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New Neutral and Anionic Alkynylgold(I) Complexes *via* New Synthetic Methods. Crystal and Molecular Structures of $[(PPh_3)_2N][Au(C{\equiv}CCH_2OH)_2]$, $[Au(C{\equiv}CSiMe_3)(CN^tBu)]$, and $[Au(C{\equiv}CR)PR'_3]$ (R' = Cyclohexyl, R = CH_2Cl, CH_2Br; R' = Ph, R = $SiMe_3$, ^tBu)[†]

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$[(PPh_3)_2N][Au(acac)_2]$ (acac = acetylacetonate) reacts with terminal alkynes $RC{\equiv}CH$ to give $[(PPh_3)_2N][Au(C{\equiv}CR)_2]$ (R = H, ^tBu, $SiMe_3$, CH_2X (X = Cl, Br, OH)) complexes. The reactions between $[(PPh_3)_2N][Au(C{\equiv}CH)_2]$ and $[(PPh_3)_2N][AuX_2]$ (X = Cl, Br, I) give $[(PPh_3)_2N][Au(C{\equiv}CH)X]$ complexes. Neutral mononuclear $[Au(C{\equiv}CR)(NHEt_2)]$ (R = $SiMe_3$, ^tBu), $[Au(C{\equiv}CR)(PR'_3)]$ (R = H, R' = Ph, C_6H_4OMe-4; R = CH_2Cl, CH_2Br, CH_2OH, R' = Cy = cyclohexyl; R = $SiMe_3$, R' = Ph, C_6H_4OMe-4, Cy; R = ^tBu, R' = Ph, Cy, C_6H_4OMe-4), $[Au(C{\equiv}CR)(CN^tBu)]$ (R = $SiMe_3$, ^tBu), and $[Au(C{\equiv}CR)\{C(NH^tBu)(NEt_2)\}]$ (R = H, $SiMe_3$, ^tBu) or dinuclear $[(AuL)_2\{\mu\text{-}C{\equiv}C(CH_2)_5C{\equiv}C\}]$ (L = PPh_3, CN^tBu, $C(NH^tBu)(NEt_2)$) are obtained via a variety of synthetic methods: (i) reaction between $[(PPh_3)_2N][Au(C{\equiv}CH)_2]$ and $[Au(PR_3)_2]ClO_4$, (ii) reaction of terminal alkynes with [Au(acac)(L)], (iii) reaction of [AuClL] complexes with terminal alkynes in diethylamine, (iv) substitution reactions (*e.g.*, $[Au(C{\equiv}CR)(NHEt_2)] + PR'_3$), (v) reaction of diethylamine with alkynyl isocyanide derivatives to give alkynylcarbene complexes. The crystal structures of $[(PPh_3)_2N][Au(C{\equiv}CCH_2OH)_2]$, $[Au(C{\equiv}CSiMe_3)(CN^tBu)]$, and $[Au(C{\equiv}CR)(PR'_3)]$ (R' = Cy, R = CH_2Cl, CH_2Br; R' = Ph, R = $SiMe_3$, ^tBu) were determined.

Introduction

The preference of gold(I) for a linear coordination geometry, together with the linearity of the C≡C bond in alkynyl ligands, make alkynylgold(I) complexes attractive candidates for the design of linear-chain metal-containing polymers with extended backbone electronic conjugation. The expectation that these electronically flexible rigid-rod polymers might exhibit interesting properties either difficult or impossible to achieve with conventional organic polymers justifies the rapidly growing interest in alkynylgold(I) complexes. Among the many alkynylgold(I) complexes described, some show liquid-crystalline properties[1,2] or nonlinear-optical behavior.[3] In addition, some alkynylgold(I) derivatives belong to a new class of luminophores with interesting photophysical and photochemical properties.[4−8]

Although a few of the reported alkynylgold(I) complexes are anionic or cationic,[2,9−19] most of them are neutral and the majority correspond to the type $[Au(C{\equiv}CR)(L)]$ (R = Ph, ^tBu, CF_3, $C_6H_{10}OH$; L = tertiary phosphine)[13,20−26] or $[Au_2(\mu\text{-}C{\equiv}C)L_2]$ (L = phosphines or L_2 = diphosphines).[4−7,10,27−31] The few gold(I) com-

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plexes with other alkynyl groups include two ethynyl (R = H) complexes[9,32,33] as well as some derivatives with R = Me, Et,[21] CF_3,[34] *para*-substituted aryls,[3,35] $MeOCH_2$,[36] dialkynyls $-C\equiv C-(C_6H_4)_2C\equiv C-$,[31] or C_6H_3-$(C\equiv C-)_3$-1,3,5[37] derivatives. A limited number of alkynylgold(I) complexes with isocyanide,[1,2,8,34,38] amine,[13,39] or ylide ligands[40] have also been reported.

We describe here a wide variety of anionic and neutral alkynylgold(I) complexes with ethynyl, propargyl, (trimethylsilyl)ethynyl, *tert*-butylethynyl, and 1,5-nonadiyndiyl groups and amine, phosphine, isocyanide, or carbene ligands. We have explored a wide variety of synthetic methods. Some of these results have been the subject of preliminary reports.[41−43]

Experimental Section

Unless otherwise stated, NMR spectra were recorded in $CDCl_3$ in a Varian Unity 300 at room temperature. Chemical shifts are referred to TMS (^1H, ^{13}C) or H_3PO_4 (^{31}P). All of the anionic complexes show, with very small differences, IR absorptions at 1581 (m), 1320−1220 (s, br), 544 (s), 527 (s), and 491 (s) cm^{-1} and ^1H NMR resonances at 7.3−7.7 (m) and $^{13}C\{^1H\}$ NMR resonances at 127 (dd of an AA′ system, $^1J_{CP}$ = 108 Hz, $^4J_{CP}$ = 0.8 Hz, *ipso*-C), 130 (m, *o*-C), 132 (m, *m*-C), and 134 (m, *p*-C) assignable to the $[(PPh_3)_2N]$ cation and are not given below. Molar conductivities are measured in acetone solutions ($1-6 \times 10^{-4}$ mol L^{-1}). Unless otherwise stated, the neutral complexes show molar conductivities (Λ_M) in the range 0−2 Ω^{-1} cm^2 mol^{-1}. The synthesis, spectroscopic and analytical data, and the crystal structure of **24** were preliminarly reported by us.[42]

$[(PPh_3)_2N][Au(C\equiv CR)_2]$ (R = H (1), ^{t}Bu (2), $SiMe_3$ (3), CH_2Cl (4), CH_2Br (5), CH_2OH (6)). Complexes **1**−**6** were obtained by reacting $[(PPh_3)_2N][Au(acac)_2]$ (acac = acetylacetonate) (0.1−0.3 mmol) with an excess of the corresponding alkyne (molar ratio *ca.* 1:40) in dichloromethane; for the synthesis of **1**, a saturated solution of acetylene in degassed dichloromethane (20 mL) was used and bubbling of acetylene was continued during the reaction. After 30 min of stirring, the reaction mixtures were filtered through Celite, the solutions concentrated under vacuum (to *ca.* 5 mL), and diethyl ether (20 mL) added to precipitate white solids, which were recrystallized from dichloromethane/diethyl ether. **1**: Yield 91%. Mp: 225 °C. Anal. Calcd for $C_{40}H_{32}AuNP_2$: C, 61.15; H, 4.10; N, 1.80. Found: C, 60.57; H, 4.34; N, 1.92. Λ_M (Ω^{-1} cm^2 mol^{-1}): 108. IR (cm^{-1}): ν(CH), 3266 (vw); ν(C≡C), 1962 (w). ^1H NMR: δ 1.37 (s, 2H, CH) $^{13}C\{^1H\}$ NMR: δ 87.10 (s, CH), 127.02 (s, CAu). **2:** Yield 95%. Mp: 181 °C. Anal. Calcd for $C_{48}H_{48}AuNP_2$: C, 64.21; H, 5.39; N, 1.56. Found: C, 64.32; H, 5.47; N, 1.58. Λ_M (Ω^{-1} cm^2 mol^{-1}): 85. IR (cm^{-1}): ν(C≡C), 2090 (w). ^1H NMR: δ 1.18 (s, 18H, ^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 28.25 (s, *C*Me$_3$), 32.71 (s, Me), 111.11 (s, *C*^{t}Bu), 117.35 (s, CAu). **3**: Yield 57%. Mp: 180 °C. Anal. Calcd for $C_{46}H_{48}AuNP_2Si_2$: C, 59.61; H, 5.20; N, 1.51. Found: C, 58.99; H, 5.18; N, 1.67. Λ_M (Ω^{-1} cm^2 mol^{-1}): 95. IR (cm^{-1}): ν(C≡C), 2025 (w). ^1H NMR: δ 0.03 (s, 18 H, Me). **4:** Yield 92%. Mp: 135 °C (dec). Anal. Calcd for $C_{42}H_{34}AuCl_2NP_2$: C, 57.16; H, 3.88; N, 1.59. Found: C, 57.12; H, 3.76; N, 1.62. Λ_M (Ω^{-1} cm^2 mol^{-1}): 107. IR (cm^{-1}): ν(C≡C), 2125 (w). ^1H NMR: δ 4.27 (s, 4H, CH_2). $^{13}C\{^1H\}$ NMR: δ 34.24 (s, CH_2), 95.70 (s, *C*CH$_2$), 130.68 (s, CAu). **5:** Yield 84%. Mp: 120 °C (dec). Anal. Calcd for $C_{42}H_{34}AuBr_2NP_2$: C, 51.93; H, 3.53; N, 1.44. Found: C, 51.54; H, 3.37; N, 1.45. Λ_M (Ω^{-1} cm^2 mol^{-1}): 134. IR (cm^{-1}): ν(C≡C), 2120 (w). ^1H NMR (200 MHz): δ 4.136 (s, 4H, CH_2). $^{13}C\{^1H\}$ NMR: δ 20.35 (s, CH_2), 114.10 (s, *C*CH$_2$). **6:** Yield 83%. Mp: 143 °C (dec). Anal. Calcd for $C_{42}H_{36}AuNO_2P_2$: C, 59.65; H, 4.29; N, 1.66. Found: C, 59.76; H, 4.31; N, 1.69. Λ_M (Ω^{-1} cm^2 mol^{-1}): 80. IR (cm^{-1}): ν(O−H), 3416 (m); ν(C≡C), 2110 (m). ^1H NMR: δ 4.27 (s, 4H, CH_2). $^{13}C\{^1H\}$ NMR: δ 52.41 (s, CH_2), 100.13 (s, *C*CH$_2$), 127.29 (s, CAu). Single crystals of **6** were obtained by slow diffusion of diethyl ether into a solution of **6** in dichloromethane.

