neutral. A few cationic[23] and some 2D-graphite-like polymers[24] have also been reported, but anionic polymers were unknown so far. Our previous experience on the use of the "acac method"[25] for the synthesis of alkynylgold(I) derivatives[26−28] prompted us to prepare a family of bis(alkynyl)Pt(II) derivatives bearing C≡CH units that could be used as starting materials for the synthesis of new heteronuclear $Pt^{II}Au^{I}$ alkynyl compounds, including anionic polymeric species.

Experimental Section

The IR spectra, elemental analyses, and melting point determinations were carried out as described earlier.[29] Technical grade solvents were purified by standard procedures. Unless otherwise stated, the reactions were carried out at room temperature without any special precautions to exclude oxygen or moisture. The complexes *cis*-[$PtCl_2(PR_3)_2$] were prepared from *trans*-[$PtCl_2(NCPh)_2$] and the appropriate phosphine (2:1, in CH_2Cl_2, 1 h at room temperature) and [Au(acac)PR_3] as previously described for R = Ph.[30] The syntheses of C_6Me_4(C≡CH)$_2$-1,4,[28] 1,3,5-C_6Me_3(C≡CH)$_3$-1,3,5,[31] and PPN[Au(acac)$_2$][30] were previously described. The NMR spectra were measured in $CDCl_3$ with Bruker Avance 200, 300, or 400 spectrometers. Chemical shifts are referred to TMS (^{1}H), $CDCl_3$ (^{13}C), or H_3PO_4 (^{31}P). The FAB^+ mass spectra were measured with a Fisons VG-Autospec spectrometer using 3-nitrobenzyl alcohol as the matrix.

Synthesis of $C_6Me_4(C{\equiv}CSiMe_3)_2$-1,2. $Me_3SiC{\equiv}CH$ (9 mL, 64 mmol) was added to a mixture of $C_6Me_4I_2$-1,2,[32] (6.24 g, 16 mmol), *cis*-[$PdCl_2(PPh_3)_2$] (449 mg, 0.64 mmol), and CuI (245 mg, 1.29 mmol) in degassed $NHEt_2$ (70 mL). The mixture was stirred under nitrogen for 6.5 days, and the solvent was removed under reduced pressure. The residue was stirred with Et_2O (120 mL) and filtered. The solution was concentrated to ca. 50 mL and chromatographed on neutral Al_2O_3 to give a

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red solution, which was concentrated to dryness. Recrystallization of the crude product from EtOH (40 mL) gave colorless needles of the title compound. Yield: 4.3 g, 81%. Mp: 136 °C. Anal. Calcd for $C_{20}H_{30}Si_2$: C 73.54, H 9.26. Found: C 73.30, H 9.67. IR (cm^{-1}): ν(C≡C) 2150 (s). ^1H NMR (200 MHz, $CDCl_3$): δ 2.42 (s, 6 H, Me), 2.22 (s, 6 H, Me), 0.31 (s, 18 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 136.2 (Ar), 135.6 (Ar), 123.0 (Ar), 103.9 (CSi), 100.7 (*C*≡CSi), 18.5 (Me), 16.7 (Me), 0.2 (Si*Me*$_3$).

Synthesis of $C_6Me_4(C{\equiv}CH)_2$-1,2. A solution of KOH (1 g, 18 mmol) in H_2O (3 mL) was added to a suspension of C_6Me_4-$(C{\equiv}CSiMe_3)_2$-1,2 (3 g, 9.12 mmol) in MeOH (50 mL), and the mixture was refluxed for 4 h. After diluting with H_2O (50 mL), the mixture was extracted with Et_2O (2 × 50 mL). The combined extracts were dried over anhydrous $MgSO_4$, and the solvent was removed under reduced pressure to give a purple solid, which was washed with cold EtOH (−70 °C, 10 mL), filtered, and air-dried to give colorless needles of the title compound. Yield: 1.38 g, 83%. Mp: 102 °C. Anal. Calcd for $C_{14}H_{14}$: C 92.26, H 7.74. Found: C 91.99, H 8.04. IR (cm^{-1}): ν(CH) 3310 (s), 3280 (s), ν(C≡C) 2098 (s). ^1H NMR (200 MHz, $CDCl_3$): δ 3.47 (s, 2 H, ≡CH), 2.42 (s, 6 H, Me), 2.20 (s, 6 H, Me). $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 136.6 (Ar), 136.0 (Ar), 122.3 (Ar), 83.6 (≡CH), 82.3 (*C*≡CH), 18.6 (Me), 16.7 (Me).

Synthesis of *trans*-[Pt(C≡CC$_6$Me$_4$C≡CH-4)$_2$(PAr$_3$)$_2$] [Ar = Ph (1a), To (1b)]. A mixture of $C_6Me_4(C{\equiv}CH)_2$-1,4 (for **1a**: 908 mg, 4.98 mmol; for **1b**: 1.22 g, 6.67 mmol), *cis*-$[PtCl_2(PR_3)_2]$ (R = Ph, 985 mg, 1.25 mmol; To, 1.460 g, 1.67 mmol), and CuI (**1a**: 24 mg, 0.12 mmol; **1b**: 32 mg, 0.17 mmol) in degassed $NHEt_2$ (**1a**: 30 mL; **1b**: 65 mL) was stirred under nitrogen for 16.5 (**1a**) or 65 (**1b**) h. The solvent was removed under reduced pressure, and the residue was stirred with $CHCl_3$ (**1a**: 10 mL; **1b**: 13 mL). The resulting suspension was added slowly dropwise into rapidly stirred EtOH (100 mL) and filtered. The solid was washed with EtOH (10 mL) and *n*-pentane (20 mL). The crude product was stirred in a mixture of $CHCl_3$ and Et_2O (2:1, 90 mL) and the resulting suspension filtered through Celite. The solution was concentrated under vacuum until a yellow solid began to precipitate, at which point *n*-pentane (50 mL) was added. The suspension was filtered and the solid was air-dried to give a pale yellow powder. **1b** was additionally dried under reduced pressure (ca. 1 mbar) for 1 h.

1a: Yield 1.16 g, 86%. Mp: 185 °C (dec). Anal. Calcd for $C_{64}H_{56}P_2Pt$: C 71.03, H 5.22. Found: C 70.79, H 5.35. IR (cm^{-1}): ν(CH) 3302 (s), ν(C≡C) 2094 (s). ^1H NMR (200 MHz, $CDCl_3$): δ 7.81−7.71 (m, 15 H, PPh_3), 7.27−7.18 (m, 15 H, PPh_3), 3.38 (s, 2 H, ≡CH), 2.21 (s, 12 H, Me), 1.64 (s, 12 H, Me). APT $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 134.9 (d, *o*-CH, PPh_3, $^2J_{CP}$ = 6 Hz), 134.7 (Ar), 133.9 (Ar), 131.3 (d, *i*-C, PPh_3, $^1J_{PC}$ = 29 Hz), 130.1 (*p*-CH, PPh_3), 127.6 (d, *m*-CH, PPh_3, $^3J_{CP}$ = 5 Hz), 129.4 (Ar), 120.9 (≡CPt, $^1J_{CPt}$ = 30 Hz), 117.4 (Ar), 112.6 (*C*≡CPt, $^2J_{CPt}$ = 2 Hz), 83.6 (≡CH), 18.2 (Me), 17.7 (Me). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ 18.94 PPh_3 (s, $^1J_{PPt}$ = 2672 Hz). MS (FAB$^+$), *m/z* (%): 1083 (M^+, 55). Crystals of **1a**·$CHCl_3$ suitable for an X-ray diffraction study were obtained by the liquid diffusion method using CH_2Cl_2 and *n*-pentane.

1b: Yield 1.38 g, 71%. Mp: 218 °C (dec). Anal. Calcd for $C_{70}H_{68}P_2Pt$: C 72.09, H 5.88. Found: C 71.72, H 5.91. IR (cm^{-1}): ν(CH) 3310 (s), ν(C≡C) 2088 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.66−7.61 (m, 12 H, PTo_3), 7.00−6.98 (m, 12 H, PTo_3), 3.38 (s, 2 H, ≡CH), 2.23 (s, 30 H, Me, PTo_3, C_6Me_4), 1.66 (s, 12 H, C_6Me_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.1 (m, *p*-CH, PTo_3), 135.0 (d, *o*-CH, PTo_3, $^2J_{CP}$ = 7 Hz), 134.6 (Ar), 133.8 (Ar), 129.8 (Ar), 128.7 (d, *i*-C, PTo_3, $^1J_{CP}$ = 30 Hz), 128.3 (m, *m*-CH, PTo_3, $^3J_{CP}$ = 6 Hz), 117.3 (Ar), 112.8 (C≡CPt), 83.7 (≡CH), 83.3 (*C*≡CH), 21.2 (Me, PTo_3), 18.1 (Me), 17.6 (Me). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 16.91 (s, $^1J_{PPt}$ = 2644 Hz). MS (FAB$^+$), *m/z* (%): 1166 (M^+, 26).

