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The first anionic arenediethynylgold(I) complexes

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Dedicated to Professor Pascual Royo on the occasion of his 65th birthday.

Abstract

We report synthetic methods for the preparation of mono-, di-, tri- and polyanionic alkynylgold(I) complexes, derived from diethynylarenes. The reaction between PPN[Au(acac)$_2$] and 1,3-diethynylbenzene [HC≡C(mphen)C≡CH] (1:1 M ratio) afforded the polymeric complex (PPN)$_n$[Au{C≡C(mphen)C≡C}]$_n$ (**1**) while the monomeric complexes (PPN)[Au{C≡C(Ar)C≡CH}$_2$] [Ar = mphen (**2**), mes (**3**)] resulted when the same dialkyne or 1,3-diethynylmesitylene [HC≡C(mes)C≡CH] were used in a 1:2 M ratio. Complexes PPN[XAuC≡C(Ar)C≡CH] [Ar = mphen, X = Cl (**4**), Ar = mes, X = Cl (**5**), SCN (**6**)] were obtained from the metathesis reactions between complexes **2** or **3** and the appropriate PPN[AuX$_2$] salts. The C≡CH groups in complexes **2** or **4** are acidic enough as to react with [Au(acac)PPh$_3$] (1:2) or with PPN[Au(acac)$_2$] (1:1) to give complexes PPN[Au{C≡C(mphen)C≡CAuPPh$_3$}$_2$] (**7**) or (PPN)$_3$[Au{C≡C(mphen)C≡CAuCl}$_2$] (**8**), respectively. Complexes (PPN)$_2$[XAuC≡C(Ar)C≡CAuX)] [Ar = mphen, X = Cl (**9**); Ar = mes, X = Cl (**10**), SCN (**11**)] have been prepared by reacting [Ph$_3$PAuC≡C(mphen)C≡CAuPPh$_3$] with PPN[AuCl$_2$] (1:2) (**9**) or [AuC≡C(mes)C≡CAu]$_n$ with the appropriate PPNX (1:2) salt (**10**, **11**).

Keywords: Anionic; Arenediethynyl; Gold(I)

1. Introduction

Metal complexes with bridging –C≡C(Ar)C≡C– spacers (Ar being various aromatic rings) have been shown to display electrical conductivity, nonlinear optical or liquid crystalline properties [1]. Among them, all the reported gold complexes are neutral which is also the case for the vast majority of alkynylgold(I) complexes. So far, arenediethynylgold(I) complexes of the types [Au{C≡C(Ar)C≡C}Au]$_n$ [2–4], [LAuC≡C(Ar)C≡CAuL}], (L = phosphine [3–5], isocyanide) [2–4], [AuC≡C(Ar)C≡CAu(LL)]$_n$, (LL = diphosphines [1,3], diisocyanide) [2,3], [ClAuP(R$_2$)CH$_2$(R$_2$)PAuC≡C(Ar)C≡CAuP(R$_2$)CH$_2$(R$_2$)PAuCl] [1] and [{AuC≡C(Ar)C≡CAu}$_2${μ-{CH$_2$(PR$_2$)$_2$}$_2$}] [5] have been described Ar being 1,4-C$_6$H$_4$, 1,4-(C$_6$H$_2$Me$_2$-2,5) or 3,5-C$_6$H$_3$Me. Three of them [3,6] have been studied by X-ray diffraction methods and all show infinite chain or ribbon structures and display interesting photophysical properties [6,7]. These have been attributed in part [8–11] to the existence of short intermolecular Au···Au contacts that are present in most of the structurally characterized luminescent gold(I) complexes [3,6,8,12]. Puddephatt has recently reviewed this chemistry [13].

