Alkynyl Gold(I) Complexes. The First Family of Ethynyl Gold(I) Complexes

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Complexes $[N(PPh_3)_2][Au(C{\equiv}CH)_2]$ or $[Au(C{\equiv}CH)(PR_3)]$ (R = Ph or C_6H_4OMe-4) or $[N(PPh_3)_2][Au(C{\equiv}CH)X]$ (X = Cl or Br) have been prepared by reacting $[N(PPh_3)_2][Au(acac)_2]$ or $[Au(acac)(PR_3)]$ (Hacac = acetylacetone) with acetylene, respectively, or $[N(PPh_3)_2][Au(C{\equiv}CH)_2]$ with $[N(PPh_3)_2][AuX_2]$.

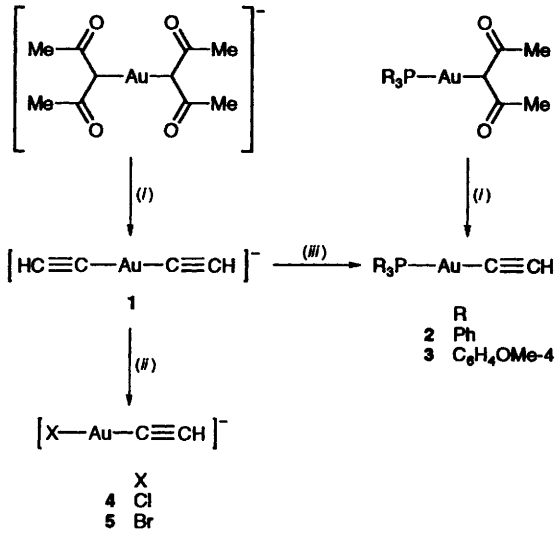
There is a rapidly growing interest in acetylide (or alkynyl) metal complexes. In particular, those complexes having a polyyne structure are expected to have non-linear optical behaviour or liquid-crystalline properties,[1] and those having bridging acetylide ligands are models for reactive intermediates on heterogeneous catalyst surfaces[2] or show luminescent properties for photochemical C–H bond activation.[3]

The main interest in alkynyl gold complexes[4] is based on the synthesis of rigid-rod gold(I) complexes (*i.e.*, linear-chain metal-containing polymers, with extended backbone conjugation through dπ–pπ bonding) for potential applications as advanced materials.[4d–f] In addition, some acetylide gold(I) complexes belong to a new class of luminophores with interesting photophysical and photochemical properties.[4c,g]

In spite of the great number of alkynyl gold(I) complexes reported,[4,5] there is, as far as we are aware, only one well characterized ethynyl gold(I) complex, $[Au(C{\equiv}CH)(PPr^i)_3]$.[5a] Although, $K[Au(C{\equiv}CH)_2]$ and $K_2[HC{\equiv}CAuC{\equiv}CAuC{\equiv}CH]$ were prepared some time ago by Nast and Kirner,[5b] owing to the low stabilities of the complexes to moisture and light, they were only characterized by IR spectroscopy, conductivity in solution and elemental analyses (Au, K and C_2H). Later, Nast *et al.*[5c] described the synthesis of $[PPh_4]_2[HC{\equiv}CAuC{\equiv}CAuC{\equiv}CH]$ from its potassium homologue but only ν(C≡C), elemental analyses and conductivity were reported. Finally, attempts to isolate $[Au(C{\equiv}CH)(PR_3)]$ (R = aryl) failed.[5d] Here we describe the synthesis of a family of ethynyl gold(I) complexes of the types $[Au(C{\equiv}CH)X]^-$ (X = C≡CH, Cl or Br) and $[Au(C{\equiv}CH)(PR_3)]$ (R = aryl).