Synthesis of *trans*-[Pt(C≡CC$_6$Me$_4$C≡CH-4)$_2$(PR$_3$)$_2$] [R = Me (1c), Et (1d), ^{n}Bu (1e)]. To a solution of **1c** (190 mg, 0.18 mmol), **1d** (522 mg, 0.48 mmol), or **1e** (1.32 g, 1.22 mmol) in dry THF (10 mL for **1c**,**d**; 15 mL for **1e**) was added the appropriate phosphine (**1c**, PMe_3, 1 mL, 1 M in toluene, 1 mmol; **1d**, PEt_3, 0.43 mL, 2.9 mmol; **1e**, P^nBu_3, 1.8 mL, 7.32 mmol). The solution was stirred under nitrogen for 15 (**1c**) or 23 (**1d**,**e**) h and concentrated under vacuum to ca. 2 mL. Then *n*-pentane (15 mL) was added to precipitate a colorless solid, which was filtered off, washed with *n*-pentane (5 mL), and air-dried. In the case of **1e**, concentrating the solution to 1 mL, adding *n*-pentane (20 mL), and cooling to −78 °C was necessary; the resulting suspension was filtered and the colorless solid washed with cold *n*-pentane and dried at ca.1 mbar for 1 h.

1c: Yield 101 mg, 81%. Mp: 261 °C (dec). Anal. Calcd for $C_{34}H_{44}P_2Pt$: C 57.54, H 6.25. Found: C 57.24, H 6.63. IR (cm^{-1}): ν(CH) 3314 (s), 3268 (s), ν(C≡C) 2086 (s). ^1H NMR (200 MHz, $CDCl_3$): δ 3.5 (s, 2 H, ≡CH), 2.46 (s, 12 H, C_6Me_4), 2.41 (s, 12 H, C_6Me_4), 1.72 (m, 18 H, PMe_3, $^3J_{HPt}$ = 31 Hz). APT $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 136.2 (Ar), 134.7 (Ar), 129.4 (Ar), 119.2 (Ar), 118.7 (≡CPt, $^1J_{CPt}$ = 31 Hz), 107.7 (*C*≡CPt, $^2J_{CPt}$ = 4 Hz), 84.6 (≡CH), 83.5 (*C*≡CH), 19.2 (Me), 18.8 (Me), 16.2 (virtual t, Me, PMe_3, $|^1J_{CP} + {}^3J_{CP}|$ = 40 Hz, $^2J_{CPt}$ = 45 Hz). $^{31}P\{^1H\}$ NMR (81 MHz, $CDCl_3$): δ −21.1 (s, $^1J_{PPt}$ = 2312 Hz). MS (FAB$^+$), *m/z* (%): 709 (M^+, 26).

1d: Yield 250 mg, 66%. Mp: 185 °C (dec). Anal. Calcd for $C_{40}H_{56}P_2Pt$: C 60.52, H 7.11. Found: C 60.36, H 7.48. IR (cm^{-1}): ν(CH) 3306 (s), 3240 (s), ν(C≡C) 2082 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 3.46 (s, 2 H, ≡CH), 2.44 (s, 12 H, C_6Me_4), 2.41 (s, 12 H, C_6Me_4), 2.08 (m, 12 H, CH_2), 1.16 (m, 18 H, Me, PEt_3). APT $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 135.70 (Ar), 134.06 (Ar), 129.49 (Ar), 119.27 (≡CPt, $^1J_{CPt}$ = 29 Hz), 118.32 (Ar), 108.37 (*C*CPt), 83.99 (≡CH), 83.24 (*C*≡CH), 18.54 (Me), 18.41 (Me), 16.29 (virtual t, CH_2, $|^1J_{CP} + {}^3J_{CP}|$ = 36 Hz,), 8.27 (Me, PEt_3). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 11.36 (s, $^1J_{PPt}$ = 2385 Hz). MS (FAB$^+$), *m/z* (%): 793 (53, M^+).

1e: Yield 650 mg, 56%. Mp: 120 °C. Anal. Calcd for $C_{52}H_{80}P_2Pt$: C 64.91, H 8.38. Found: C 65.07, H 8.29. IR (cm^{-1}): ν(CH) 3308 (s), ν(C≡C) 2086 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 3.46 (s, 2 H, ≡CH), 2.43 (s, 12 H, C_6Me_4), 2.41 (s, 12 H, C_6Me_4), 2.03 (m, 12 H, P*CH*$_2$Pr), 1.57 (m, 12 H, PCH_2CH_2Et), 1.35 (m, 12 H, $P(CH_2)_2CH_2$Me), 0.87 (t, 18 H, $P(CH_2)_3Me$, $^3J_{HH}$ = 7 Hz). APT $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ: 135.6 (Ar), 133.9 (Ar), 129.6 (Ar), 119.2 (Ar), 118.0 (C≡CPt), 107.8 (C≡CPt), 83.9 (≡CH), 83.4 (*C*≡CH), 26.5 [$P(CH_2)_2CH_2$Me], 24.3 (virtual t, PCH_2CH_2Et, $|^2J_{CP} + {}^4J_{CP}|$ = 14 Hz), 24.0 (virtual t, P*CH*$_2$Pr, $|^1J_{CP} + {}^3J_{CP}|$ = 36 Hz), 18.6 (Me), 18.4 (Me), 13.8 [$P(CH_2)_3Me$]. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 3.48 (s, $^1J_{PPt}$ = 2366 Hz). MS (FAB$^+$), *m/z* (%): 963 (52) (M^+).

Synthesis of *trans*-[Pt(C≡CC$_6$Me$_4$C≡CH-2)$_2$(PAr$_3$)$_2$] [Ar = Ph (2a), To (2b)]. A mixture of $C_6Me_4(C{\equiv}CH)_2$-1,2 (for **2a**: 236 mg, 1.29 mmol; for **2b**: 454 mg, 2.5 mmol), *cis*-$[PtCl_2(PR_3)_2]$ (for **2a**: 256 mg, 0.32 mmol; for **2b**: 545 mg, 0.62 mmol), and CuI (for **2a**: 6 mg, 0.031 mmol, for **2b**: 12 mg, 0.062 mmol) in degassed $NHEt_2$ (for **2a**: 20 mL, for **2b**: 30 mL) was stirred under nitrogen for 15 (**2a**) or 26 (**2b**) h. The solvent was removed under reduced pressure, the residue was stirred with $CHCl_3$ (ca. 3 mL), and the resulting suspension was added slowly dropwise into EtOH (40 mL) with vigorous stirring. The suspension was filtered and the colorless solid was air-dried to give **2a** or **2b**·$0.5H_2O$. Complex **2b** was not dehydrated after treating it under reduced pressure (1 mbar) for 0.5 h.

2a: Yield 248 mg, 72%. Mp 236 °C (dec). Anal. Calcd for $C_{64}H_{56}P_2Pt$: C 71.03, H 5.22. Found: C 70.72, H 5.51. IR (cm^{-1}): ν(CH) 3284 (s), ν(C≡C) 2102 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.87−7.82 (m, 15 H, PPh_3), 7.26−7.20 (m, 15 H, PPh_3), 3.01 (s, 2 H, ≡CH), 2.31 (s, 6 H, C_6Me_4), 2.07 (s, 6 H, C_6Me_4), 1.98 (s, 6 H, C_6Me_4), 1.55 (s, 6 H, C_6Me_4). APT $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 135.3 (m, *m*-CH, PPh_3), 134.7 (Ar), 134.4 (Ar), 134.1 (Ar), 131.5 (m, *i*-C, PPh_3), 130.5 (Ar), 129.8 (m, *p*-CH, PPh_3), 129.6 (Ar), 127.5 (m, *o*-CH, PPh_3), 120.0

(Ar), 118.6 (≡CPt, $^1J_{PtC}$ = 31 Hz), 112.4 (*C*≡CPt, $^2J_{PtC}$ = 5 Hz), 84.3 (≡CH), 81.2 (*C*≡CH), 18.5 (Me), 17.9 (Me), 16.6 (Me), 16.4 (Me). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 17.17 (s, $^1J_{PtP}$ = 2671 Hz).