$[(PPh_3)_2N][Au(C\equiv CH)X]$ (X = Cl (7), Br (8), I (9)). Complexes **7**−**9** were obtained by reacting equimolar amounts of **1** (*ca.* 0.2 mmol) and the corresponding $[(PPh_3)_2N][AuX_2]$ complexes in dichloromethane for 1 h. The resulting solutions were filtered through Celite and concentrated (*ca.* 3 mL), and diethyl ether (20 mL) was added to precipitate white solids, which were recrystallized from dichloromethane/diethyl ether. **7**: Yield 86%. Mp: 192 °C. Anal. Calcd for $C_{38}H_{31}AuClNP_2$: C, 57.37; H, 3.93; N, 1.76. Found: C, 56.91; H, 3.91; N, 1.78. Λ_M (Ω^{-1} cm^2 mol^{-1}): 116. IR (cm^{-1}): ν(CH), 3270 (vw); ν(C≡C), 1982 (w). ^1H NMR (200 MHz): δ 1.63 (s, 1H, CH). $^{13}C\{^1H\}$ NMR: δ 83.75 (s, CH). **8**: Yield 93%. Mp: 186 °C. Anal. Calcd for $C_{38}H_{31}AuBrNP_2$: C, 54.30; H, 3.72; N, 1.67. Found: C, 54.29; H, 3.74; N, 1.71. Λ_M (Ω^{-1} cm^2 mol^{-1}): 139. IR (cm^{-1}): ν(CH), 3266 (vw); ν(C≡C), 1980 (w). ^1H NMR: δ 1.65 (s, 1H, CH). $^{13}C\{^1H\}$ NMR (50 MHz): δ 83.37 (s, CH). **9:** Yield 85%. Mp: 185 °C. Anal. Calcd for $C_{38}H_{31}AuINP_2$: C, 51.43; H, 3.53; N, 1.58. Found: C, 51.75; H, 3.53; N, 1.63. Λ_M (Ω^{-1} cm^2 mol^{-1}): 131. IR (cm^{-1}): ν(CH), 3268 (vw); ν(C≡C), 1964 (w). ^1H NMR (200 MHz): δ 1.63 (s, 1H, CH). $^{13}C\{^1H\}$ NMR: δ 82.20 (s, CH).

$[Au(C\equiv CR)(NHEt_2)]$ (R = $SiMe_3$ (10), ^{t}Bu (11)). $[AuCl(tht)]$ (tht = tetrahydrothiophene) (*ca.* 1 mmol) was treated with an equimolar amount of the corresponding alkyne in diethylamine (15 mL) for 30 min. The resulting suspensions were filtered to remove $(NH_2Et_2)Cl$, and the solutions were concentrated (*ca.* 2 mL) and cooled at −10 °C for 2 h to give white solids, which were filtered off and dried in the air. **10:** Yield 73%. Mp: 20 °C (dec). Anal. Calcd for $C_9H_{20}AuNSi$: C, 29.43; H, 5.49; N, 3.81. Found: C, 29.41; H, 5.42; N, 3.70. IR (cm^{-1}): ν(N−H), 3156 (m); ν(C≡C), 2054 (m). ^1H NMR (200 MHz): δ 0.07 (s, 9H, $SiMe_3$), 1.39 (m, 6H, CH$_2$*Me*), 2.92 (m, 4H, CH_2), 4.87 (s, 1H, NH). $^{13}C\{^1H\}$ NMR: δ 0.87 (s, $SiMe_3$),

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14.70 (s, CH_2Me), 48.67 (s, CH_2), 108.85 (s, CSi), 126.56 (s, CAu). **11**: Yield 48%. Mp: 65 °C (dec). Anal. Calcd for $C_{10}H_{20}AuN$: C, 34.20; H, 5.74; N, 3.99. Found: C, 33.64; H, 5.55; N, 3.72. IR (cm^{-1}): ν(N−H), 3154 (w). ^1H NMR (200 MHz): δ 1.25 (s, 9H, ^{t}Bu), 1.45 (m, 6H, CH_2Me), 2.98 (m, 4H, CH_2), 4.99 (s, 1H, NH). $^{13}C\{^1H\}$ NMR: δ 14.64 (s, CH_2Me), 28.40 (s, CMe_3), 32.24 (s, Me), 48.76 (s, CH_2), 90.46 (s, C^tBu), 112.96 (s, CAu).

[Au(C≡CH)(PPh_3)] (12). To a solution of $[Au(PPh_3)_2]ClO_4$ (205 mg, 0.25 mmol) in acetone (20 mL) was added **1** (196 mg, 0.25 mmol), and the reaction mixture was stirred for 24 h. **12** (132 mg, 0.27 mmol) precipitated as a white solid, which was filtered off, washed with *n*-hexane (5 mL), and air dried. The solution was concentrated to dryness, and the residue was extracted 3 times with a mixture of acetone (5 mL) and Et_2O (20 mL) to give insoluble $[(PPh_3)_2N]ClO_4$ (130 mg, 0.20 mmol) and a solution which, upon concentration (2 mL) and addition of *n*-hexane (20 mL), gave a second crop of **12** (63 mg, 0.13 mmol). Yield: 80%. Mp: 168 °C. Anal. Calcd for $C_{20}H_{16}AuP$: C, 49.60; H, 3.33. Found: C, 49.70; H, 3.25. IR (cm^{-1}): ν(CH), 3272 (vw); ν(C≡C), 1981 (w). ^1H NMR: δ 1.83 (s, 1H, CH), 7.4−7.6 (m, 15H, PPh_3). $^{13}C\{^1H\}$ NMR (50 MHz): δ 90.06 (d, CH, $^3J_{CP}$ = 10 Hz), 129.20 (d, PPh_3, $^3J_{CP}$ = 11.4 Hz), 129.59 (d, PPh_3, $^1J_{CP}$ = 56 Hz), 131.66 (d, PPh_3, $^4J_{CP}$ = 2.5 Hz), 134.30 (d, PPh_3, $^2J_{CP}$ = 14.1 Hz). $^{31}P\{^1H\}$ NMR: δ 42.43 (s).