Addition of a dichloromethane solution (20 cm^3) of $[N(PPh_3)_2][Au(acac)_2]$[6] (Hacac = acetylacetone) (701 mg, 0.75 mmol) to a saturated solution of acetylene in the same solvent (10 cm^3) leads to the formation of $[N(PPh_3)_2][Au(C{\equiv}CH)_2]$ **1**† in high yield (90–95%) (see Scheme 1). This, and some reactions below, are new examples of the synthetic utility of acetylacetonatogold(I) complexes.[7]

Contrary to $K[Au(C{\equiv}CH)_2]$ previously reported,[5b] complex **1** is stable to moisture and daylight. Our method is also much simpler than that used to prepare the potassium salt which involves three steps and the use of liquid ammonia, acetylene, $KC{\equiv}CH$, $Au_2(C{\equiv}C){\cdot}NH_3$ and $K_2[Au_2(\mu\text{-}C{\equiv}C)(C{\equiv}CH)_2]$.[5b]



Scheme 1 The cation for all complexes is $[N(PPh_3)_2]^+$. (*i*) $+C_2H_2$; (*ii*) $+[AuX_2]^-$; (*iii*) $+[Au(PR_3)_2]ClO_4$

By reacting **1** with $[Au(PR_3)_2]ClO_4$ (1:1, acetone, room temperature, 24 h) or $[Au(acac)(PR_3)]$ with an excess of acetylene (dichloromethane, ice-bath, 3 h) complexes $[Au(C{\equiv}CH)(PR_3)]$ [R = Ph **2**‡ (80%) or C_6H_4OMe-4 **3**§ (69%)] can be obtained (see Scheme 1). Cross and Davidson[5d] had reported that the reaction between $[AuCl(PPh_3)]$ and acetylene in alcoholic sodium ethoxide produced complex **2** but as it was impure they were unable to recrystallize it. Similar reactions with other $[AuCl(PR_3)]$ complexes (R = C_6H_4Me-4 or C_6H_4-

† **1**: M.p. 225 °C (Found: C, 60.60; H, 4.35; N, 1.90. Calc. for $C_{40}H_{32}AuNP_2$: C, 61.15; H, 4.10; N, 1.80%). Λ_M = 108 Ω^{-1} cm^2 mol^{-1} (10^{-4} mol l^{-1} in Me_2CO). NMR: ^1H δ 1.37 (s, 2 H, CH); ^{13}C δ 87.10 (s, CH), 127.02 (s, CAu); ^{31}P δ 20.88 (s). IR (cm^{-1}): ν(CH) 3266vw, ν(C≡C) 1962w.

‡ **2**: M.p. 168 °C (Found: C, 49.70; H, 3.25. Calc. for $C_{20}H_{16}AuP$: C, 49.60; H, 3.30%). Λ_M = 3 Ω^{-1} cm^2 mol^{-1} (5×10^{-4} mol l^{-1} in Me_2CO). NMR: ^1H δ 1.83 (s, 1 H, CH), 7.4–7.6 (m, 15 H, Ph); ^{31}P δ 42.43 (s). IR (cm^{-1}): ν(CH) 3272, ν(C≡C) 1982.

§ **3**: M.p. 123 °C (Found: C, 48.05; H, 3.75. Calc. for $C_{23}H_{22}AuO_3P$: C, 48.10; H, 3.85%). Λ_M = 0 Ω^{-1} cm^2 mol^{-1} (5×10^{-4} mol l^{-1} in Me_2CO). NMR: ^1H δ 1.81 (d, 1 H, CH, $^4J_{PH}$ 4.8), 3.82 (s, 9 H, OMe), 6.94 (m, 6 H, C_6H_4OMe-4), 7.43 (m, 6 H, C_6H_4OMe-4); ^{13}C δ 55.42 (s, OMe), 90.48 (d, CH, $^3J_{PC}$ 26.2), 114.67 [d, P(C_6H_4OMe-4)$_3$, $^3J_{PC}$ 12.6], 121.3 [d, P(C_6H_4OMe-4)$_3$, $^1J_{PC}$ 61.5], 126.3 (d, CAu, $^2J_{PC}$ 140), 135.6 [d, P(C_6H_4OMe-4)$_3$, $^2J_{PC}$ 15.1], 162.0 [d, P(C_6H_4OMe-4)$_3$, $^4J_{PC}$ 2 Hz]; ^{31}P δ 37.93 (s). IR (cm^{-1}): ν(CH) 3268, ν(C≡C) 1982.