2b·0.5H$_2$O: Yield 467 mg, 65%. Mp: 229 °C (dec). Anal. Calcd for $C_{70}H_{69}O_{0.5}P_2Pt$: C 71.50, H 5.96. Found: C 71.36, H 5.84. IR (cm^{-1}): ν(CH) 3308, 3284 (s), ν(C≡C) 2098 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.73−7.69 (m, 12 H, PTo_3), 7.00−6.98 (m, 12 H, PTo_3), 3.02 (s, 2 H, ≡CH), 2.33 (s, 6 H, C_6Me_4), 2.20 (s, 18 H, Me, PTo_3), 2.07 (s, 6 H, C_6Me_4), 2.01 (s, 6 H, C_6Me_4), 1.60 (s, 6 H, C_6Me_4), 1.53 (s, 1 H, H_2O). APT $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 139.6 (*p*-C, PTo_3), 135.1 (m, *o*-CH, PTo_3), 134.5 (Ar), 134.2 (Ar), 134.0 (Ar), 130.1 (Ar), 129.9 (Ar), 128.7 (d, *i*-C, PTo_3, $^1J_{CP}$ = 30 Hz), 128.1 (m, *m*-CH, PTo_3), 120.4 (≡CPt, $^1J_{CPt}$ = 31 Hz), 120.0 (Ar), 112.2 (*C*≡CPt, $^2J_{CPt}$ = 4 Hz), 84.3 (≡CH), 81.1 (*C*≡CH), 21.2 (Me, PTo_3), 18.5 (Me), 17.8 (Me), 16.6 (Me), 16.3 (Me). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 16.35 (s, $^1J_{PPt}$ = 2650 Hz). MS (FAB^+) *m/z* (%): 1166 (M^+, 26). Single crystals of **2b**·2$CHCl_3$ suitable for an X-ray diffraction study were obtained by the liquid diffusion method using $CDCl_3$ and *n*-pentane.

Synthesis of *trans*-[Pt(C≡CC$_6$Me$_4$C≡CH-2)$_2$(PMe$_3$)$_2$] (2c).[15] To a solution of **2a** (0.418 g, 0.39 mmol) in dry THF (15 mL) under nitrogen was added PMe_3 (1 M in toluene, 2.32 mL, 2.32 mmol). After 14.5 h of stirring, the reaction mixture was concentrated under vacuum to ca. 3 mL, *n*-pentane (15 mL) was added, and after a few minutes of stirring, the suspension was filtered. The solid was washed with *n*-pentane (5 mL) and dried under reduced pressure (ca. 1 mbar) for 1 h to give **2c** as a colorless microcrystalline powder. Yield: 243 mg, 88%. Mp: 234 °C (dec). Anal. Calcd for $C_{34}H_{44}P_2Pt$: C 57.54, H 6.25. Found: C 57.71, H 6.67. IR (cm^{-1}): ν(CH) 3234 (s), ν(C≡C) 2084 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 3.32 (s, 2 H, ≡CH), 2.48 (s, 6 H, C_6Me_4), 2.42 (s, 6 H, C_6Me_4), 2.20 (s, 6 H, C_6Me_4), 2.17 (s, 6 H, C_6Me_4), 1.77 (virtual t, 18 H, Me, PMe_3, $|^2J_{HP} + {}^4J_{HP}|$ = 8 Hz, $^3J_{HPt}$ = 30 Hz). APT $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 136.0 (Ar), 135.5 (Ar), 134.7 (Ar), 131.8 (Ar), 129.0 (Ar), 120.8 (Ar), 116.0 (*C*≡CPt, $^2J_{CPt}$ = 31 Hz), 106.8 (≡CPt, $^1J_{CPt}$ = 267 Hz), 84.8 (≡CH), 82.4 (*C*≡CH), 19.0 (Me), 18.6 (Me), 16.9 (Me), 16.5 (Me), 16.0 (virtual t, Me, PMe_3, $|^1J_{CP} + {}^3J_{CP}|$ = 40 Hz). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ −21.62 (s, $^1J_{PtP}$ = 2320 Hz). MS (FAB^+), *m/z* (%): 709 (M^+, 24).

Synthesis of *trans*-[Pt{C≡CC$_6$Me$_3$(C≡CH)$_2$-3,5}$_2$(PAr$_3$)$_2$] [Ar = Ph (3a), To (3b)]. A mixture of $C_6Me_3(C{\equiv}CH)_3$-1,3,5 (for **3a**: 255 mg, 1.3 mmol; for **3b**: 357 mg, 1.86 mmol), the appropriate *cis*-$[PtCl_2(PR_3)_2]$ (R = Ph, 262 mg, 0.33 mmol; To, 406 mg, 0.46 mmol), and CuI (for **3a**: 6 mg, 0.033 mmol; for **3b**: 9 mg, 0.05 mmol) in degassed $NHEt_2$ (25 mL) was stirred under nitrogen for 13 (**3a**) or 22 (**3b**) h. The suspension was concentrated to dryness, the residue was dissolved in $CHCl_3$ (5 mL), and the solution was added slowly dropwise into rapidly stirred EtOH (50 mL). The resulting suspension was filtered and the solid recrystallized from a 1:1 mixture of $CHCl_3/Et_2O$ and *n*-pentane and dried under reduced pressure (1 mbar) for 1 h to give **3a**·H_2O or **3b**·H_2O as colorless powders.

3a·H$_2$O: Yield 168 mg, 46%. Mp: 212 °C (dec). Anal. Calcd for $C_{66}H_{54}OP_2Pt$: C 70.77, H 4.86. Found: C 70.74, H 4.88. IR (cm^{-1}): ν(CH) 3304 (s), ν(C≡C) 2098 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.78−7.18 (m, 30 H, PPh_3), 3.34 (s, 4 H, ≡CH), 2.45 (s, 6 H, C_6Me_3), 1.84 (s, 12 H, C_6Me_3), 1.55 (s, 2 H, H_2O). APT $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.70 (Ar), 138.72 (Ar), 135.02 (m, *o*-CH, PPh_3), 131.19 (m, *i*-C, PPh_3), 130.24 (m, *p*-CH, PPh_3), 127.63 (m, *m*-CH, PPh_3), 119.84 (Ar), 118.48 (C≡CPt), 110.42 (C≡CPt), 83.54 (≡CH), 81.87 (*C*≡CH), 19.68 (Me), 19.63 (Me). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 18.63 (s, $^1J_{PPt}$ = 2657 Hz). MS (FAB^+), *m/z* (%): 1102 (M^+, 10).

3b·H$_2$O: Yield 357 mg, 65%. Mp: 248 °C (dec). Anal. Calcd for $C_{72}H_{66}OP_2Pt$: C 71.80, H 5.52. Found: C 71.55, H 5.77. IR (cm^{-1}): ν(CH) 3280 (s), 3270 (s), ν(C≡C) 2088 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.65−7.60 (m, 12 H, PTo_3), 7.02−7.00 (m, 12 H, PTo_3), 3.34 (s, 4 H, ≡CH), 2.46 (s, 6 H, C_6Me_3), 2.24 (s, 18 H, Me, PTo_3), 1.84 (s, 12 H, C_6Me_3), 1.54 (s, 2H, H_2O). APT $^{13}C\{^1H\}$ NMR (50 MHz, $CDCl_3$): δ 141.67 (Ar), 140.29 (m, *p*-C, PTo_3), 138.40 (Ar), 134.92 (m, *o*-CH, PTo_3), 128.28 (m, *m*-CH, PTo_3), 128.27 (d, *i*-C, PTo_3, $^1J_{CP}$ = 60 Hz), 118.45 (C≡CPt), 110.19 (C≡CPt), 83.43 (≡CH), 81.92 (*C*≡CH), 21.22 (Me, PTo_3), 19.61 (Me), 19.58 (Me). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 17.13 (s, $^1J_{PPt}$ = 2633 Hz). MS (FAB^+), *m/z* (%): 1186 (M^+, 90).

Synthesis of *trans*-[Pt(C≡CC$_6$Me$_4$C≡CAuPR$_3$-4)$_2$(PAr$_3$)$_2$] [Ar = Ph (4a), To (4b)]. To a solution of *trans*-[Pt{C≡C(C_6Me_4)C≡CH-4}$_2$(PAr_3)$_2$] [Ar = Ph (**1a**) 125 mg, 0.12 mmol; To (**1b**) 99 mg, 0.08 mmol] in degassed CH_2Cl_2 (**1a**, 20 mL) or acetone (**1b**, 20 mL) was added the appropriate [Au(acac)PR_3] complex [R = Ph (193 mg, 0.35 mmol), To (153 mg, 0.25 mmol)], and the mixture was stirred under nitrogen for 6 (**4a**) or 10.5 (**4b**) h. In the case of **4a** a light suspension formed, which was filtered, the filtrate concentrated under vacuum to ca. 10 mL, and Et_2O (15 mL) added to give a yellow precipitate, which was filtered, washed with Et_2O (2 × 5 mL), and dried under reduced pressure (ca. 1 mbar) for 1 h to give **4a**·H_2O. In the case of **4b** a copious suspension formed, which was concentrated under vacuum to ca. 10 mL, and the yellow solid collected upon filtration was air-dried.