In this paper we report mono-, di-, tri-, and polyanionic alkynylgold(I) complexes of the types (PPN)[Au{C≡C(Ar)C≡CH}$_2$], PPN[XAuC≡C(Ar)C≡CH], PPN[Au{C≡C(Ar)C≡CAuL)$_2$], (PPN)$_2$[XAuC≡C(Ar)C≡CAuX)], (PPN)$_3$[Au{C≡C(Ar)C≡CAuCl}$_2$], and (PPN)$_n$[Au{C≡C(Ar)C≡C}]$_n$, [PPN = bis(triphenyl)phosphoranylidenammonium, Ar = phenylendiyl-1,3 (mphen), mesitylendiyl-1,3 (mes); X = Cl, SCN, L = PPh$_3$] that we have prepared with the aim of extending the short family of anionic alkynylgold(I) complexes and with the hope of finding among them some peculiar structural features. These are the first

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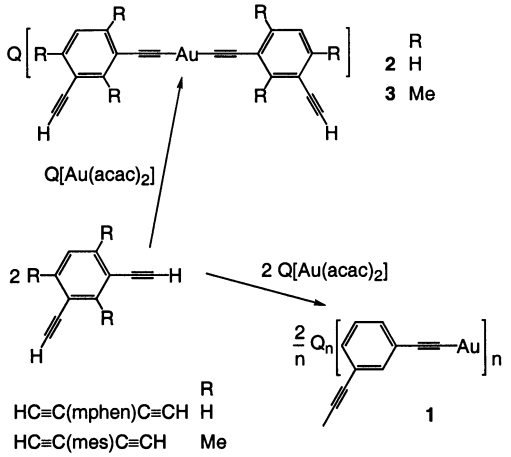
anionic arenediethynylgold(I) complexes and, although we have unfortunately failed to obtain single crystals suitable for diffraction studies they have been structurally characterized by NMR techniques.

2. Results and discussion

2.1. Synthesis of complexes

We have previously reviewed [14] the ability of acetylacetonatogold(I) complexes of the types [Au(acac)(PR_3)] or PPN[Au(acac)$_2$] (PPN = $Ph_3P{=}N{=}PPh_3$) to deprotonate organic substrates containing even weakly acidic hydrogen atoms. These reactions gave rise to a great variety of gold(I) complexes with phosphorus ylide, methanide, methanediide, sulfur ylide, amino, amido, nitrido, alkyl, phosphido, thiolato, hydrosulfido, trithiocarbonato, dithiocarbamato, 1,1-dithiolato and alkynyl (including ethynyl) ligands. As an extension of 'the acac method', the reactions of PPN[Au(acac)$_2$] with the dialkynes HC≡C(Ar)C≡CH [Ar = C_6H_4-1,3 (mphen) [15], {C_6HMe_3-2,4,6}-1,3 (mes) [4] allowed us to prepare different alkynylaurategold(I) complexes depending on the reaction conditions. Thus, while the polymeric complex (PPN)$_n$[AuC≡C(mphen)C≡C]$_n$ (**1**) results from the 1:1 reaction between PPN[Au(acac)$_2$] and the corresponding dialkyne, the mononuclear derivatives (PPN)$_2$[Au{C≡C(Ar)C≡CH}$_2$] [Ar = mphen (**2**), mes (**3**)] were isolated from the 1:2 reactions (Scheme 1). An slight excess of PPN[Au(acac)$_2$] must be used for the synthesis of **1** (see Section 3) because otherwise it is contaminated with a small amount of **2** that cannot be separated. Although the excess of PPN[Au(acac)$_2$] precipitates along with **1** upon addition of Et_2O and it cannot be removed by recrystallization we fortunately found an alternative way to purify **1** which consists in heating the mixture **1** + PPN[Au(acac)$_2$] in an oven at 60–70 °C for 2 h which causes the PPN[Au(acac)$_2$] to decompose to metallic gold. After recrystallizing the heated mixture from CH_2Cl_2 and Et_2O pure **1** could be isolated in 36% yield.