[Au(C≡CR)(PR′$_3$)] (R = H, R′ = C_6H_4OMe-4 (13); R′ = Cy, R = CH_2Cl (14), CH_2Br (15), CH_2OH (16)). A solution of [Au(acac)(PR′$_3$)] (*ca.* 0.5 mmol) in CH_2Cl_2 (15 mL) was slowly added to a solution of the corresponding alkyne (molar ratio 1:1.1) in dichloromethane (5 mL) under a nitrogen atmosphere. For the synthesis of **13**, a saturated solution of acetylene in degassed dichloromethane (20 mL) was used and bubbling of acetylene was continued during the reaction. After 3 (**13**−**15**) or 4.5 h (**16**) of stirring, the resulting suspensions were filtered through anhydrous $MgSO_4$, the solutions were concentrated (1 mL), and *n*-hexane (20 mL) was added to precipitate white solids, which were filtered off and air dried. **13:** Yield 70%. Mp: 123 °C. Anal. Calcd for $C_{23}H_{22}AuO_3P$: C, 48.10; H, 3.86. Found: C, 48.07; H, 3.76. IR (cm^{-1}): ν(CH), 3268 (vw); ν(C≡C), 1971 (w). ^1H NMR: δ 1.81 (d, 1H, CH, $^4J_{HP}$ = 4.8 Hz), 3.82 (s, 9H, Me), 6.94 (m, 6H, Ph), 7.43 (m, 6H, Ph). $^{13}C\{^1H\}$ NMR: δ 55.42 (s, Me), 90.48 (d, CH, $^3J_{CP}$ = 26.2 Hz), 114.67 (d, Ph, $^3J_{CP}$ = 12.6 Hz), 121.3 (d, Ph, $^1J_{CP}$ = 61.5 Hz), 126.3 (d, CAu, $^2J_{CP}$ = 140 Hz), 135.6 (d, Ph, $^2J_{CP}$ = 15.1 Hz), 162.0 (d, Ph, $^4J_{CP}$ = 2 Hz). $^{31}P\{^1H\}$, 37.93 (s). **14**: Yield 57%. Mp: 142 °C. Anal. Calcd for $C_{21}H_{35}AuClP$: C, 45.78; H, 6.40. Found: C, 45.49; H, 6.44. IR (cm^{-1}): ν(C≡C), 2132 (w). ^1H NMR: δ 1.20−2.05 (m, 33 H, Cy), 4.29 (d, 2 H, CH_2, $^4J_{HP}$ = 1.5 Hz). $^{13}C\{^1H\}$ NMR (50 MHz): δ 25.81 (s, Cy), 27.05 (d, Cy, $^2J_{CP}$ = 11.9 Hz), 30.65 (s, Cy), 32.50 (s, CH_2), 32.60 (d, Cy, $^1J_{CP}$ = 28.1 Hz), 97.47 (d, ≡CCH_2, $^3J_{CP}$ = 24.3 Hz), 133.77 (d, CAu, $^2J_{CP}$ = 130.9 Hz). $^{31}P\{^1H\}$ NMR: δ 55.63 (s). **15**: Yield 54%. Mp: 140 °C. Anal. Calcd for $C_{21}H_{35}AuBrP$: C, 42.37; H, 5.92. Found: C, 42.58; H, 6.15. IR (cm^{-1}): ν(C≡C), 2128 (w). ^1H NMR (200 MHz): δ 1.26−2.05 (m, 33 H, Cy), 4.10 (d, 2 H, ≡CCH_2, $^4J_{HP}$ = 1.2 Hz). $^{13}C\{^1H\}$ NMR (50 MHz): δ 17.45 (d, ≡CCH_2, $^4J_{CP}$ = 2.5 Hz), 25.81 (s, Cy), 27.05 (d, Cy, $^2J_{CP}$ = 11.8 Hz), 30.67 (s, Cy), 33.15 (d, Cy, $^1J_{CP}$ = 27.4 Hz). $^{31}P\{^1H\}$ NMR: δ 55.58 (s). **16**: Yield 72%. Mp: 147 °C. Anal. Calcd for $C_{21}H_{36}AuOP$: C, 47.37; H, 6.81. Found: C, 47.32; H, 6.97. IR (cm^{-1}): ν(O−H), 3470 (vw); ν(C≡C), 2126 (w). ^1H NMR: δ 1.23−2.01 (m, 33 H, Cy), 4.36 (d, 2 H, ≡CCH_2, $^4J_{HP}$ = 6 Hz). $^{13}C\{^1H\}$ NMR (50 MHz): δ 25.69 (s, Cy), 26.91 (d, Cy, $^2J_{CP}$ = 11.7 Hz), 30.52 (s, Cy), 32.91 (d, Cy, $^1J_{CP}$ = 27.9 Hz), 51.73 (s, ≡CCH_2), 101.78 (d, ≡CCH_2, $^3J_{CP}$ = 23.3 Hz), 130.89 (d, CAu, $^2J_{CP}$ = 128.5 Hz). $^{31}P\{^1H\}$ NMR: δ 55.81 (s). Single crystals of **14** and **15** were obtained by slow evaporation of *n*-hexane solutions.

[Au(C≡CR)(PR′$_3$)] (R = $SiMe_3$, R′ = Ph (17), Cy (18); R = ^{t}Bu, R′ = Ph (19), Cy (20)). To a suspension of [AuCl(PR′$_3$)] (*ca.* 1 mmol) in diethylamine (10 mL) was added the corresponding alkyne in a 1:1.05 molar ratio. After 24 h of stirring, the resulting suspension was filtered to remove the insoluble $(NH_2Et_2)Cl$. The solution was concentrated (*ca.* 1 mL), and *n*-hexane (20 mL) was added to precipitate white solids, which were filtered off, washed with *n*-hexane (2 mL), and air dried. **17:** Yield 87%. Mp: 149 °C. Anal. Calcd for $C_{23}H_{24}AuPSi$: C, 49.64; H, 4.21. Found: C, 49.84; H, 4.34. IR (cm^{-1}), ν(C≡C), 2060 (s). ^1H NMR (200 MHz): δ 0.17 (s, 9 H, $SiMe_3$), 7.38−7.46 (m, 15 H, Ph). $^{13}C\{^1H\}$ NMR (50 MHz): δ 0.75 (s, $SiMe_3$), 109.47 (d, $CSiMe_3$, $^3J_{CP}$ = 19.8 Hz), 128.91 (d, Ph, $^3J_{CP}$ = 11.2 Hz), 129.39 (d, Ph, $^1J_{CP}$ = 55.4 Hz), 131.39 (d, Ph, $^4J_{CP}$ = 2.4 Hz), 134.00 (d, Ph, $^2J_{CP}$ = 13.7 Hz), 149.77 (d, CAu, $^2J_{CP}$ = 131.6 Hz). $^{31}P\{^1H\}$, 41.29 (s). **18**: Yield 77%. Mp: 115 °C. Anal. Calcd for $C_{23}H_{42}AuPSi$: C, 48.08; H, 7.37. Found: C, 48.35; H, 7.58. IR (cm^{-1}), ν(C≡C), 2056 (s). ^1H NMR: δ 0.13 (s, 9 H, $SiMe_3$), 1.18−1.92 (m, 33 H, Cy). $^{13}C\{^1H\}$ NMR (50 MHz): 0.83 (s, $SiMe_3$), 25.70 (s, Cy), 26.95 (d, Cy, $^2J_{CP}$ = 11.7 Hz), 30.43 (s, Cy), 32.95 (d, Cy, $^1J_{CP}$ = 27.6 Hz), 108.16 (d, $CSiMe_3$, $^3J_{CP}$ = 19.9 Hz), 154.48 (d, CAu, $^2J_{CP}$ = 122 Hz). $^{31}P\{^1H\}$ NMR: δ 55.20 (s). **19:** Yield 80%. Mp: 193 °C (lit.[35] 181−2 °C). Anal. Calcd for $C_{24}H_{24}AuP$: C, 53.34; H, 4.48. Found: C, 52.98; H, 4.48. IR (cm^{-1}): ν(C≡C), 2118 (w) (lit.[35] 2140). ^1H NMR: δ 1.33 (s, 9 H, ^{t}Bu), 7.42−7.53 (m, 15 H, Ph). $^{13}C\{^1H\}$ NMR: δ 28.12 (s, CMe_3), 32.23 (s, Me), 114.50 (d, C^tBu, $^3J_{CP}$ = 25.7 Hz), 116.41 (d, CAu, $^2J_{CP}$ =141 Hz), 128.91 (d, Ph, $^3J_{CP}$ = 11.0 Hz), 129.86 (d, Ph, $^1J_{CP}$ = 55.4 Hz), 131.32 (d, Ph, $^4J_{CP}$ = 2.6 Hz), 134.18 (d, Ph, $^2J_{CP}$ = 14.1 Hz). $^{31}P\{^1H\}$, 42.09 (s). **20**: Yield 54%. Mp: 195 °C. Anal. Calcd for $C_{24}H_{42}AuP$: C, 51.61; H, 7.58. Found: C, 51.20; H, 7.80. IR (cm^{-1}): ν(C≡C), 2109 (vw). ^1H NMR (200 MHz): δ 1.20−1.90 (m, 33 H, Cy), 1.25 (s, 9 H, ^{t}Bu). $^{13}C\{^1H\}$ NMR (50 MHz): 25.83 (s, Cy), 27.09 (d, Cy, $^2J_{CP}$ = 11.7 Hz), 28.08 (d, CMe_3, $^4J_{CP}$ = 1.7 Hz), 30.52 (s, Cy), 32.33 (s, Me), 33.11 (d, Cy, $^1J_{CP}$ = 27.6 Hz), 113.46 (d, C^tBu, $^3J_{CP}$ = 23.9 Hz), 120.89 (d, CAu, $^2J_{CP}$ = 131.2 Hz). $^{31}P\{^1H\}$, 55.30 (s). Single crystals of **17** and **19** were obtained by slow evaporation of *n*-hexane solutions.

[$(AuPPh_3)_2$\{μ-C≡C(CH_2)$_5$C≡C\}] (21). HC≡C(CH_2)$_5$C≡CH (31 μL, 0.21 mmol) was added to a suspension of [AuCl(PPh_3)] (207 mg, 0.42 mmol) in $HNEt_2$ (15 mL), and the reaction mixture was stirred for 24 h. The resulting suspension was filtered, and the solid residue was washed with distilled water (2 × 5 mL) and dissolved in CH_2Cl_2 (10 mL). This solution was filtered through $MgSO_4$ and concentrated to 1 mL. Addition of *n*-hexane (15 mL) gave **21** as a white solid. Yield: 52%. Mp: 82 °C. Anal. Calcd for $C_{45}H_{40}Au_2P_2$: C, 52.14; H, 3.89. Found: C, 52.04; H, 3.96. ^1H NMR: δ 1.58−1.65 (m, 6H, CH_2), 2.38 (t, 4 H, CH_2, $^3J_{HH}$ = 6.9 Hz), 7.39−7.55 (m, 30 H, PPh_3). $^{13}C\{^1H\}$ NMR: δ 19.87 (s, CH_2), 28.92 (s, CH_2), 29.85 (s, CH_2), 105.71 (d, ≡C−CH_2, $^3J_{CP}$ = 25.7 Hz), 119.28 (d, CAu, $^2J_{CP}$ = 142 Hz), 128.99 (d, Ph, $^3J_{CP}$ = 11.1 Hz), 129.78 (d, Ph, $^1J_{CP}$ = 55.9 Hz), 131.37 (s, Ph), 134.25 (d, Ph, $^2J_{CP}$ = 14.1 Hz) $^{31}P\{^1H\}$, 41.96 (s).