4a·H$_2$O: Yield 115 mg, 48%. Mp: 174 °C (dec). Anal. Calcd for $C_{100}H_{86}Au_2OP_4Pt$: C 59.56, H 4.30. Found: C 59.38, H, 4.32. IR (cm^{-1}): ν(C≡C) 2088 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.78−7.19 (m, 60 H, PPh_3), 2.35 (s, 12 H, C_6Me_4), 1.64 (s, 12 H, C_6Me_4), 1.55 (s, 2 H, H_2O). $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ 42.57 (s, $AuPPh_3$), 18.43 (s, $PtPPh_3$, $^1J_{PPt}$ = 2667 Hz).

4b: Yield 152 mg, 88%. Mp: 174 °C (dec). Anal. Calcd for $C_{112}H_{108}Au_2P_4Pt$: C 62.08, H 5.02. Found: C 62.01, H 5.25. IR (cm^{-1}): ν(C≡C) 2094 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 7.67−7.62 (m, 12 H, PTo_3), 7.45−7.40 (m, 12 H, PTo_3), 7.23−7.21 (m, 12 H, PTo_3), 6.99−6.97 (m, 12 H, PTo_3), 2.38 (s, 18 H, Me, PTo_3), 2.36 (s, 12 H, C_6Me_4), 2.22 (s, 18 H, Me, PTo_3), 1.64 (s, 12 H, C_6Me_4). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 141.6 (d, *p*-C, PTo_3, $^4J_{CP}$ = 2 Hz), 140.0 (Ar), 139.9 (m, *p*-C, PTo_3), 135.0 (d, *m*-CH, PTo_3, $^3J_{CP}$ = 12 Hz,), 134.2 (d, *o*-CH, PTo_3, $^2J_{CP}$ = 14 Hz), 133.7 (d, *i*-C, PTo_3, $^1J_{CP}$ = 86 Hz), 129.7 (d, *o*-CH, PTo_3, $^2J_{CP}$ = 11 Hz), 128.8 (Ar), 128.5 (Ar), 128.2 (d, *m*-CH, PTo_3, $^3J_{CP}$ = 6 Hz), 127.9 (Ar), 127.2 (d, *i*-C, PTo_3, $^1J_{CP}$ = 57 Hz), 120.7 (C≡C), 120.5 (C≡C), 112.8 (C≡C), 103.4 (d, ≡CAu, $^2J_{CP}$ = 27 Hz), 21.4 (Me, PTo_3), 21.3 (Me, PTo_3), 18.9 (Me), 17.8 (Me). $^{31}P\{^1H\}$ NMR: (162 MHz, $CDCl_3$): δ 40.52 (s, $AuPTo_3$), 16.94 (s, $PtPTo_3$, $^1J_{PPt}$ = 2654 Hz). MS (FAB^+), *m/z* (%): 2167 (M^+, 6). Crystals of **4b**·5CH_2Cl_2 suitable for an X-ray diffraction study were obtained by the liquid diffusion method using CH_2Cl_2 and *n*-pentane.

Synthesis of *trans*-[Pt(C≡CC$_6$Me$_4$C≡CAuPR$_3$-4)$_2$(PMe$_3$)$_2$] (4c). To a suspension of **4b** (301 mg, 0.14 mmol) in dry THF (5 mL) was added PMe_3 (1 M in toluene, 1.2 mL, 1.2 mmol), and the mixture was stirred under nitrogen for 25 h. The resulting suspension was filtered and the colorless solid collected, washed with *n*-pentane (2 × 10 mL), and dried successively in an oven at 80 °C for 0.5 h and under reduced pressure (ca. 1 mbar) for 0.5 h to give **4c**·1.5THF. Yield: 147 mg, 84%. Mp: 231 °C (dec). Anal. Calcd for $C_{46}H_{72}Au_2O_{1.5}P_4Pt$: C 40.56, H 5.32. Found: C 40.44, H 5.50. IR (cm^{-1}): ν(C≡C) 2088 (s). ^1H NMR (400 MHz, $CDCl_3$): δ 3.75 (m, 6 H, THF), 2.50 (s, 12 H, C_6Me_4), 2.44 (s, 12 H, C_6Me_4), 1.85 (m, 6 H, THF), 1.72 (m, 18 H, $PtPMe_3$), 1.52 (d, 18 H, $AuPMe_3$, $^2J_{HP}$ = 10 Hz). APT $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.2 (Ar), 138.8 (Ar), 135.5 (Ar), 135.2 (Ar), 133.8 (Ar), 127.0 (*C*≡CPt), 122.0 (d, *C*≡CAu, $^3J_{CP}$ = 9 Hz), 116.5 (≡CPt, $^1J_{PtC}$ = 30 Hz), 103.3 (d, CAu, $^2J_{CP}$ = 29 Hz), 68.0 (CH_2, THF), 25.6 (CH_2, THF), 19.1 (Me), 18.9 (Me), 15.9 (virtual t, $PtPMe_3$, $|^1J_{CP} + {}^3J_{CP}|$ = 40 Hz), 15.8 (d, $AuPMe_3$, $^1J_{CP}$ = 36 Hz). $^{31}P\{^1H\}$ NMR: (162 MHz, $CDCl_3$): δ 1.25 (s, $AuPMe_3$), −21.46 (s, $PtPMe_3$, $^1J_{PPt}$ = 2316 Hz). MS (FAB^+), *m/z* (%): 1252 (M^+, 13).

Synthesis of *trans*-[Pt{C≡CC$_6$Me$_3$(C≡CAuPTo$_3$)$_2$-3,5}$_2$-(PTo$_3$)$_2$] (5b). To a suspension of **3b** (102 mg, 0.09 mmol) in a 1:1 CH_2Cl_2/acetone mixture (10 mL) was added a solution of [Au(acac)PTo$_3$] (310 mg, 0.52 mmol) in degassed acetone (10 mL). The mixture was stirred under nitrogen for 24 h, the resulting suspension was filtered and the colorless solid washed with Et_2O (5 mL) and air-dried. Yield: 226 mg, 79%. Mp: 223 °C (dec). Anal. Calcd for $C_{156}H_{144}Au_4P_6Pt$: C 58.78, H 4.55. Found: C 59.13, H 4.62. IR (cm^{-1}): ν(C≡C) 2096 (s). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70−7.64 (m, 12 H, Ar, PtPTo$_3$), 7.46−7.41 (m, 24 H, AuPTo$_3$), 7.26−7.22 (m, 24 H, AuPTo$_3$), 6.99−6.97 (m, 12 H, PtPTo$_3$), 2.71 (s, 6 H, C$_6$Me$_3$), 2.39 (s, 36 H, Me, AuPTo$_3$), 2.21 (s, 18 H, Me, PtPTo$_3$), 2.07 (s, 12 H, C$_6$-Me$_3$). APT ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 141.6 (d, *p*-C, AuPTo$_3$, $^4J_{CP}$ = 2 Hz), 140.0 (m, *p*-C, PtPTo$_3$), 139.3 (Ar), 136.9 (Ar), 134.9 (m, *o*-CH, PtPTo$_3$), 134.2 (d, *o*-CH, AuPTo$_3$, $^2J_{CP}$ = 14 Hz), 129.7 (d, *m*-CH, AuPTo$_3$, $^3J_{CP}$ = 12 Hz), 128.5 (Ar), 128.2 (m, *m*-CH, PtPTo$_3$), 127.3 (d, *i*-C, AuPTo$_3$, $^1J_{CP}$ = 57 Hz), 127.1 (d, *i*-C, PtPTo$_3$, $^1J_{CP}$ = 56 Hz), 126.1 (Ar), 120.8 (d, *C*CAu, $^3J_{CP}$ = 2 Hz), 117.7 (C≡CPt), 111.8 (C≡CPt), 102.6 (d, CAu, $^2J_{CP}$ = 27 Hz), 21.45 (Me, PTo$_3$), 21.34 (Me, PTo$_3$), 21.14 (Me), 20.46 (Me). ^{31}P{^{1}H} NMR: (162 MHz, $CDCl_3$): δ 40.51 (s, AuPTo$_3$), 17.01 (s, PtPTo$_3$, $^1J_{PPt}$ = 2653 Hz). MS (FAB$^+$), *m/z* (%): 3184 (M$^+$, 22).