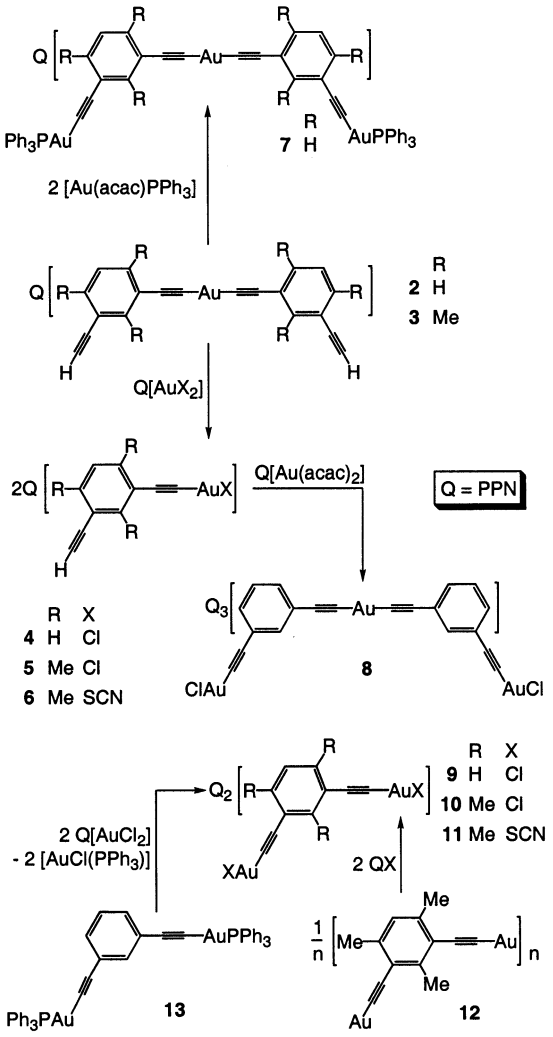
Scheme 1.

The 1:1 reaction between PPN[Au(acac)$_2$] and HC≡C(mes)C≡CH, analogous to that leading to **1**, gave a yellow product which ^{1}H-NMR spectrum shows the expected resonances for the homologous complex (PPN)$_n$[AuC≡C(mes)C≡C]$_n$ [δ 2.26 (s, 6H, Me), 2.44 (s, 3H, Me), 6.63 (s, 1H, mes), 7.33–3.62 (m 30H. PPN)] along with other very small singlet resonances at 2.13, 2.33, 2.40 and 6.77 ppm that we attribute to the formation of a small amount of an open chain oligomer (PPN)$_{n+1}$[HC≡C(mes)C≡C{AuC≡C(mes)C≡C}$_n$AuC≡C(mes)C≡CH]. The syntheses of **2** or **3** can be carried out in the presence of an excess of the appropriate dialkyne, which is removed easily along with the by-product acacH by washing with Et_2O. The low yield in the synthesis of **3** is due to the necessity of recrystallizing it from acetone, which is the only way to remove a small amount of a contaminant observed in its ^{1}H-NMR spectrum, which we could not identify.

By reacting complexes **2** or **3** with one equivalent of the appropriate PPN[AuX_2] salt, complexes PPN[XAuC≡C(Ar)C≡CH] [X = Cl, Ar = mphen (**4**), mes (**5**); X = SCN, Ar = mes (**6**); Scheme 2] were obtained in high yield. Metathesis reactions between dialkynylaurate(I) and dihaloaurate(I) complexes to give the corresponding alkynyl(halo)aurate(I) derivatives have been previously described by us [16,17].

The anionic trinuclear derivative PPN[Au{C≡C(mphen)C≡CAuPPh_3}$_2$] (**7**) or (PPN)$_3$[Au{C≡C(mphen)C≡CAuCl}$_2$] (**8**) was obtained in high yield by reacting two equivalents of [Au(acac)PPh_3] or half equivalent of PPN[Au(acac)$_2$] with complexes **2** or **4**, respectively. These reactions provide new examples of the utility of the 'acac method' [14].

The anionic dinuclear complexes (PPN)$_2$[XAuC≡C(Ar)C≡CAuX] [Ar = mphen, X = Cl, (**9**); Ar = mes, X = Cl (**10**), SCN (**11**)] can be obtained by reacting the appropriate neutral polymer [AuC≡C(Ar)C≡CAu] (Ar = mphen (**12a**), mes (**12b**)) [4] with two equivalents of the corresponding PPNX salt. Most probably, complexes **9**–**11** result from the cleavage of the weak π(C≡C)→Au interactions by the anionic X ligand. Although this is the most straightforward method to prepare complex **9**, a better yield is achieved (82 vs. 72%) by reacting [Ph_3PAuC≡C(mphen)C≡CAuPPh_3] (**13**) [4] with two equivalents of PPN[$AuCl_2$]. The success in this ligand exchange reaction could be attributed in part to the great stability of the by-product [AuCl(PPh_3)] that can be recovered almost quantitatively from the mother liquor in which complex **9** precipitates.