[Au(C≡CR)(PR′$_3$)] (R′ = C_6H_4OMe-4; R = $SiMe_3$ (22), ^{t}Bu (23)). To yellow solutions of **10** or **11** (*ca.* 1 mmol) in dichloromethane (10 mL) was added an equimolar amount of solid $P(C_6H_4OMe\text{-}4)_3$. The solutions were stirred for 15 min and concentrated to 1 mL, and *n*-hexane (20 mL) was added to give white solids, which were filtered off and air dried. **22**: Yield 78%. Mp: 116 °C. Anal. Calcd for $C_{26}H_{30}AuO_3PSi$: C, 48.30; H, 4.68. Found: C, 48.38; H, 4.66. IR (cm^{-1}): ν(C≡C), 2056 (s). ^1H NMR: δ 0.20 (s, 9 H, $SiMe_3$), 3.81 (s, 9 H, OMe), 6.91 (m, 6 H, C_6H_4), 7.40 (m, 6 H, C_6H_4). $^{13}C\{^1H\}$ NMR: δ 0.90 (s, $SiMe_3$), 55.35 (s, OMe), 109.71 (d, $CSiMe_3$, $^3J_{CP}$ = 21.6 Hz), 114.58 (d, C_6H_4, $^3J_{CP}$ = 12.6 Hz), 121.42 (d, C_6H_4, $^1J_{CP}$ = 60.9 Hz), 135.62 (d, C_6H_4, $^2J_{CP}$ = 15.1 Hz), 150.36 (d, CAu, $^2J_{CP}$ = 131.9 Hz), 161.96 (d, C_6H_4, $^4J_{CP}$ = 2 Hz). $^{31}P\{^1H\}$, 37.86 (s). **23:** Yield 83%. Mp: 172 °C. Anal. Calcd for $C_{27}H_{30}AuO_3P$: C, 51.44; H, 4.80. Found: C, 51.45; H, 4.83. IR (cm^{-1}): ν(C≡C), 2112 (vw). ^1H NMR (200 MHz): δ 1.33 (s, 9 H, ^{t}Bu), 3.82 (s, 9 H, OMe), 6.91 (m, 6 H, C_6H_4), 7.43 (m, 6 H, C_6H_4). $^{13}C\{^1H\}$ NMR (50 MHz): δ 28.19 (s, CMe_3), 32.31 (s, CMe_3), 55.32 (s, OMe), 102.41 (d, C^tBu, $^3J_{CP}$ = 21.4 Hz), 114.46

(d, C_6H_4, $^3J_{CP} = 12.3$ Hz), 116.78 (d, CAu, $^2J_{CP} = 141.6$ Hz), 121.7 (d, C_6H_4, $^1J_{CP} = 60.6$ Hz), 135.64 (d, C_6H_4, $^2J_{CP} = 15.4$ Hz), 161.84 (d, C_6H_4, $^4J_{CP} = 1.7$ Hz). $^{31}P\{^1H\}$ NMR: δ 38.39 (s).

[Au(C≡C^{t}Bu)(CN^{t}Bu)] (25). To a suspension of [AuCl(CN^{t}Bu)] (316 mg, 1.00 mmol) in triethylamine (5 mL), ^{t}BuC≡CH was added (90 mg, 1.10 mmol). After 72 h, the suspension was filtered, the solid washed with water (5 mL) to remove ($NHEt_3$)Cl dissolved in CH_2Cl_2 (10 mL), and the solution filtered through $MgSO_4$. Concentration of the solution (*ca.* 1 mL) and addition of *n*-hexane (20 mL) gave **25** as a white solid. Yield: 221 mg, 61%. Mp: 82 °C. Anal. Calcd for $C_{11}H_{18}AuN$: C, 36.57; H, 5.02; N, 3.88. Found: C, 36.57; H, 5.02; N, 3.81. IR (cm^{-1}): ν(CN), 2226 (s). ^1H NMR (200 MHz): δ ^1H, 1.18 (s, 9 H, $C_2{}^tBu$), 1.46 (s, 9 H, CN^{t}Bu). $^{13}C\{^1H\}$ NMR: δ 28.02 (s, *C*^{t}Bu), 29.76 (s, Me (CN^{t}Bu)), 32.17 (s, Me ($C_2{}^tBu$)), 58.32 (s, N*C*Me_3), 106.52 (s, *C*^{t}Bu), 114.07 (s, Au*C*≡C), 147.50 (t, Au*C*N, $^1J_{CN} = 20$ Hz).

[(AuCN^{t}Bu)$_2$\{μ-C≡C(CH$_2$)$_5$C≡C\}] (26). To a suspension of [AuCl(CN^{t}Bu)] (325 mg, 1.03 mmol) in NEt_3 (10 mL) was added HC≡C(CH_2)$_5$C≡CH (75 μL, 0.51 mmol). After 24 h of stirring, the reaction mixture was worked up as described above for **25**, giving **26** as a white solid. Yield: 234 mg, 67%. Mp: 117 °C (dec). Anal. Calcd for $C_{19}H_{28}Au_2N_2$: C, 33.64; H, 4.16; N, 4.13. Found: C, 33.76; H, 4.21; N, 4.54. IR (cm^{-1}): ν(CN), 2224 (s). ^1H NMR (200 MHz): δ ^1H, 1.50−1.69 (m, 6 H, CH_2), 1.56 (s, 18 H, ^{t}Bu), 2.32 (t, 4 H, CH_2). $^{13}C\{^1H\}$ NMR: δ 19.81 (s, CH_2), 28.64 (s, CH_2), 29.71 (s, CH_2), 29.78 (s, Me), 57.75 (s, *C*Me_3), 104.80 (s, *C*≡CAu), 109.55 (s, *C*Au).

[Au(C≡CR)\{C(NH^{t}Bu)(NEt$_2$)\}] (R = SiMe$_3$ (27), ^{t}Bu (28)). To a solution of [AuCl(CN^{t}Bu)] (1 mmol) in diethylamine (10 mL) was added the corresponding alkyne (molar ratio of 1:1), and the mixture was stirred for 17 (**27**) or 24 (**28**) h. The resulting suspension was filtered and washed with water (2 mL) to remove (NH_2Et_2)Cl. The remaining solid was treated with dichloromethane (10 mL) and filtered through $MgSO_4$. The solution was concentrated (*ca.* 1 mL), and *n*-hexane (15 mL) was added to give white solids, which were filtered off, washed with *n*-hexane (2 mL), and air dried. **27**: Yield: 79%. Mp: 143 °C. Anal. Calcd for $C_{14}H_{29}AuN_2Si$: C, 37.33; H, 6.49; N, 6.22. Found: C, 37.50; H, 6.50; N, 6.31. IR (cm^{-1}): ν(N−H), 3344 (m); ν(C≡C), 2050 (s); ν(C=N), 1538 (s). ^1H NMR (200 MHz): δ 0.18 (s, 9 H, $SiMe_3$), 1.16 (t, 3 H, CH_2*Me*, $^3J_{HH} = 7.3$ Hz), 1.25 (t, 3 H, CH_2*Me*, $^3J_{HH} = 7.1$ Hz), 1.61 (s, 9 H, ^{t}Bu), 3.24 (q, 2 H, CH_2, $^3J_{HH} = 7.3$ Hz), 4.0 (q, 2 H, CH_2, $^3J_{HH} = 7.1$ Hz), 5.84 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR: δ 1.13 (s, $SiMe_3$), 11.80 (s, CH_2*Me*), 14.82 (s, CH_2*Me*), 31.92 (s, Me (^{t}Bu)), 39.88 (s, CH_2), 53.81 (s, *C*Me_3), 54.01 (s, CH_2), 110.24 (s, *C*$SiMe_3$), 145.82 (s, C≡*C*Au), 205.45 (s, *C*N_2). **28**: Yield: 83%. Mp: 116 °C. Anal. Calcd for $C_{15}H_{29}AuN_2$: C, 41.48; H, 6.73; N, 6.45. Found: C, 41.24; H, 6.81; N, 6.48. IR (cm^{-1}): ν(N−H), 3350 (m); ν(C≡C), 2106 (vw); ν(C=N), 1538 (s). ^1H NMR (200 MHz): δ 1.15 (t, 3 H, CH_2*Me*, $^3J_{HH} = 7.3$ Hz), 1.24 (t, 3 H, CH_2*Me*, $^3J_{HH} = 7.4$ Hz), 1.29 (s, 9 H, Me (C≡C-^{t}Bu)), 1.61 (s, 9 H, Me (NH^{t}Bu)), 3.22 (q, 2 H, CH_2, $^3J_{HH} = 7.3$ Hz), 4.02 (q, 2 H, CH_2, $^3J_{HH} = 7.1$ Hz), 5.81 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR: δ 11.84 (s, CH_2*Me*), 14.79 (s, CH_2*Me*), 28.25 (s, C≡C*C*Me_3), 31.95 (s, Me (NH^{t}Bu)), 32.61 (s, Me (C≡C^{t}Bu)), 39.76 (s, CH_2), 53.81 (s, NH*C*Me_3), 54.05 (s, CH_2), 109.72 (s, C≡*C*^{t}Bu), 115.40 (s, C≡*C*Au), 206.09 (s, *C*N_2).