Synthesis of *trans*-[Pt{C≡C(C$_6$Me$_3$)(C≡CAuPMe$_3$)$_2$-3,5}$_2$(PMe$_3$)$_2$] (5c). To a suspension of **5b** (105 mg, 0.033 mmol) in dry THF (15 mL) was added PMe$_3$ (1 M in toluene, 0.29 mL, 0.29 mmol), and the mixture was stirred under nitrogen for 6 h. The solution was concentrated under reduced pressure to ca. 5 mL, and *n*-pentane (5 mL) was added to precipitate a colorless solid, which was filtered, washed with *n*-pentane (5 mL), and vacuum-dried (ca. 1 mbar) for 1 h. Yield: 58 mg, 91%. Mp: 196 °C (dec). Anal. Calcd for $C_{48}H_{72}$-Au_4P_6Pt: C 31.71, H 3.99. Found: C 32.07, H 4.02. IR (cm^{-1}): ν(C≡C) 2086 (s). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.74 (s, 6 H, C$_6$Me$_3$), 2.71 (s, 12 H, C$_6$Me$_3$), 1.71 (virtual t, 18 H, PtP*Me*$_3$, $|^2J_{HP} + {}^4J_{HP}|$ = 8 Hz, $^3J_{HPt}$ = 28 Hz), 1.51 (d, 36 H, AuP*Me*$_3$, $^2J_{HP}$ = 10 Hz). APT ^{13}C{^{1}H} NMR (50 MHz, $CDCl_3$): δ 140.6 (Ar), 140.0 (Ar), 139.5 (Ar), 137.6 (Ar), 122.3 (*C*≡CAu), 114.8 (C≡CPt), 106.9 (C≡CPt), 102.9 (d, CAu, $^2J_{CP}$ = 30 Hz), 21.87 (Me), 21.59 (Me), 16.29 (virtual t, PtP*Me*$_3$, $|^1J_{CP} + {}^3J_{CP}|$ = 38 Hz), 16.20 (d, AuP*Me*$_3$, $^1J_{CP}$ = 36 Hz). ^{31}P{^{1}H} NMR: (121 MHz, $CDCl_3$): δ 1.63 (s, AuPMe$_3$), −21.10 (PtPMe$_3$, $^1J_{PPt}$ = 2329 Hz). MS (FAB$^+$), *m/z* (%): 1817 (M$^+$, 10).

Synthesis of (PPN)$_n$[*trans*-Pt{(C≡CC$_6$Me$_4$C≡C-4)$_2$Au}-(PR$_3$)$_2$]$_n$ [R = Ph (6a), Me (6c), ^{n}Bu (6e)]. To a solution of the appropriate complex **1** (**1a**: 161 mg, 0.15 mmol; **1c**: 91 mg, 0.13 mmol; **1e**: 155 mg, 0.16 mmol) in degassed CH_2Cl_2 (15 mL) was added a solution of PPN[Au(acac)$_2$] (for **6a**: 153 mg, 0.16 mmol; for **6c**: 132 mg, 0.14 mmol; for **6e**: 158 mg, 0.17 mmol) in the same solvent (10 mL). The mixture was stirred under nitrogen for 15.5 (**6a**), 5 (**6c**), or 26 (**6e**) h. In the first two cases a copious precipitate formed, which was filtered, washed with CH_2Cl_2 (10 mL), and dried in the air and then under reduced pressure (ca. 1 mbar) for 0.5 h to give a bright orange (**6a**) or bright yellow (**6c**) powder insoluble in all common organic solvents; thus further purification proved impossible. For **6e** a solution resulted that was filtered through Celite, the solvent removed under vacuum to ca. 5 mL, and *n*-pentane added (20 mL) to precipitate a colorless solid, which was filtered, washed with *n*-pentane (2 × 5 mL), and dried successively in the air and under reduced pressure (ca. 1 mbar) for 0.5 h.

6a: Yield 183 mg, 67%. Mp: 159 °C (dec). IR (cm^{-1}): ν(C≡C) 2086(w).

6c: Yield 128 mg, 68%. Mp: 142 °C (dec). IR (cm^{-1}): ν(C≡C) 2082(s). ^{31}P{^{1}H} NMR (121 MHz, solid): δ 21.02 (br, PPN), −22.22 (s, PMe$_3$, $^1J_{PPt}$ = 2324 Hz).

6e: Yield 207 mg, 76%. Mp: 194 °C (dec). Anal. Calcd for $C_{88}H_{108}AuNP_4Pt$: C 62.33, H 6.42, N 0.83. Found: C 62.00, H 6.39, N 0.86. IR (cm^{-1}): ν(C≡C) 2086(s). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.47−7.26 (m, 30 H, PPN), 2.21−2.14 (three s, 24 H, C$_6$Me$_4$), 1.87 (m, 12 H, CH_2, Bu), 1.41 (m, 12 H, CH_2, Bu), 1.20 (m, 12 H, CH_2, Bu), 0.70 (m, 18 H, Me, Bu). APT ^{13}C{^{1}H} NMR (100 MHz, CD_2Cl_2): δ 137.70, 134.55 (quaternary carbon nuclei, C$_6$Me$_4$), 134.16 (m, *p*-CH, PPN), 133.56, 133.47 (quaternary carbon nuclei, C$_6$Me$_4$) 132.51 (m, *m*-CH, PPN), 129.90 (m, *o*-CH, PPN), 127.38 (m, *i*-C, PPN), 26.91 (s, P(CH$_2$)$_2$*C*H$_2$-Me), 24.75 (virtual t, PCH$_2$*C*H$_2$Et, $|^2J_{CP} + {}^4J_{CP}|$ = 13.6 Hz), 24.32 (virtual t, P*C*H$_2$Pr, $|J_{CP} + {}^3J_{CP}|$ = 34.6 Hz), 19.15, 19.10, 19.07 (s, C$_6$*Me$_4$*), 14.06 (s, Me, Bu). ^{31}P{^{1}H} NMR (162 MHz, CD_2Cl_2): δ 21.13 (s, PPN), 3.53 (br s, P(^{n}Bu)$_3$, $^1J_{PPt}$ = 2377 Hz).

Synthesis of (PPN)$_{2n}$[*trans*-Pt{C≡CC$_6$Me$_3$(C≡C)$_2$-3,5}$_2$Au$_2$(PTo$_3$)$_2$]$_n$ (7). To a solution of **3b** (108 mg, 0.09 mmol) in degassed CH_2Cl_2 (15 mL) was added a solution of PPN[Au-(acac)$_2$] (0.179 g, 0.19 mmol) in the same solvent (5 mL), and the mixture was stirred under nitrogen for 24 h. The resulting suspension was filtered and the solid washed with CH_2Cl_2 (2 × 5 mL) and dried under reduced pressure (ca. 1 mbar) for 0.5 h to give a colorless powder insoluble in all common organic solvents. Yield: 184 mg, 77%. Mp: 206 °C (dec). IR (cm^{-1}): ν(C≡C), 2084(w).

X-ray Structure Determinations. Numerical details are presented in Table 1. Data were recorded at −140 °C on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation (λ = 0.71073 Å). Absorption corrections were based on multiple scans (program SADABS). Structures were refined anisotropically on F^2 using the program SHELXL-97 (Prof. G. M. Sheldrick, University of Göttingen). Acetylenic H atoms were refined freely; other H atoms, using a riding model or rigid methyl groups. *Special features of refinement*. **1a**: The chloroform molecule is disordered over an inversion center. **4b**: There are three dichloromethane sites, one of which is disordered over an inversion center.