Scheme 2.

2.2. Structure of complexes

2.2.1. NMR spectroscopy

In the ^{1}H-NMR spectra of those complexes that contain C≡C(Ar)C≡CH fragments the acetylene proton appears at chemical shifts (Ar = mphen, **2**: 2.93, **4**: 2.95; Ar = mes, **3**: 3.35; **5**: 3.36; **6**: 3.38 ppm) similar to the corresponding dialkynes (Ar = mphen, 3.05 [15]; mes, 3.40 [4] ppm).

The resonances due to the protons in the aromatic mphen fragments cannot be assigned unambiguously since they are obscured by those due to the PPh_3 ligands or the PPN cation.

The resonances in the ^{13}C{^{1}H}-NMR spectra have been assigned (see Section 3) based on those of the corresponding free alkynes [4,18] and some other alkynylgold complexes reported previously by us [17,19] but in some cases the assignment was prevented due to overlapping with resonances of the PPN cation (**2**) or to the limited stability of complexes (**1**, **7**, **8**) that prevented sufficient data acquisition. The *C*–Au and *C*≡CAu resonances appear in the ranges 132–122 and 128–98 ppm, respectively, downfield shifted with respect to their homologous in the free alkyne as previously observed in other alkynyl complexes [17].

2.2.2. IR spectroscopy

The IR spectra of complexes **1**–**11** show one weak or medium absorption assignable to the ν(C≡C) stretching mode in the range 2090–2110 (Ar = mphen) or 2096–2106 (Ar = mes) cm^{-1} very slightly shifted to lower energy with respect to those in the corresponding free alkynes (2120 (Ar = mphen) and 2102 (Ar = mes) cm^{-1}). In the spectra of complexes containing C≡CH fragments two (**2**, **3**, **5**) or one (**4**) weak bands are observed in the ranges 3225–3280 (Ar = mphen) or 3280–3320 (Ar = mes) cm^{-1} that could be assigned to ν(CH). No band assignable to this stretching mode is observed in the spectrum of **6**. Although the AuCl bond is expected to weaken with increasing negative charge of the complex and this expectation has been confirmed by the descent of the corresponding IR absorption [20,21], the mono- (**4**, **5**), di- (**9**, **10**) and trianionic (**8**) chlorogold complexes here described show one ν(AuCl) band in the narrow range 321 (**8**)–326 (**5**, **10**) cm^{-1}. The sulfocyano derivatives **6** and **11** show one intense ν(C≡N) absorption at 2114 and 2118 cm^{-1}, respectively, which obscure the corresponding ν(C≡C) band expected in the same region. The presence of PPh_3 in complex **7** is evidenced by intense bands in the 1100 and 500–550 cm^{-1} regions.

3. Experimental

3.1. General

The IR spectra, elemental analyses and melting point determinations were carried out as described earlier [22]. Technical grade solvents were purified by standard procedures. Unless otherwise stated, the reactions were carried out at room temperature (r.t.) without special precautions against moisture. The ^{1}H- and ^{31}P{^{1}H}-NMR spectra were recorded in $CDCl_3$ with Varian Unity 300 or Bruker AC-200 spectrometers. Chemical shifts, given in ppm, are referred to TMS (^{1}H) or H_3PO_4 [^{31}P{^{1}H}]. All the anionic complexes show, with very small differences, IR absorptions [1320–1220 (s, br), 544 (s), 527 (s) and 491 (s) cm^{-1}] as well as ^{1}H (7.3–7.7, m, ppm) and ^{13}C{^{1}H} [127 (dd, $^{1}J_{CP}$ = 108 Hz, $^{3}J_{CP}$ = 1.8 Hz, *ipso*-C), 130 (m, *o*-C), 132 (m, *m*-C), and 134 (m, *p*-C) NMR resonances assignable to the PPN[N(PPh$_3$)$_2$] cation which are not given below. Molar conductivities were measured in acetone solution (ca. 5×10^{-4} mol l^{-1}) except for complexes **7** and **8** that do not give stable solutions in this solvent. Diethynylbenzene [15], diethy-

nylmesitylene and complexes **12** and **13** [4] were prepared by following published procedures.