[\{AuC(NH^{t}Bu)(NEt$_2$)\}$_2$\{μ-C≡C(CH$_2$)$_5$C≡C\}] (29). To a solution of [AuCl(CN^{t}Bu)] (457 mg, 1.45 mmol) in diethylamine (10 mL), HC≡C(CH_2)$_5$C≡CH (89 mg, 0.72 mmol) was added. After 14 h of stirring, the resulting suspension was filtered and the solid washed with water to remove (NH_2Et_2)Cl. The residue was treated with dichloromethane (15 mL), the solution filtered through $MgSO_4$ and concentrated (*ca.* 1 mL), and *n*-hexane (20 mL) added to precipitate a white solid, which was filtered off, washed with *n*-hexane (2 mL), and air dried. Yield: 332 mg, 56%. Mp: 90 °C. Anal. Calcd for $C_{27}H_{50}Au_2N_4$: C, 39.32; H, 6.11; N, 6.79. Found: C, 39.59; H, 6.27; N, 6.80. IR (cm^{-1}): ν(N−H), 3338 (m); ν(C=N), 1538 (s). ^1H NMR (200 MHz): δ 1.16 (t, 3 H, *Me*CH_2, $^3J_{HH} = 7.3$ Hz), 1.25 (t, 3 H, *Me*CH_2, $^3J_{HH} = 7.2$ Hz), 1.61 (s, 18 H, C*Me*$_3$), 2.36 (t, 4 H, CH_2, $^3J_{HH} = 7.6$ Hz), 3.23 (q, 4 H, NCH_2, $^3J_{HH} = 7.3$ Hz), 3.996 (q, 4 H, NCH_2, $^3J_{HH} = 7.2$ Hz), 5.83 (s, 2 H, NH). $^{13}C\{^1H\}$ NMR: δ 11.79 (s, Me), 14.79 (s, Me), 20.35 (s, CH_2), 29.18 (s, CH_2), 30.17 (s, CH_2), 31.88 (s, C*Me*$_3$), 39.82 (s, NCH_2), 53.77 (s, *C*Me_3), 53.95 (s, NCH_2), 106.53 (s, ≡*C*−CH_2), 112.63 (s, ≡CAu), 205.80 (s, CN_2).

[AuCl\{C(NH^{t}Bu)(NEt$_2$)\}] (30). A solution of [AuCl(CN^{t}Bu)] (370 mg, 1.17 mmol) in diethylamine (5 mL) was stirred for 5 h. The solvent was removed *in vacuo*, and the residue was extracted with CH_2Cl_2 (10 mL) and filtered through $MgSO_4$. Addition of *n*-hexane (15 mL) to the solution gave an oily material, which upon stirring for 1 h gave a white solid. Yield: 381 mg, 84%. Mp: 82 °C. Anal. Calcd for $C_9H_{20}AuClN_2$: C, 27.81; H, 5.19; N, 7.21. Found: C, 27.87; H, 5.18; N, 7.08. IR (cm^{-1}): ν(NH), 3360 (w); ν(C=N), 1538 (s); ν(Au−Cl), 328 (s). ^1H NMR (200 MHz): δ 1.21 (t, 3 H, CH_2*Me*, $^3J_{HH} = 7.3$ Hz), 1.29 (t, 3 H, CH_2*Me*, $^3J_{HH} = 7.0$ Hz), 1.64 (s, 9 H, ^{t}Bu), 3.33 (q, 2 H, CH_2, $^3J_{HH} = 7.3$ Hz), 3.98 (q, 2 H, CH_2, $^3J_{HH} = 7.0$ Hz), 5.82 (s, 1 H, NH). $^{13}C\{^1H\}$ NMR: δ 11.75 (s, CH_2*Me*), 14.61 (s, CH_2*Me*), 31.65 (s, Me (^{t}Bu)), 40.38 (s, CH_2), 54.08 (s, *C*Me_3), 54.99 (s, CH_2), 188.95 (s, *C*Au).

[Au(C≡CH)\{C(NH^{t}Bu)(NEt$_2$)\}] (31). To a solution of **30** (298 mg, 0.77 mmol) in acetone (20 mL), [Tl(acac)] (317 mg, 1.05 mmol) was added, and the resulting suspension was stirred for 40 min and filtered through Celite. After C_2H_2 was bubbled into the solution for 2 h, it was filtered through Celite and concentrated (1 mL) and diethyl ether (20 mL) was added to precipitate a white solid. Yield: 140 mg, 48%. Mp: 115 °C. Anal. Calcd for $C_{11}H_{21}AuN_2$: C, 34.93; H, 5.59; N, 7.41. Found: C, 34.82; H, 5.82; N, 7.44. Λ_M (Ω^{-1} cm^2 mol^{-1}): 29. IR (cm^{-1}): ν(CH), 3266 (w); ν(NH), 3204 (m); ν(C≡C), 1932 (w); ν(C=N), 1562 (m). ^1H NMR (200 MHz): δ 1.18 (t, 3H, CH_2*Me*, $^3J_{HH} = 7.2$ Hz), 1.25 (t, 3H, CH_2*Me*, $^3J_{HH} = 7.0$ Hz), 1.58 (s, 1H, CH), 1.62 (s, 9H, ^{t}Bu), 3.35 (q, 2H, CH_2, $^3J_{HH} = 7.2$ Hz), 3.95 (q, 2H, CH_2, $^3J_{HH} = 7.0$ Hz). $^{13}C\{^1H\}$ NMR: δ 11.76 (s, CH_2*Me*), 14.93 (s, CH_2*Me*), 31.86 (s, Me (^{t}Bu)), 40.41 (s, CH_2), 53.81 (s, *C*Me_3), 54.15 (s, CH_2), 77.21 (s, H*C*≡C), 142.64 (s, Au*C*≡C), 199.31 (s, *C*N_2).

X-Ray Structure Determinations of Compounds 6, 14, 15, 17, and 19. *Crystal data*: See Table 1. *Data collection and reduction:* Crystals were mounted on glass fibers in inert oil and transferred to the cold gas stream of a Siemens R3 diffractometer. Data were registered in ω-scan mode to $2\theta_{max} = 50°$ (Mo Kα radiation). Cell constants were refined from setting angles of ca. 65 reflections to $2\theta = 25°$. Absorption corrections were based on ψ-scans. *Structure solution and refinement*: The structures were solved by the heavy-atom method and refined anisotropically on F^2 using the program SHELXL-93 (G. M. Sheldrick, University of Göttingen). H atoms were included using a riding model. *Special features of refinement*: In compound **6**, the hydroxyl H were not located; one OH group is disordered (there are no short O···O contacts suggestive of H bonds). Compounds **14** and **15** are isostructural; the Br atom of **15** has a high *U* value. Residual electron density near an inversion center in **19** was tentatively interpreted as a disordered molecule of $NHEtCH_2Cl$.

Results and Discussion

Synthesis. We have previously shown that acetylacetonatogold(I) complexes are able to deprotonate organic substrates containing even weakly acidic hydrogen atoms to give a variety of gold(I) complexes containing ylide, thiolato, phosphide, bis(diphenylphosphino)methanide, alkyl (CHRR′ (R = R′ = CN, CO_2Me; R = CN, R′ = CO_2Me)), or alkynyl ligands.[41,43−50] The extension of this method to the preparation of new

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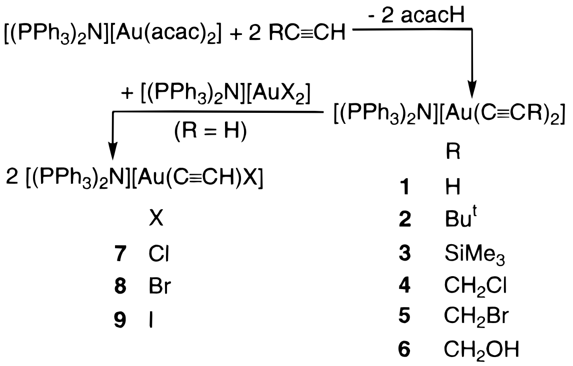
Table 1. Crystal Data for Complexes 6, 14, 15, 17 and 19

	6	**14**	**15**	**17**	**19**
molecular formula	$C_{42}H_{36}AuNO_2P_2$	$C_{21}H_{35}AuClP$	$C_{21}H_{35}AuBrP$	$C_{23}H_{24}AuPSi$	$C_{25.50}H_{28}AuCl_{0.50}N_{0.50}P$
mol wt	845.62	550.88	595.34	556.45	587.15
space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$C2/c$
a (Å)	10.892(2)	11.119(3)	11.314(2)	6.7192(10)	30.518(6)
b (Å)	21.823(2)	16.732(3)	16.674(3)	21.571(3)	8.601(2)
c (Å)	16.072(2)	12.967(4)	12.959(2)	15.962(2)	17.885(4)
α (deg)	90	90	90	90	90
β (deg)	108.413(10)	114.92(2)	115.060(10)	96.625(10)	93.61(2)
γ (deg)	90	90	90	90	90
V (Å^3)	3624.8(9)	2187.8(10)	2214.6(6)	2322.7(5)	4686(2)
Z	4	4	4	4	8
T (K)	173(2)	173(2)	173(2)	173(2)	173(2)
λ (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
ρ_{calc} (Mg/m^3)	1.550	1.672	1.786	1.591	1.665
F(000)	1680	1088	1160	1080	2296
μ (mm^{-1})	4.183	6.921	8.520	6.458	6.415
no. of indep reflns	6357	4984	3719	5335	4119
no. of param	439	217	112	247	133
no. of restraints	407	39	21	87	24
R1[a]	0.0378	0.0369	0.0630	0.0274	0.0382
wR2[b]	0.0580	0.0870	0.1788	0.0446	0.0923
$S(F^2)$	0.819	0.942	1.037	0.831	0.915
max $\Delta\rho$ (e Å^{-3})	0.837	2.220	2.483	0.709	1.105

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for reflections with $I > 2\sigma I$. [b] $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{0.5}$ 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.