OMe-4) gave the dinuclear complexes $[Au_2(\mu\text{-}C{\equiv}C)(PR_3)_2]$ and no intermediate $[Au(C{\equiv}CH)(PR_3)]$ could be detected. The only previously reported $[Au(C{\equiv}CH)(PR_3)]$ complex has been prepared by reacting $[Au(\sigma\text{-}C_5H_5)(PPr^i_3)]$ with acetylene.[5a]

Reactions between **1** and $[N(PPh_3)_2][AuX_2]$ (1 : 1, dichloromethane, room temperature, 1–2 h) give the mixed-ligand complexes $[N(PPh_3)_2][Au(C{\equiv}CH)X]$ [X = Cl **4*** (86%) or Br† (93%)]. Related complexes $[Au(C{\equiv}CR)X]^-$ [R = Ph; X = Cl, Br or I] have been prepared by Abu-Salah and Al-Ohaly,[8] by reacting polymeric $[\{Au(C{\equiv}CPh)\}_n]$ with the corresponding halide anions. The reaction of complex **4** with PPh_3 (1 : 1) gives complex **2** but the difficulty in separating it from the by-product $[N(PPh_3)_2]Cl$ leads to a very low yield (28%).

Proton NMR spectra of complexes **2**–**5** show the ethynyl proton chemical shift in the δ 1.63–1.83 region. The lower value for δ(CH) in complex **1** (δ 1.37) could be due to the shielding effect of both C≡C bonds. The ^1H and ^{31}P NMR spectra of complex **2** show the chemical shifts of the methine proton and phosphorus (δ 1.83 and 42.43, respectively) at similar values to those reported for the impure sample of this complex (δ 1.75 and 41.9, respectively).[5d]

The IR spectra of the ethynyl complexes show bands assignable to the ν(C≡C) and ν(CH) vibration modes in the regions 1957–1982 and 3256–3272 cm^{-1}, respectively.

In conclusion, contrary to the previous impression that ethynyl gold(I) compounds could be unstable and difficult to prepare, the synthetic methods developed here refute such a hypothesis. Thus, by reacting acetylacetonatogold(I) complexes with acetylene it is possible to isolate $[N(PPh_3)_2][Au(C{\equiv}CH)_2]$ and $[Au(C{\equiv}CH)(PR_3)]$ (R = Ph or C_6H_4OMe-4) as pure and stable compounds. Previous attempts to prepare $[Au(C{\equiv}CH)(PR_3)]$ (R = aryl) had failed. A second method to prepare these complexes is also given. Finally, we have synthesized a new type of ethynyl gold(I) complex, $[Au(C{\equiv}CH)X]^-$ (X = Cl or Br). All these complexes are now being studied as precursors for the synthesis of di- and polynuclear complexes.

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* **4**: M.p. 192 °C (Found: C, 56.90; H, 3.90; N, 1.80. Calc. for $C_{38}H_{31}AuClNP_2$: C, 57.35; H, 3.95; N, 1.75%). Λ_M = 116 Ω^{-1} cm^2 mol^{-1} (5 × 10^{-4} mol l^{-1}). NMR: ^1H δ 1.63 (s, 1 H, CH); ^{13}C δ 83.75 (s, CH); ^{31}P δ 20.93 (s). IR (cm^{-1}): ν(CH) 3282, ν(C≡C) 1975.

† **5**: M.p. 186 °C (Found: C, 54.30; H, 3.75; N, 1.70. Calc. for $C_{38}H_{31}AuBrNP_2$: C, 54.30; H, 3.70; N, 1.65%). Λ_M = 139 Ω^{-1} cm^2 mol^{-1} (5 × 10^{-4} mol l^{-1} in Me_2CO). NMR: ^1H, δ 1.65 (s, 1 H, CH); ^{31}P, δ 21.68 (s), IR (cm^{-1}): ν(CH) 3266, ν(C≡C) 1980.

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