3.2. Preparation of (PPN)$_n$[Au{C≡C(mphen)C≡C}]$_n$ (**1**)

PPN[Au(acac)$_2$] [PPN = bis(triphenyl)phosphoranylydenammonium, acac = acetylacetonato, 775 mg, 0.83 mmol] was added to a solution of 1,3-diethynylbenzene (100 mg, 0.79 mmol) in degassed CH_2Cl_2 (30 ml) and the reaction mixture was stirred at r.t. for 5 h. The resulting suspension was filtered through Celite, the solution was concentrated under vacuum (2 ml) and Et_2O (40 ml) was added to give a white solid that was heated in an oven at 60–70 °C for 2 h and then recrystallized from CH_2Cl_2 and Et_2O to give **1** as a white solid. Yield 36%. M.p. 105 °C. Anal. Calc. for $C_{46}H_{34}AuNP_2$: C, 64.27; H, 3.99; N, 1.63. Found: C, 64.26; H, 4.26; N, 1.74%. IR (cm^{-1}): ν(C≡C), 2090. ^{1}H-NMR (200 MHz): δ 7.40–7.70 (m, PPN+mphen).

3.3. Preparation of (PPN)[Au{C≡C(Ar)C≡CH}$_2$] [Ar = mphen (**2**), mes (**3**)]

PPN[Au(acac)$_2$] (**2**: 402 mg, 0.43 mmol; **3**: 1307 mg, 1.4 mmol) was added to a solution of the appropriate diethynylarene (**2**: 114 mg, 0.90 mmol; **3**: 495 mg, 2.94 mmol) in degassed CH_2Cl_2 (**2**: 30 ml; **3**: 15 ml). The reaction mixture was stirred at r.t. for 1 (**2**) or 5 (**3**) h, the resulting suspension was filtered through Celite (**2**) or anhydrous $MgSO_4$ (**3**) and the solution was concentrated under vacuum to 2 ml (**2**) or to dryness (**3**). Et_2O (40 ml) was added, the resulting white suspension was filtered under vacuum and the solid was air dried. Compound **2** was recrystallized from CH_2Cl_2–Et_2O. Both complexes are white solids.

3.3.1. Compound **2**

Yield 93%. M.p. 112 °C. Anal. Calc. for $C_{56}H_{40}AuNP_2$: C, 68.23; H, 4.09; N, 1.42. Found: C, 67.94; H, 3.91; N, 1.59%. Λ_M (Ω^{-1} cm^2 mol^{-1}): 105. IR (cm^{-1}): ν(CH), 3268, 3234; ν(C≡C), 2091. ^{1}H-NMR (200 MHz): δ 2.93 (s, 2H, CH), 7.04 [t, 2H, H5 (mphen), $^3J_{HH} = 8$ Hz], 7.16 [m, 2H, H4 (mphen)], 7.35 [m, 2H, H6 (mphen)], 7.39–7.65 [m, 32H, PPN+H2 (mphen)]. ^{13}C{^{1}H}-NMR (50.3 MHz): δ 83.97 (≡CH), 101.56 (C≡CH), 121.13 [C3 (mphen)], 127.47 [C5 (mphen)], 127.68 (C≡CAu), 128.53 [C1(mphen)], 132.76 [C4 (mphen)], 135.67 [C2 (mphen)].