Scheme 1



bisalkynylaurate(I) complexes $[(PPh_3)_2N][Au(C{\equiv}CR)_2]$ (R = H (**1**), ^{t}Bu (**2**), $SiMe_3$ (**3**), CH_2Cl (**4**), CH_2Br (**5**), CH_2OH (**6**)) by reacting $[(PPh_3)_2N][Au(acac)_2]$ with the corresponding alkyne provides a further example of the synthetic utility of acetylacetonatogold(I) complexes (see Scheme 1). The reactions were carried out using excess alkyne (molar ratio *ca.* 1:40) in order to prevent the formation of insoluble polymeric $[Au(C{\equiv}CR)]_n$ species. The complexes were obtained in high yield (83−95%) and the excess of alkyne and the byproduct (acacH) were easily removed. $K[Au(C{\equiv}CH)_2]$ was reported long ago by Nast *et al.* as a compound of very low stability to moisture and light. In contrast, complex **1** is stable to moisture and daylight. Our method of synthesis is much simpler than that used to prepare the potassium salt, which involved three steps and the use of liquid ammonia, acetylene, KC≡CH, $Au_2(C{\equiv}C){\cdot}NH_3$, and $K_2[Au_2(\mu\text{-}C{\equiv}C)(C{\equiv}CH)_2]$.[33] As far as we are aware, the only other $[Au(C{\equiv}CR)_2]^-$ complex known is that with R = Ph, prepared by Nast *et al.* by reacting $[Au(C{\equiv}CPh)]_n$ with KC≡CH in liquid ammonia.[33,51]

Alkynylhaloaurate(I) complexes $[(PPh_3)_2N][Au(C{\equiv}CH)X]$ (X = Cl (**7**), Br (**8**), I (**9**)) were prepared in high yield (84−95%) by reacting equimolar amounts of **1** and the corresponding $[(PPh_3)_2N][AuX_2]$ salts (see Scheme 1). The only reported $[Au(C{\equiv}CR)X]^-$ complexes are those with R = Ph and X = Cl, Br, I obtained by reacting $[Au(C{\equiv}CPh)]_n$ with X^-.[9,52] However, no experimental details were reported.

We have attempted the synthesis of the mixed alkynyl complex $[(PPh_3)_2N][Au(C{\equiv}CH)(C{\equiv}C^tBu)]$ by reacting equimolar amounts of **1** and **2** in dichloromethane, but only a mixture of the starting complexes (by ^{1}H NMR) was recovered. The reaction of **1** with $[(PPh_3)_2N][Au(SH)_2]$[46] (1:1, dichloromethane) seems to produce an equilibrium mixture (by ^{1}H NMR) of the starting complexes and, probably, $[(PPh_3)_2N][Au(C{\equiv}CH)(SH)]$, which we could not separate. Scheme 1 summarizes the reactions that lead to anionic alkynylgold(I) complexes **1**−**9**.

For the syntheses of neutral $[Au(C{\equiv}CR)L]$ (L = amine, phosphine, isocyanide, or carbene) complexes, we have used a variety of synthetic procedures (see Schemes 2 and 3). Thus, moderate to high (48−73%) yields of the alkynyl(diethylamine)gold(I) complexes $[Au(C{\equiv}CR)(NHEt_2)]$ (R = $SiMe_3$ (**10**), ^{t}Bu (**11**)) were achieved by reacting equimolar amounts of [AuCl(tht)] (tht = tetrahydrothiophene) and the corresponding alkyne in diethylamine. The alkynyl ligand generated *in situ* (on deprotonation of the alkyne by the amine) and the amine itself replace both tht and chloro ligands, forming the desired complexes along with $(NH_2Et_2)Cl$. This ammonium salt is easily removed because of its insolubility in diethylamine, and the corresponding complex

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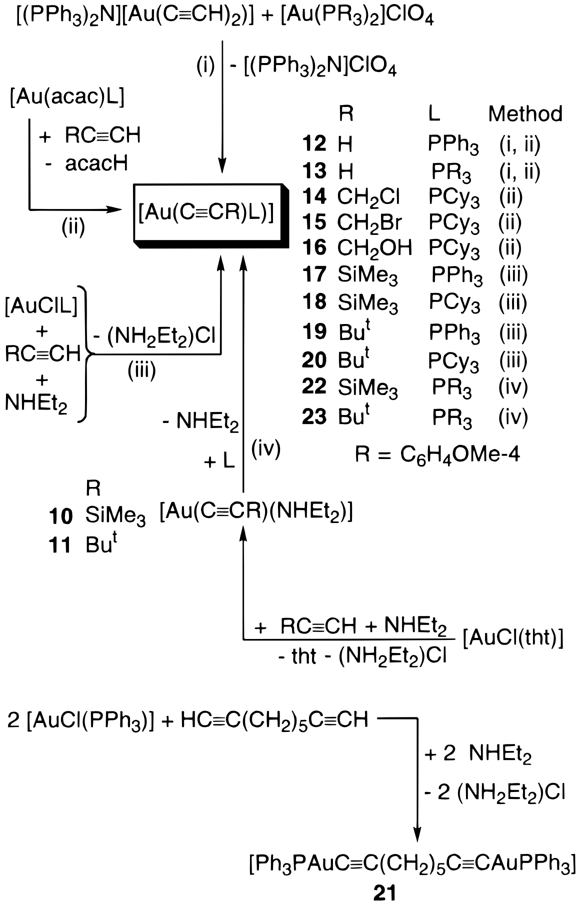
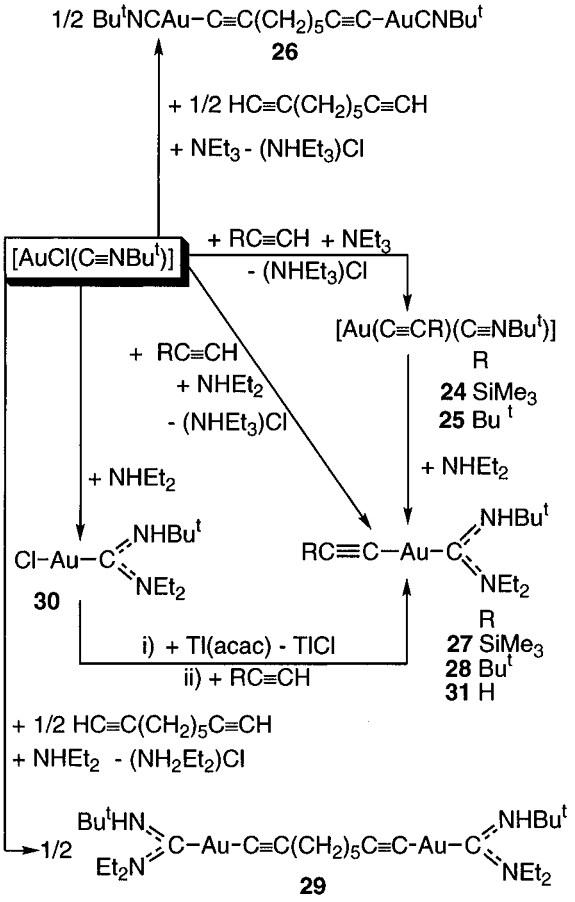
Scheme 2



Scheme 3



precipitates on cooling the solution. Complexes [Au(C≡CR)(L)] (R = Ph, L = NH_3, $^iPrNH_2$, $^tBuNH_2$, $C_5H_{11}NH_2$, $C_8H_{15}NH_2$, $C_9H_{17}NH_2$, $^nBu_2NH$, piperidine, pyridine; R = ^tBu, L = $^tBuNH_2$; R = ^tBu, C_6H_4Me-4, L = NH_3 have been prepared by reacting $[Au(C{\equiv}CR)]_n$ with the corresponding ligand[13,39] or the alkyne with $[AuL_2]^+$.[39]

We have not been able to prepare [Au(C≡CH)($NHEt_2$)] because the reaction of [AuCl(tht)] with C_2H_2 in diethylamine or triethylamine gives instead a brown complex that detonates after drying when touched by a spatula. We believe this complex to be the same reported long ago as Au_2C_2.[53] If Na_2CO_3 is used instead of the amine, metallic gold is obtained. The same explosive compound was formed in the following reactions: $[(PPh_3)_2N][Au(C{\equiv}CH)Cl]$ + $[Au(acac)(PCy_3)]$ (but not with $[Au(acac)\{P(C_6H_4OMe\text{-}4)_3\}]$); $[Au(C{\equiv}CSiMe_3)(NHEt_2)]$ + C_2H_2; $[(PPh_3)_2N][Au(C{\equiv}CH)_2]$ + [AuCl(tht)]; $[(PPh_3)_2N][AuCl_4]$ + C_2H_2 + $HNEt_2$; $[Au(C{\equiv}CSiMe_3)(PPh_3)]$ + $AgClO_4$. Because of the extreme instability of this compound, we have not attempted to characterize it. However, we have carried out limited investigations on its reactivity. Thus, the product from the reaction of [AuCl(tht)] with C_2H_2 in diethylamine reacts with $P(C_6H_4OMe\text{-}4)_3$ to give a complex mixture that we could not separate. However, the ^{31}P NMR spectrum of one of the fractions showed the presence of **13** and $[AuCl(P(C_6H_4OMe\text{-}4)_3)]$. The reaction with ^tBuNC gave a mixture with two resonances in the ^tBu region of the ^1H NMR. It does not react with $[(PPh_3)_2N][AuCl_2]$. The reaction of $[AuCl(AsPh_3)]$ with $Me_3SiC{\equiv}CH$ in diethylamine, intended to produce $[Au(C{\equiv}CSiMe_3)(AsPh_3)]$, gives **10** instead.