Results and Discussion

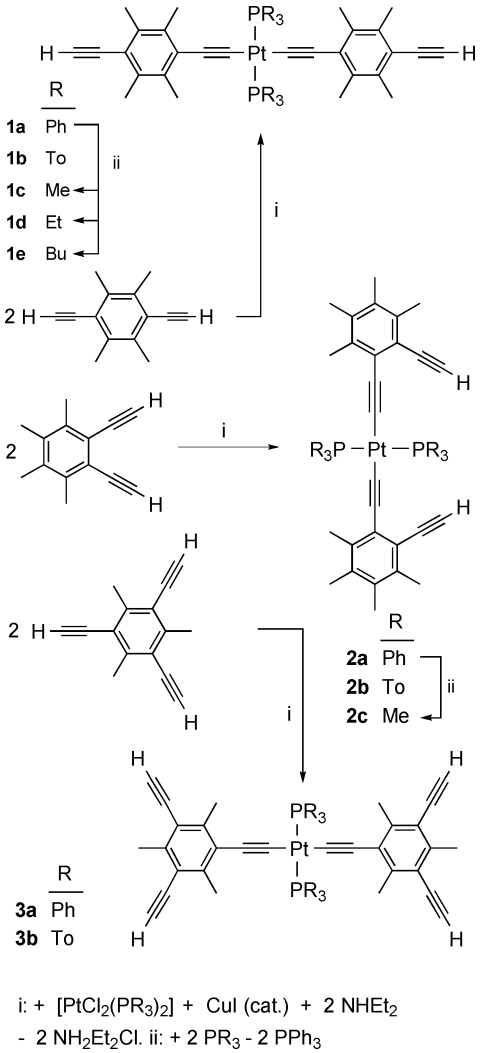
Synthesis. The complexes *trans*-[Pt(C≡CC$_6$Me$_4$-C≡CH-4)$_2$(PAr$_3$)$_2$] [Ar = Ph (**1a**), To (**1b**)], *trans*-[Pt-(C≡CC$_6$Me$_4$C≡CH-2)$_2$(PAr$_3$)$_2$] [Ar = Ph (**2a**), To (**2b**)], and *trans*-[Pt(C≡CC$_6$Me$_3$(C≡CH)$_2$-3,5)$_2$(PAr$_3$)$_2$] [Ar = Ph (**3a**), To (**3b**)] were prepared by dehydrohalogenation reactions, catalyzed by 0.1% mol CuI, between the appropriate *cis*-[PtCl$_2$(PR$_3$)$_2$] complexes and excess of the alkynes C$_6$Me$_4$(C≡CH)$_2$-1,4, C$_6$Me$_4$(C≡CH)$_2$-1,2, or C$_6$Me$_3$(C≡CH)$_3$-1,3,5 (approximately 1:4 molar ratio), respectively, in diethylamine (Scheme 1). Some of the complexes crystallized with half (**2b**) or one (**3a**,**b**) molecule of water that we could not remove even after repeated recrystallization from $CHCl_3$/Et_2O mixtures. The PPh_3 ligands in complexes **1a** and **2a** can be replaced by more basic trialkylphosphines to give the homologous derivatives with PMe$_3$ (**1c**, **2c**), PEt$_3$ (**1d**), or P(^{n}Bu)$_3$ (**1e**) (Scheme 1).

Our previous experience of the synthetic utility of the "acac method"[25] to prepare alkynylgold(I) complexes[26,28] from the acetylacetonatogold(I) complexes [Au(acac)-PAr$_3$] or [Au(acac)$_2$]$^-$ and a variety of terminal alkynes prompted us to study the possibility of preparing heteronuclear Pt^{II}Au^I σ-alkynyl complexes from the alkynyl derivatives **1**−**3**, which could behave as terminal alkynes. Thus, the reactions of complexes **1a**, **1b**, and **3b** with an excess of the appropriate [Au(acac)PAr$_3$] gave, respectively, trinuclear Pt^{II}Au$^I_2$ or pentanuclear Pt^{II}Au$^I_4$ σ-alkynyl complexes *trans*-[Pt(C≡CC$_6$Me$_4$C≡CAuPAr$_3$-4)$_2$(PAr$_3$)$_2$] [Ar = Ph (**4a**), To (**4b**)] or *trans*-[Pt{C≡CC$_6$Me$_3$(C≡CAuPAr$_3$)$_2$-3,5}$_2$(PAr$_3$)$_2$] [Ar = Ph (**5a**), To (**5b**)], respectively, in good yield (Scheme 2).

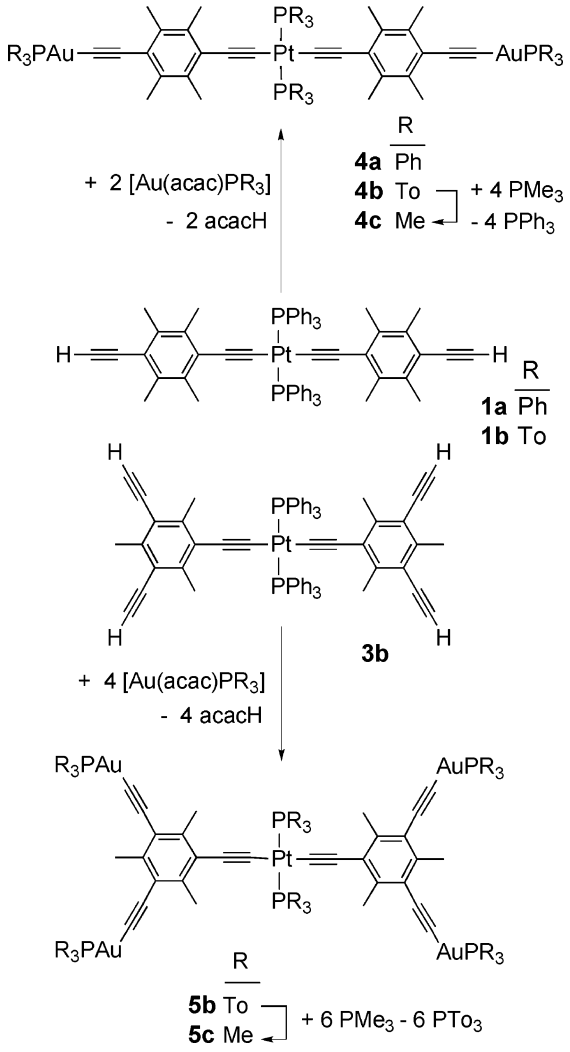
Table 1. Crystal Data and Structure Refinement

	1a·$CHCl_3$	**2b**·$2CHCl_3$	**4b**·$5CH_2Cl_2$
formula	$C_{65}H_{57}Cl_3P_2Pt$	$C_{72}H_{70}Cl_6P_2Pt$	$C_{117}H_{118}Au_2Cl_{10}P_4Pt$
fw	1201.49	1405.01	2591.52
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	9.0753(6)	10.2862(6)	12.3981(11)
b (Å)	11.5861(8	12.7169(8)	15.1902(12)
c (Å)	14.3546(11)	13.5664(11)	16.3181(14)
α (deg)	96.168(4)	77.919(4)	92.748(4)
β (deg)	102.756(4)	70.307(4)	104.496(4)
γ (deg)	104.817(4	76.817(4)	107.755(4
volume (Å^3)	1401.48(17)	1609.71(19)	2807.8(4)
Z	1	1	1
ρ_{calcd} (Mg m^{-3})	1.424	1.449	1.533
μ (Mo Kα) (mm^{-1})	2.743	2.520	4.190
F(000)	606	712	1286
cryst size (mm)	0.30 × 0.14 × 0.10	0.23 × 0.21 × 0.07	0.20 × 0.16 × 0.07
θ range (deg)	1.48 to 30.03	1.61 to 30.03	1.30 to 26.37
no. of reflns coll	28 596	33 598	47 189
no. of indep reflns	8158	9391	11442
R_{int}	0.0260	0.0305	0.0521
max. and min. transmsn	0.819 and 0.663	0.862 and 0.667	0.802 and 0.669
no. of restraints/params	105/343	106/378	198/604
goodness-of-fit on F^2	1.023	1.037	0.986
R1 [$I>2\sigma(I)$]	0.0275	0.0229	0.0393
wR2 (all reflns)	0.0688	0.0543	0.1101
largest diff peak and hole (e Å^{-3})	1.800 and −1.583	0.982 and −0.799	2.719 and −1.576

Scheme 1



Scheme 2



However, although its NMR spectra show **5a**·$2H_2O$ to be pure, the %C found is low (Anal. Calcd for $C_{138}H_{112}Au_4O_2P_6Pt$: C 55.79, H 3.80. Found: C 54.33, H 3.77), which we could not improve even after repeated recrys-