3.3.2. Compound **3**

Yield 31%. M.p. 198 °C. Anal. Calc. for $C_{62}H_{52}NAuP_2$: C, 69.60; H, 4.90; N, 1.31. Found: C, 69.25; H, 5.12; N, 1.54%. Λ_M (Ω^{-1} cm^2 mol^{-1}): 84. IR(cm^{-1}): ν(CH), 3284, 3318; ν(C≡C), 2096. ^{1}H-NMR (200MHz): δ 2.33 (s, 6H, Me), 2.41 (s, 6H, Me), 2.59 (s, 6H, Me), 3.35 (s, 2H, CH), 6.79 [s, 2H (mes)], 7.38–7.69 (m, 30H, PPN). ^{13}C{^{1}H}-NMR (75.4 MHz): δ 20.3 (Me), 20.9 (Me), 22.1 (Me), 82.7 (CH), 83.1 (C≡CH), 99.0, 118.3, 125.6 (CAu), 127.1 (C≡CAu), 136.4, 141.3, 142.7, 144.2.

3.4. Preparation of PPN[XAuC≡C(Ar)C≡CH] [Ar = mphen, X = Cl (**4**), Ar = mes, X = Cl (**5**), SCN (**6**)]

To a solution of **2** (ca. 0.1 mmol) in CH_2Cl_2 (30 ml) or **3** (ca. 0.1 mmol) in acetone (15 ml) was added the appropriate PPN[AuX$_2$] complex in 1:1 molar ratio. The reaction mixture was stirred for 90 min (**4**) or 5.5 h (**5**) or 4.5 h (**6**) and then filtered through Celite. The solution was concentrated to ca. 2–3 ml (**4**, **6**) or to dryness (**5**) and Et_2O (**4**, 40 ml) or *n*-pentane (**5**, 20 ml) or *n*-hexane (**6**, 40 ml) was added. The resulting suspension was stirred for a few minutes (**4**, **5**) or 2 h (**6**) and filtered to give a white solid which was vacuum filtered and air dried.

3.4.1. Compound **4**

Yield 98%. M.p. 140 °C. Anal. Calc. for $C_{46}H_{35}AuClNP_2$: C, 61.65; H, 3.94; N, 1.56. Found: C, 61.83; H, 3.76; N, 1.70%. Λ_M (Ω^{-1} cm^2 mol^{-1}): 126. IR (cm^{-1}): ν(CH), 3273; ν(C≡C), 2106; ν(AuCl), 324. ^{1}H-NMR (200 MHz): δ 2.95 (s, 1H, CH), 7.06 [t, 1H, H5 (mphen), $^3J_{HH} = 8$ Hz], 7.19 [m, 1H, H4 (mphen)], 7.36 [m, 1H, H6 (mphen)], 7.42–7.69 [m, 31H, PPN+H2 (mphen)]. ^{13}C{^{1}H}-NMR (50.3 MHz): δ 83.78 (≡CH), 97.12 (C≡CH), 121.19 [C3 (mphen)], 126.65 (CAu), 127.49 [C5 (mphen), 127.66 (C≡CAu), 128.72 [C1 (mphen)], 132.70 [C4 (mphen)], 135.64 [C2 (mphen)].

3.4.2. Compound **5**

Yield 87%. M.p. 80 °C. Anal. Calc. for $C_{49}H_{41}AuClNP_2 \cdot H_2O$: C, 61.54; H, 4.53; N, 1.47. Found: C, 61.47; H, 4.31; N, 1.52%. Λ_M (Ω^{-1} cm^2 mol^{-1}): 111. IR(cm^{-1}): ν(CH), 3288, 3228; ν(C≡C), 2106; ν(AuCl), 326. ^{1}H-NMR (200 MHz): δ 1.65 (s, 2H, H_2O), 2.33 (s, 3H, Me), 2.41 (s, 3H, Me), 2.59 (s, 3H, Me), 3.36 (s, 1H, CH), 6.79 (s, 1H, mes), 7.40–7.70 (m, 30H, PPN). ^{13}C-NMR (50.3 MHz): δ 20.6 (Me), 21.3 (Me), 22.3 (Me), 82.8 (≡CH), 83.8 (C≡CH), 95.1, 118.8, 119.1, 127.6 (*C*≡CAu), 137.2, 141.2, 143.2.