Alkynylgold(I) complexes with phosphine ligands have been prepared (see Scheme 2) by four different synthetic methods, namely (i) the reaction between equimolar amounts of **1** and $[Au(PR_3)_2]ClO_4$ to give $[Au(C{\equiv}CH)(PR_3)]$ (R = Ph (**12**), C_6H_4OMe-4 (**13**)) and $[(PPh_3)_2N]ClO_4$, which could be separated because of the insolubility of the latter in diethyl ether; (ii) reaction of terminal alkynes with $[Au(acac)PR_3]$ to give acacH and complexes $[Au(C{\equiv}CR)(PR'_3)]$ (R = H, R′ = Ph (**12**), C_6H_4OMe-4 (**13**); R′ = Cy = cyclohexyl, R = CH_2Cl (**14**), CH_2Br (**15**), CH_2OH (**16**)). A slight excess of the alkyne was used, except in the case of acetylene, which was used in large excess to prevent the formation of mixtures that we attribute to the reaction $2[Au(C{\equiv}CH)L] \rightarrow [LAuC{\equiv}CAuL] + C_2H_2$. Although the synthesis of **12** has been reported, it was not obtained in pure form.[21] (iii) The reaction of $[AuCl(PR_3)]$ complexes with terminal alkynes in diethylamine to give complexes $[Au(C{\equiv}CR)(PR'_3)]$ (R = $SiMe_3$, R′ = Ph (**17**), Cy (**18**); R = ^tBu, R′ = Ph (**19**), Cy (**20**)) and $[(AuPPh_3)_2\{\mu\text{-}C{\equiv}C(CH_2)_5C{\equiv}C\}]$ (**21**). In this case, the alkynyl ligand resulting from deprotonation of the alkyne by the diethylamine solvent coordinates to gold with concomitant formation of insoluble $(NH_2Et_2)Cl$, and (iv) the displacement of the $NHEt_2$ ligand present in complexes **10** or **11** by $P(C_6H_4OMe\text{-}4)_3$ to give complexes $[Au(C{\equiv}CR)(P(C_6H_4OMe\text{-}4)_3)]$ (R = $SiMe_3$ (**22**), ^tBu (**23**)) in high yield (78−83%). These reactions must be favored by the low affinity of the soft-acid gold(I) for hard-base nitrogen donor

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ligands.[54] All four methods generally give high yields (70−87%) of the organometallic complexes except for those partially soluble in *n*-hexane, such as **14**, **15**, **20**, and **21** (50−60%). Complexes $[\mathrm{Au(C{\equiv}CR)(PR'_3)}]$ (R′ = Ph, R = Ph, $\mathrm{C_6H_4Me}$-4, Me, Et, ^{i}Pr, Pr, ^{n}Bu, ^{t}Bu, $\mathrm{CF_3}$, $\mathrm{C_6F_5}$, $\mathrm{CH_2OH}$, $\mathrm{(CH_2)_2OH}$, $\mathrm{C_6H_{10}OH}$, $\mathrm{CO_2Me}$; R′ = Me, R = Me, ^{t}Bu; R′ = ^{i}Pr, R = H, $\mathrm{CO_2Me}$; R = Ph, R′ = Me, OPh, Et, $\mathrm{R'_3} = \mathrm{Ph_2\{CH_2(anthracenyl)\}}$, $\mathrm{Ph(OMe)_2}$; R = $\mathrm{CF_3}$, $\mathrm{R'_3} = \mathrm{PhMe_2}$) are among the best known alkynylgold(I) derivatives. They have been prepared by reacting (i) $[\mathrm{Au(C{\equiv}CR)}]_n$ with the corresponding phosphine,[8,13,35] (ii) [AuCl(L)] with $\mathrm{LiC{\equiv}CR}$[13] or with $\mathrm{NaC{\equiv}CR}$[21,35] or $\mathrm{KC{\equiv}CR}$,[35] (iii) the alkyne with [AuMe(L)][25,26] or with $[\mathrm{Au(NR_2)(L)}]$ ($\mathrm{HNR_2}$ = imidazole)[55] or $[\mathrm{Au(C_5R''_5)(L)}]$ (R″ = H, Me),[22] (iv) [AuCl(L)] with the alkyne in $\mathrm{NHEt_2}$ in the presence of CuCl.[35] In our experience, this last method does not in fact require the presence of CuCl as catalyst.

$[\mathrm{AuCl(CN^tBu)}]$ reacts with terminal alkynes in triethylamine to give moderate yields (36−67%) of the corresponding alkynyl(isocyanide)gold(I) complexes $[\mathrm{Au(C{\equiv}CR)(CN^tBu)}]$ (R = $\mathrm{SiMe_3}$ (**24**),[42] ^{t}Bu (**25**)) and $[\mathrm{(AuCN^tBu)_2\{\mu\text{-}C{\equiv}C(CH_2)_5C{\equiv}C\}}]$ (**26**). The reactions are similar to those described above for the syntheses of complexes **17**−**21**, except for the use of triethylamine instead of diethylamine. It is well-known that primary or secondary amines, and also alcohols, add to isocyanidegold(I) complexes to give the corresponding carbene derivatives.[56−59] Therefore, the use of diethylamine must be avoided for the syntheses of isocyanide complexes. In fact, when $[\mathrm{AuCl(CN^tBu)}]$ and the same alkynes that in triethylamine lead to isocyanide complexes **24**−**26** are reacted in diethylamine, the corresponding alkynyl(carbene)complexes $[\mathrm{Au(C{\equiv}CR)\{C(NH^tBu)(NEt_2)\}}]$ (R = $\mathrm{SiMe_3}$ (**27**), ^{t}Bu (**28**)) and $[\mathrm{(Au\{C(NH^tBu)(NEt_2)\})_2\{\mu\text{-}C{\equiv}C(CH_2)_5C{\equiv}C\}}]$ (**29**) are obtained as the result of the double role of diethylamine as a deprotonating agent toward the alkyne and as a nucleophile adding to the isocyanide ligand. Similarly, the isocyanide complex $[\mathrm{AuCl(CN^tBu)}]$ reacts with diethylamine to give the carbene complex $[\mathrm{AuCl\{C(NH^tBu)(NEt_2)\}}]$ (**30**).

All attempts to prepare $[\mathrm{Au(C{\equiv}CH)(CN^tBu)}]$ failed. Thus, from the reaction of $[\mathrm{AuCl(CN^tBu)}]$ with acetylene in triethylamine, the above-mentioned brown explosive complex $\mathrm{Au_2C_2}$ was obtained. The reaction of $[\mathrm{AuCl(CN^tBu)}]$ with Tl(acac) in dichloromethane gives insoluble TlCl and a solution presumably containing $[\mathrm{Au(acac)(CN^tBu)}]$, which, however, could not be isolated because of its oily nature. This complex was expected to react with acetylene to give acacH and the ethynyl complex, but unfortunately, on bubbling acetylene through this solution, immediate partial decomposition to metallic gold was observed and the resulting mixture could not be separated. The same occurred when acetylene was bubbled through a solution containing a 1:1 mixture of $[\mathrm{AuCl(CN^tBu)}]$ and proton sponge. When NaOH or NaH was used as a base, total decomposition to metallic gold occurred. Other attempts also failed. For example, the reaction between [AuCl(tht)], $\mathrm{C_2H_2/Na_2CO_3}$, and $\mathrm{CNBu^t}$ gave $[\mathrm{AuCl(CNBu^t)}]$, whereas no reaction took place between $[\mathrm{AuCl(CN^tBu)}]$ and $\mathrm{C_2H_2/Na_2CO_3}$ or **12** and ^{t}BuNC. The ethynyl(carbene)gold(I) complex $[\mathrm{Au(C{\equiv}CH)\{C(NH^tBu)(NEt_2)\}}]$ (**31**) was obtained by treating **30** with Tl(acac), removing TlCl, and bubbling acetylene through the resulting solution. Scheme 3 summarizes the reactions leading to isocyanide and carbene alkynylgold(I) complexes.

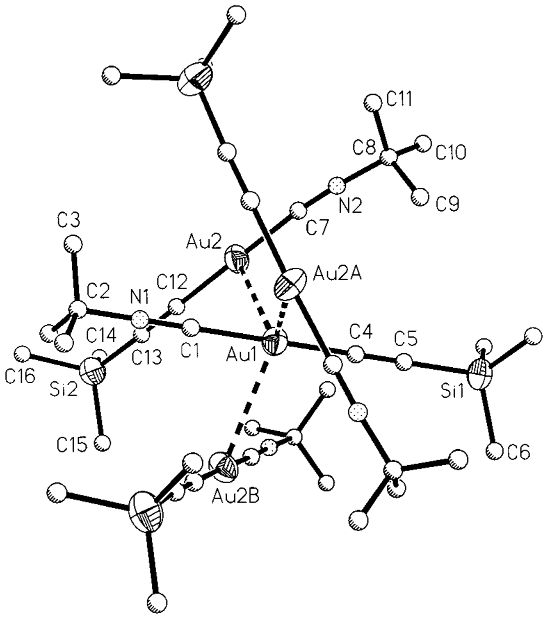

Figure 1. Ellipsoid plot of compound **24** with labeling scheme (50% probability levels). H atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Au(1)−C(4) 1.95(5), Au(1)−C(1) 1.98(5), Au(1)−Au(2) 3.1244(10), Au(2)−C(7) 1.96(3), Au(2)−C(12) 2.02(2), N(1)−C(1) 1.17(5), N(2)−C(7) 1.15(3), C(4)−C(5) 1.18(6), C(12)−C(13) 1.21(3), C(4)−Au(1)−C(1) 180.00(2), C(7)−Au(2)−C(12) 177.9(10), Au(2)−Au(1)−Au(2′) 116.32(2).