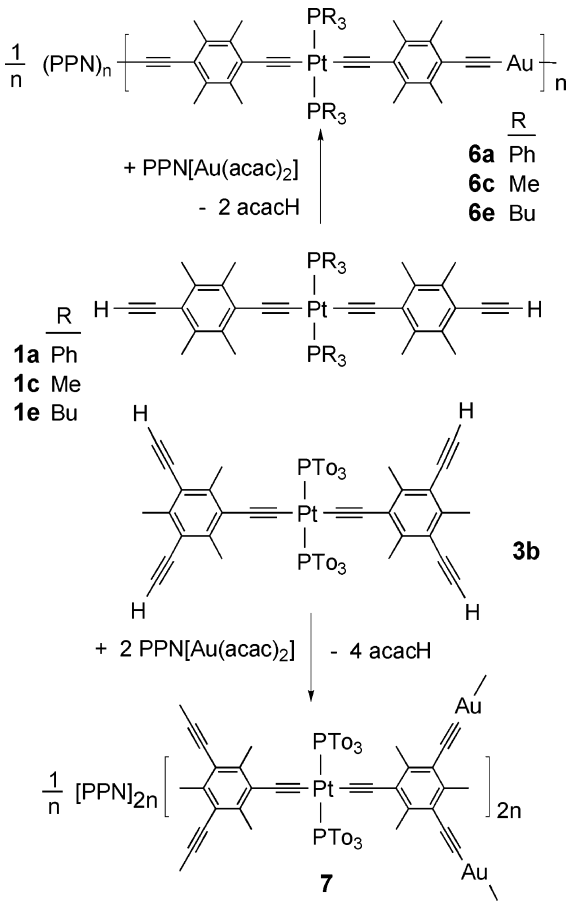
tallizations. Under the same reaction conditions, the homologous complexes *trans*-[Pt(C≡CC$_6$Me$_4$C≡CAuPAr$_3$-2)$_2$(PAr$_3$)$_2$] (Ar = Ph, To) could not be obtained from **2a** or **2b** and [Au(acac)PAr$_3$], which we attribute to the steric hindrance between the *ortho*-C≡CH substituents in **2a** or **2b** and the bulky phosphine ligands, as confirmed by the crystal structure of **2b** (see below). The replacement of the PTo$_3$ ligands in complex **4b** or **5b** by PMe$_3$ allowed the synthesis of the homologous complexes **4c** and **5c**, respectively (Scheme 2). Similarly, the reaction of **4b** with PEt$_3$ (1:4) gave the corresponding complex with this ligand, but despite many recrystallizations, its NMR spectra and elemental analyses (Anal. Calcd for C$_{52}$H$_{84}$Au$_2$P$_4$Pt: C 43.92, H 5.95. Found: C 42.80, H 5.91) showed the presence of some impurity that we could not remove.

Apart from the metallamacrocyclic Pt$^{II}_2$Au^I triangle PPN[Au{Pt(PMe$_3$)$_2$}$_2${μ-C$_6$Me$_4$(C≡C)$_2$-1,2}$_3$], the synthesis and the crystal structure of which has been recently reported by us,[15] complexes [Pt(C≡C−C≡CH)-{C≡C−C≡CAuPPh$_3$}(dppe)][14] and the square metallamacrocycle (PPN)$_4$[Pt(C≡C−C≡C−Au−C≡C−C≡C)-(dppe)]$_4$[4] are the only mixed Pt^{II}Au^I σ-alkynyl complexes previously reported. They were obtained by reacting [Pt-(C≡C−C≡CH)$_2$(dppe)] with ^{n}BuLi and [AuCl(PPh$_3$)] or with PPN[Au(acac)$_2$], respectively, but their crystal structures are unknown.

The reaction of PPN[Au(acac)$_2$] with **1a**, **1c**, **1e** (1:1) or **3b** (2:1) gave, respectively, the anionic σ-alkynyl polymers (PPN)$_n$[*trans*-Pt{(C≡CC$_6$Me$_4$C≡C-4)$_2$Au}-(PR$_3$)$_2$]$_n$ [R = Ph (**6a**), Me (**6c**), ^{n}Bu (**6e**)] and (PPN)$_{2n}$-[*trans*-Pt{C≡CC$_6$Me$_3$(C≡C)$_2$-3,5}$_2$Au$_2$(PTo$_3$)$_2$]$_n$ (**7**), which were isolated in good yield (Scheme 3). Among them, only **6e** is soluble in organic solvents so as to allow its purification and the measuring of its NMR spectra, while the extreme insolubility of **6a**, **6b**, and **7** prevented their recrystallization and, as is usual for this type of polymeric materials, good elemental analyses (**6a**: Anal. Calcd for C$_{100}$H$_{84}$AuP$_4$Pt: C 66.15, H 4.66, N 0.77. Found: C 63.75, H 4.50, N 0.59; **6c**: Anal. Calcd for C$_{70}$H$_{72}$AuNP$_4$Pt: C 58.25, H 5.03, N 0.97. Found: C 53.29, H 5.09, N 0.50; **7**: Anal. Calcd for C$_{144}$H$_{120}$-Au$_2$N$_2$P$_6$Pt: C 65.18, H 4.56, N 1.06. Found: C 60.96, H 4.69, N 0.94). A GPC study on **6e** gave an average molecular weight of 7.7 × 10^5 amu corresponding to a medium value of 667 monomeric units, a number considerably higher than those found in other alkynyl metal-containing polymers.[11,13,17,21,22] However, the great polydispersity value (I_p = 4.66) is indicative that **6e** contains a wide range of polymeric materials. The polymers **6** and **7** are (i) the first heteronuclear alkynyl polymers of any d^8/d^{10} system, (ii) the first anionic alkynyl polymers prepared to date, and (iii) the first alkynyl polymers that have been obtained by the "acac method", which turns out to be useful for the synthesis of organometallic polymers with a high degree of polymerization. In the hope of synthesizing soluble alkynyl Au^{I}Pt^{II} polymers homologous to **6** and **7** we have undertaken the study of the reactivity of the dialkynes C$_6$^{t}Bu$_4$(C≡CH)$_2$-1,4 and C$_6$(^{n}C$_4$H$_9$)$_4$(C≡CH)$_2$-1,4 toward Pt(II) and "Au^I(acac)" complexes.

Crystal Structures of 1a·CHCl$_3$, 2b·2CHCl$_3$, and 4b·5CH$_2$Cl$_2$. The complexes **1a** (Figure 1), **2b** (Figure 2), and **4b** (Figure 3) are centrosymmetric with the

Scheme 3



inversion center at the Pt atoms (Table 1). In all cases the platinum is in a square planar environment coordinated to two alkynyl fragments and two phosphine ligands in mutually *trans* positions, the C−Pt−P angles being close to 90°. In **4b** the gold atoms coordinate to an alkynyl and a phosphine ligand in a linear environment [C−Au−P 175.2(2) °]. The C≡C [1.214(3) Å (**1a**, **2b**), 1.214 (9), 1.208(8) Å (**4b**)], C−Pt [1.998(2) Å (**1a**), 1.9973 (18) Å (**2b**), 2.007 (6) Å (**4b**)], P−Pt [2.2967(6) Å (**1a**), 2.3094(4) Å (**2b**), 2.3147(15) Å (**4b**)], C−Au [1.996(6) Å (**4b**)], and P−Au [2.2797(16) (**4b**) Å] bond distances are in the ranges previously found in related complexes.[33] The structure of **2b** reveals that the C≡CH hydrogen atoms lie between two aryl substitu-

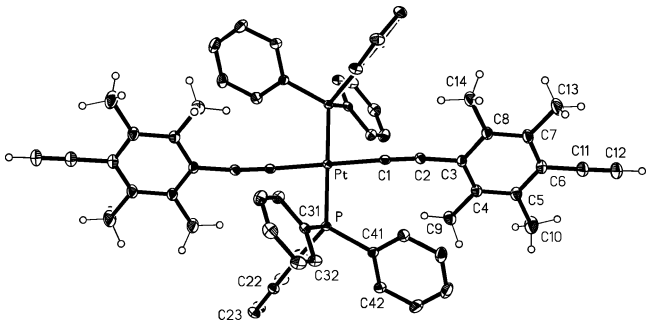


Figure 1. Thermal ellipsoid plot (50% probability) of **1a**·CHCl$_3$. Selected bond lengths (Å) and angles (deg): Pt−C(1) 1.998(2), Pt−P 2.2967(6), C(1)−C(2) 1.214(3), C(2)−C(3) 1.438(3), C(1)#1−Pt−C(1) 180.0, C(1)#1−Pt−P 86.48(6), C(1)−Pt−P 93.52(6), C(2)−C(1)−Pt 175.8(2), C(1)−C(2)−C(3) 173.8(2). Solvent and phosphine hydrogens are omitted for clarity.

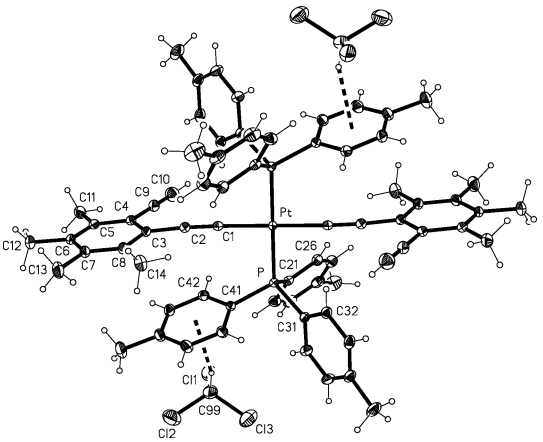


Figure 2. Thermal ellipsoid plot (40% probability) of **2b**·$2CHCl_3$. Selected bond lengths (Å) and angles (deg): Pt−C(1) 1.9973(18), Pt−P 2.3094(4), C(1)−C(2) 1.214(3), C(2)−C(3) 1.434(2), C(1)#1−Pt−C(1) 180.0, C(1)#1−Pt−P 90.34(5), C(1)−Pt−P 89.66(5), C(2)−C(1)−Pt 177.70(16), C(1)−C(2)−C(3) 176.42(19).