3.4.3. Compound **6**

Yield 78%. M.p. 65 °C. Anal. Calc. for $C_{50}H_{41}AuN_2P_2S \cdot H_2O$: C, 61.35; H, 4.43; N, 2.86; S 3.28. Found: C, 60.84; H,4.38; N, 3.10; S 3.68%. Λ_M (Ω^{-1} cm^2 mol^{-1}): 131. IR (cm^{-1}): ν(C≡N), 2114. ^{1}H-NMR (200 MHz): δ 1.61 (s, 2H, H_2O), 2.35 (s, 3H, Me), 2.42 (s, 3H, Me), 2.60 (s, 3H, Me), 3.38 (s, 1H, CH), 6.82 (s, 1H, mes), 7.41–7.70 (m, 30H, PPN). ^{13}C-NMR (50.3 MHz): δ 20.2 (Me), 21.0 (Me), 21.9 (Me), 82.2 (≡CH), 83.6 (C≡CH), 96.6, 118.6 (SCN), 124.4, 126.8, 127.3 (*C*≡CAu), 137.4, 140.7, 142.8.

3.5. Preparation of PPN[Au{C≡C(mphen)C≡CAuPPh$_3$)$_2$] (7)

To a solution of 2 (98 mg, 0.10 mmol) in CH_2Cl_2 (30 ml) was added [Au(acac)PPh_3] (112 mg, 0.20 mmol). The reaction mixture was stirred for 4.5 h and then filtered through Celite. The solution was concentrated under vacuum (to ca. 2 ml), Et_2O (40 ml) was added, the resulting suspension was stirred in an ice–water bath for 20 min and then filtered to give **7** as white solid. Yield 73%. M.p.: 135 °C. Anal. Calc. for $C_{92}H_{68}Au_3NP_4$: C, 58.09; H, 3.60; N, 0.74. Found: C, 57.97; H, 3.56; N, 0.92%. IR (cm^{-1}): ν(C≡C), 2091. ^{1}H-NMR (200 MHz): δ 7.13 [t, 2H, H5 (mphen), $^3J_{HH} = 8$ Hz], 7.37 [dd, 4H, H4+H6 (mphen), $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1.5$ Hz], 7.39–7.68 [m, 62H, PPh_3+PPN+H2 (mphen)]. $^{31}P\{^1H\}$-NMR (121 MHz): δ 42.50 (s, PPh_3), 21.39 (s, PPN).

3.6. Preparation of (PPN)$_3$[Au{C≡C(mphen)C≡CAuCl}$_2$] (8)

To a solution of **4** (98.5 mg, 0.11 mmol) in CH_2Cl_2 (30 ml) was added PPN[Au(acac)$_2$] (51.3 mg, 0.055 mmol), the reaction mixture was stirred for 15 h and then filtered through Celite. The solution was concentrated under vacuum (ca. 2 ml) and Et_2O (40 ml) was added to give **8** as a yellow solid, which was filtered, and air dried. Yield 93%. M.p. 102 °C. Anal. Calc. for $C_{128}H_{98}Au_3Cl_2N_3P_6$: C, 60.87; H, 3.91; N, 1.66. Found: C, 61.14; H, 3.77; N, 1.74%. IR (cm^{-1}): ν(C≡C), 2104; ν(AuCl), 321. ^{1}H-NMR (200 MHz): δ 6.82 [t, 2H, H5 (mphen), $^3J_{HH} = 8$ Hz], 7.06 [dd, 4H, H4+H6 (mphen), $^3J_{HH} = 8$ Hz, $^4J_{HH} = 2$ Hz], 7.42–7.68 [m, 92H, PPN+H2 (mphen)].

3.7. Preparation of (PPN)$_2$[ClAuC≡C(mphen)C≡CAuCl)] (9)

3.7.1. Method a

PPNCl (379 mg, 0.66 mmol) was added to a suspension of [AuC≡C(mphen)C≡CAu]$_n$ [4] (171 mg, 0.33 mmol) in acetone (30 ml) and the mixture was refluxed for 6.3 h. When cold, the solution was filtered through Celite and the filtrate was concentrated to dryness. The pale yellow residue was washed with Et_2O (25 ml), filtered and air dried to give **9** as a pale yellow solid in 72% yield.