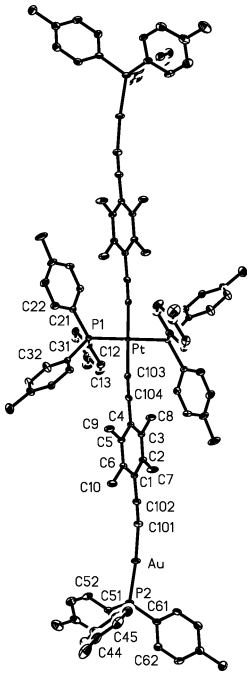


Figure 3. Thermal ellipsoid plot (30% probability) of **4b**·$5CH_2Cl_2$. Selected bond lengths (Å) and angles (deg): Pt−C(103) 2.007(6), Pt−P(1) 2.3147(15), Au−C(101) 1.996(6), Au−P(2) 2.2797(16), C(1)−C(102) 1.437(8), C(4)−C(104) 1.445(8), C(101)−C(102) 1.214(9), C(103)−C(104) 1.204(8), C(103)#1−Pt−C(103) 180.0, C(103)−Pt−P(1)#1 90.86(16), C(103)−Pt−P(1) 89.14(16), P(1)#1−Pt−P(1) 180.0, C(101)−Au−P(2) 175.2(2), C(102)−C(101)−Au 171.8(6), C(101)−C(102)−C(1) 174.7(7), C(104)−C(103)−Pt 176.6(5), C(103)−C(104)−C(4) 177.6(6). Solvent and H atoms are omitted for clarity.

ents of the phosphine, and the restricted access to these hydrogen atoms could explain why [Au(acac)PR_3] failed to react with **2a** and **2b**, as mentioned above. In compound **2b**, the chloroform is well-ordered and makes a very short contact to the centroid of the aromatic ring C41−46, as shown in Figure 2 [C−H normalized to 1.08 Å; H···Cent 2.39 Å, angle C−H···Cent 162°]. This type of X−H···π hydrogen bond is well-documented.[34] The disordered or poorly resolved solvent of the other two structures precludes meaningful analysis of corresponding contacts.

Among the many (alkynyl)Pt(II) complexes structurally characterized by X-ray diffraction methods,[33] only a few contain, as do **1a** and **2b**, C≡CH fragments and most contain the ligand −C≡C−C≡C−H.[14,35,36] Apart from our recently reported $Au^{I}Pt^{II}_2$ triangle PPN[Au{$Pt(PMe_3)_2$}$_2${μ-C_6Me_4(C≡C)$_2$-1,2}$_3$],[15] **4b** is the only heteronuclear $Pt^{II}Au^{I}$ complex structurally characterized by X-ray crystallography.

NMR Spectra. The ^{1}H NMR spectra of complexes **1**−**5** show the resonances expected for the C_6Me_4-1,4 (**1**, **4**), C_6Me_4-1,2 (**2**), or C_6Me_3-1,3,5 (**3**, **5**) fragments that they contain (see Experimental Section), and those of complexes **1**−**3** show, in addition, a singlet resonance for the C≡CH protons in the range 3.01 (**2a**) to 3.50 (**1c**) ppm. In the ^{31}P{^{1}H} NMR spectra, the $Pt(PR_3)_2$ fragment gives rise to a singlet resonance with ^{195}Pt satellites. The $^1J_{PPt}$ coupling constants are in the range 2312 (**1c**) to 2667 (**4a**) Hz, as found in other *trans*-[Pt(alkynyl)$_2$(PR_3)$_2$] complexes,[35,37] and are greater than those in the *cis*-isomers,[38] in agreement with the weaker *trans*-influence of the phosphine with respect to the alkynyl ligands. The *trans*-geometry is confirmed for complexes **1c**, **2c**, and **5c** by their ^{1}H NMR spectra, which show virtual triplets with ^{195}Pt satellites for the PMe_3 protons.[39] The $AuPR_3$ fragments in complexes **4** and **5** give rise to a singlet resonance in the ^{31}P NMR spectra. The δ(P) and the J_{PPt} values for a given phosphine depend only very slightly on the alkynyl ligand and are not affected by the substitution of the C≡CH hydrogen atoms by $AuPAr_3$.

The ^{13}C{^{1}H} NMR spectra of all complexes have been measured (see Experimental Section) with the exception of **4a**, **6a**, **6c**, and **7**, which, because of their insolubility, do not give any resonance even after 12 h of acquisition. We have assigned the C_β≡C_αPt resonances only when the C−Pt coupling was observed, based on the general assumption that J_{CPt} is greater for the α carbon, although other authors make opposite assignments[40] or describe both resonances as due to the "C≡C−Pt" fragment.[12] In our case the α carbon [δ, 116.5 (**4c**) to 120.9 (**1a**) ppm; $^1J_{CPt}$, 29−31 Hz] is at lower field than the β carbon [δ, 107.7 (**1c**) to 112.6 (**1a**) ppm; $^2J_{CPt}$, 2−4 Hz].

In the heteronuclear complexes **4** and **5**, the resonances of the alkynyl carbon nuclei of the C_β≡$C_\alpha$$AuPR_3$ fragments were assigned on the basis of the J_{CP} values.

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The α carbons give a doublet [in the range 102.6 (**5b**) to 103.4 (**4b**) ppm] with $^2J_{CP}$ values of 23−30 Hz, while the β carbons are at lower field [120.8 (**5b**) to 122.0 (**4c**) ppm] and give a singlet or a doublet with smaller $^3J_{CP}$ value (2−9 Hz).

The $^{31}P\{^1H\}$ NMR spectrum of **6e**, the only soluble polymer here described, shows one singlet resonance for the $Pt\{P(^nBu)_3\}_2$ fragments, which suggests a high polymerization degree, in agreement with the mean molecular weight ($M_w = 7.7 \times 10^5$ amu) determined by GPC, which corresponds to some 667 monomeric units. This ^{31}P resonance, including the ^{195}Pt satellites, is appreciably wider than that due to the PPN cations, but a variable-temperature study of this compound in $CDCl_3$ shows both the ^1H and $^{31}P\{^1H\}$ NMR spectra to be independent of temperature changes. The resonances from the C≡C nuclei are not observed in the $^{13}C\{^1H\}$ NMR spectrum of **6e**, which confirms their elusive detectability, as previously reported.[41]

IR Spectra. The IR spectra of complexes **1**−**7** show the $\nu_{C\equiv C}$ bands in the range 2102−2082 and those of complexes **1**−**3** show, in addition, ν_{CH} bands in the range 3314−3240 cm^{-1}, similar to those found in other (alkynyl)Pt(II) complexes.[8,12,42]

Mass Spectra. The FAB^+ MS of complexes **1**−**5** (See Experimental Section) show the molecular peaks with relative intensities ranging from 6 to 53%, the major peaks corresponding to the fragments $[Pt(PR_3)_2]^{2+}$ (**1**−**3**, 55−85%) or $[AuPR_3]^+$ and $[Au(PR_3)_2]^+$ (**4**, **5**, 90−100%). An attempted study of complex **6e** by MALDI using both linear and deflection, positive and negative modes, did not afford any conclusive results. Complex **6e** is only soluble in $CHCl_3$ or CH_2Cl_2 when freshly made. However, since a few days later it could not be dissolved in any of those solvents or in MeOH, the sample for the MALDI study was prepared by grinding the solid with a matrix of ditranol. For the low mass region only the PPN cation was detected, and when a 500 amu deflection was applied, the results show that fragmentation occurs in the tube of flight of the analyzer.

Conclusions. We report some of the few mononuclear Pt^{II} bis(σ-alkynyl) complexes of aryl di- and triacetylenes. These complexes are appropriate for the synthesis of the first σ-alkynyl trinuclear $Pt^{II}Au^{I}_2$ and pentanuclear $Pt^{II}Au^{I}_4$ complexes by reacting them with [Au(acac)PR_3] complexes. Using instead PPN[$Au(acac)_2$] it is possible to isolate the first reported anionic σ-alkynyl metal polymers described so far.

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Supporting Information Available: Listing of all refined and calculated atomic coordinates, anisotropic thermal parameters, and bond lengths and angles for **1a**·$CHCl_3$, **2b**·$2CHCl_3$, and **4b**·$5CH_2Cl_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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