3.7.2. Method b

PPN[$AuCl_2$] (147.6 mg, 0.183 mmol) was added to a solution of [Ph_3PAuC≡C(mphen)C≡$CAuPPh_3$] [4] (96 mg, 0.092 mmol) in CH_2Cl_2 (30 ml). The reaction mixture was stirred for 45 h and the resulting suspension was filtered through Celite. The solution was concentrated under vacuum (to ca. 5 ml) and Et_2O (40 ml) was added to give a solid, which was recrystallized, from CH_2Cl_2 and Et_2O to give **9** in 82% yield.

M.p.: 140 °C (dec.). Anal. Calc. for $C_{82}H_{64}Au_2Cl_2N_2P_4$: C, 59.11; H, 3.87; N, 1.68. Found: C, 58.64; H, 3.97; N, 1.74%. Λ_M (Ω^{-1} cm^2 mol^{-1}): 231.4. IR (cm^{-1}): ν(C≡C), 2110; ν(AuCl), 324. ^{1}H-NMR (200 MHz): δ 6.81 [t, 1H, H5 (mphen), $^3J_{HH} = 5.2$ Hz], 7.06 [dd, 2H, H4+H6 (mphen), $^3J_{HH} = 5.2$ Hz, $^4J_{HH} = 1.3$ Hz], 7.19 [t, 1H, H2 (mphen), $^4J_{HH} = 1.3$ Hz]. $^{13}C\{^1H\}$-NMR (75.4 MHz): δ 98.10 (s, CCAu); 109.32 [s, C1+C3 (mphen)], 126.71 (s, CAu), 135.58 [s, C2 (mphen)].

3.8. Preparation of (PPN)$_2$[XAuC≡C(mes)C≡CAuX] [X = Cl (10), SCN (11)]

To a suspension of [AuC≡C(mes)C≡CAu]$_n$ (ca. 0.8 mmol) in acetone (20 ml) was added the appropriate PPNX salt in 1:2 M ratio. The reaction mixture was refluxed for 0.75 (**10**) or 1.75 (**11**) h and the resulting suspension was filtered through Celite. The solution was concentrated under vacuum to dryness (**10**) or to 10 ml (**11**) and Et_2O (**10**, 40 ml; **11**, 15 ml) was added. The resulting suspension was stirred at r.t. (**10**) or in a cold bath (**11**, 0 °C) for 15 min and filtered. After recrystallization from acetone and Et_2O **10** and **11** were obtained as white solids.

3.8.1. Compound 10

Yield 75%. M.p. 130 °C. Anal. Calc. for $C_{85}H_{70}Au_2Cl_2N_2P_4$: C, 59.77; H, 4.13; N, 1.64. Found: C, 59.37; H, 4.29; N, 1.68%. Λ_M (Ω^{-1} cm^2 mol^{-1}): 213. IR (cm^{-1}): ν(C≡C), 2106; ν(AuCl), 326. ^{1}H-NMR (200 MHz): δ 2.32 (s, 6H, Me), 2.47 (s, 3H, Me), 6.64 [s, 1H (mes)], 7.38–7.69 (m, 60H, PPN): $^{13}C\{^1H\}$ (50.3 MHz): δ 20.9 (Me), 21.8 (Me), 95.9, 123.9, 136.5.

3.8.2. Compound 11

Yield 47%. M.p. 170 °C. Anal. Calc. for $C_{87}H_{70}Au_2N_4P_4S_2$: C, 59.59; H, 4.02; N, 3.20; S, 3.66. Found: C, 59.41; H, 4.04; N, 3.14; S, 3.30%. Λ_M (Ω^{-1} cm^2 mol^{-1}): 207. IR (cm^{-1}): ν(C≡N), 2118. ^{1}H-NMR (200 MHz): δ 2.35 (s, 6H, Me), 2.45 (s, 3H, Me), 6.69 [s, 1H, (mes)], 7.38–7.69 (m, 60H, PPN). $^{13}C\{^1H\}$-NMR (50.3 MHz): δ 20.8 (Me), 21.6 (Me), 97.5, 120.2 (SCN), 123.3, 124.7, 126.5, 137.0, 141.9.

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