Gold(I) complexes containing alkynyl and isocyanide ligands are of great interest because of their potential applications as advanced materials (luminescent compounds, liquid crystals, NLO, etc.). Compounds of the family of **24** and **25**, $[\mathrm{Au(C{\equiv}CR)(CNR')}]$ (R = Ph, R′ = ^{n}Bu, $\mathrm{C_6H_4Et}$-2, $\mathrm{C_6H_4Me}$-4,[13] $\mathrm{C_6H_3Me_2}$-2,5;[60] R = $\mathrm{C_6H_4(C_mH_{2m+1})}$-4 ($m$ = 6, 8, 10), R′ = $\mathrm{C_6H_4X}$-4 (X = H, $\mathrm{OC_nH_{2n+1}}$ (n = 2, 4, 6, 8, 10));[1] R = ^{t}Bu, R′ = $\mathrm{C_6H_4C{\equiv}CH}$, $\mathrm{C_6H_3(Me\text{-}2)(C{\equiv}CH\text{-}4)}$,[34,38]), or **26**, $[\mathrm{(AuCNR')_2\{\mu\text{-}C{\equiv}C\text{-}R\text{-}C{\equiv}C\}}]$ (R = $\mathrm{C_6H_4}$, $\mathrm{C_6H_4C_6H_4}$, $\mathrm{C_6H_2Me_2}$-2,5, $\mathrm{CH_2OC_6H_4C(Me_2)C_6H_4OCH_2}$, R′ = $\mathrm{C_6H_3Me_2}$-2,6[2]), have been prepared by reacting $[\mathrm{Au(C{\equiv}CR)}]_n$ or $[\mathrm{Au_2\{\mu\text{-}C{\equiv}C\text{-}R\text{-}C{\equiv}C\}}]_n$, respectively, with the corresponding isocyanide. We are not aware of any report of alkynyl(carbene)gold complexes such as **27**−**31**.

Crystal Structures of complexes 6, 14, 15, 17, 19, and 24. The crystal structure of **24** (see Figure 1) has recently been reported by us.[42] It shows a tetranuclear loose cluster formed through a new aurophilic structural motif: a central molecule (based on Au(1)) lying on a crystallographic 3-fold axis, with three others (based on the general Au(2)) connected to it by Au···Au contacts

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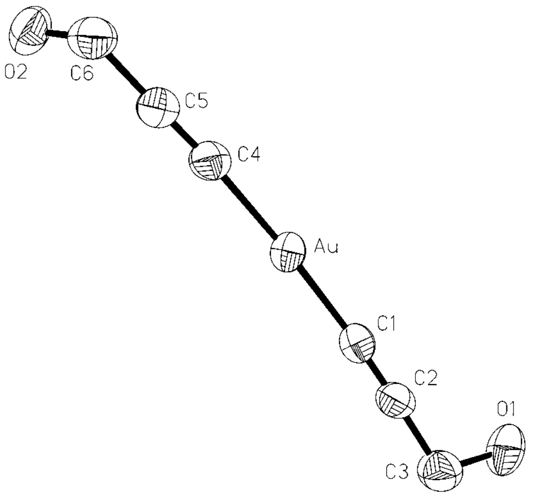

Figure 2. Ellipsoid plot of the anion of compound **6** with labeling scheme (50% probability levels). H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Au−C1 1.994(6), Au−C4 2.006(6), C1−C2 1.202(7), C2−C3 1.471(7), C3−O1 1.397(6), C3−O1′ 1.449(11), C4−C5 1.189(6), C5−C6 1.469(7), C6−O2 1.413(6), C1−Au−C4 176.2(2), C2−C1−Au 174.1(6), C5−C4−Au 176.2(5).

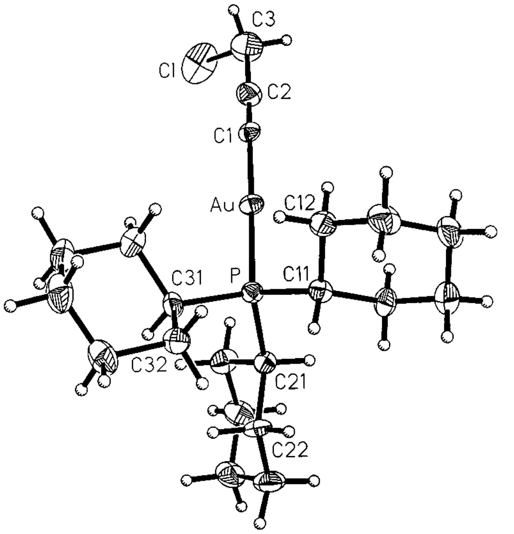

Figure 3. Ellipsoid plot of compound **14** with labeling scheme (50% probability levels). Selected bond lengths (Å) and angles (deg): Au−C1 2.051(6), Au−P 2.292(2), C1−C2 1.150(9), C1−Au−P 178.6(2), C(2)−C(1)−Au 177.8(5).

of 3.1244(10) Å. The central gold atom lies 0.61 Å out of the plane formed by the other three. The repulsion between the bulky $SiMe_3$ and ${}^tBu$ groups is avoided by rotation of the peripheral molecules by 121° (angle between the vectors C1···C4 and C7···C12) with respect to the central one. The isolated “aurophilic three-coordination” found at the central gold atom is unprecedented. In contrast, the crystal structures of **6**, **14**, **15**, **17**, and **19** (see Figures 2−6) show no intermolecular Au···Au interactions. The anionic nature of **6** and the presence of the bulky phosphine ligand PPh_3 and PCy_3 in the other complexes are probably responsible for this. The gold atoms are in essentially linear environments, with CAuC or CAuP angles of 176.2(2)° (**6**), 178.6(2)° (**14**), 179.4(4)° (**15**), 178.20(11)° (**17**), 178.0(2)° (**19**) and 180° (**24**). The AuC and AuP bond distances are in the ranges 1.994(6)−2.080(12) and 2.271(2)−2.292(2) Å, respectively, while the C≡C bond distances, necessarily imprecise, range from 1.10(2) to 1.21(3) Å. All of these

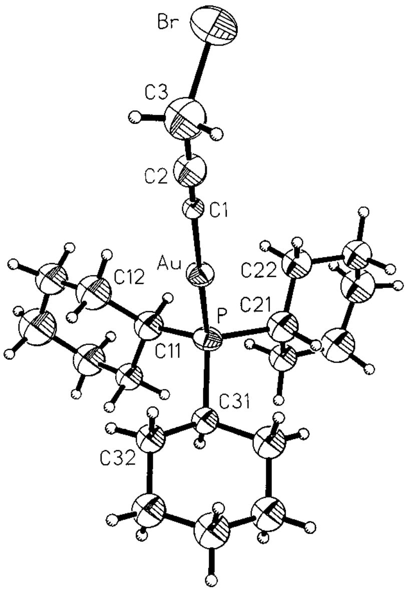

Figure 4. Ellipsoid plot of compound **15** with labeling scheme (50% probability levels). Selected bond lengths (Å) and angles (deg): Au−C1 2.080(12), Au−P 2.285(4), C1−C2 1.10(2), C1−Au−P 179.4(4), C(2)−C(1)−Au 179.1 (13).

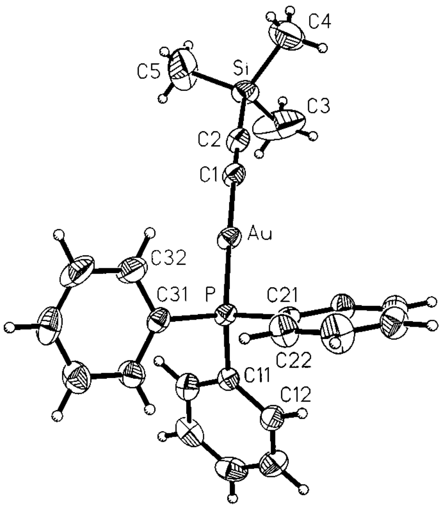

Figure 5. Ellipsoid plot of compound **17** with labeling scheme (50% probability levels). Selected bond lengths (Å) and angles (deg): Au−C1 2.000(4), Au−P 2.2786(10), C1−C2 1.196(5), C2−Si 1.836(4), C1−Au−P 178.20(11), C(2)−C(1)−Au 176.8(4), C1−C2−Si 177.6(4).

parameters are similar to those found for other crystal structures of alkynylgold(I) complexes.[10,11,28,34,61−65]

IR Spectroscopy. The band assignable to the $\nu_{C\equiv C}$ stretching mode appears as a weak (R = H, ${}^tBu$), medium (R = CH_2X, X = Cl, Br, OH), or strong (R = $SiMe_3$) absorption, slightly shifted with respect to that in the corresponding free alkyne. For the same R, the wavenumber of $\nu_{C\equiv C}$ follows the order [Au(C≡CR)(L)] (2132−1932 cm^{-1}) ≥ HC≡CR (R = CH_2Cl (2127 cm^{-1}),

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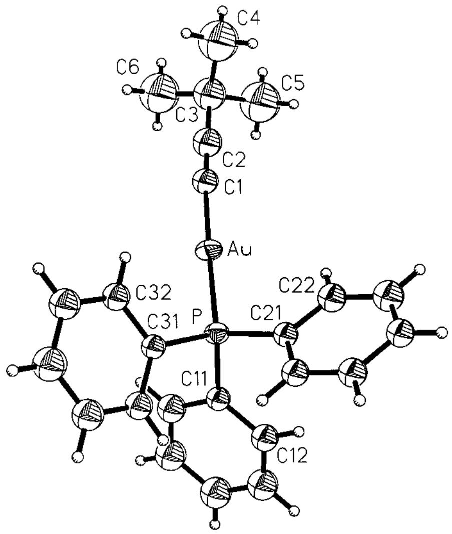

Figure 6. Ellipsoid plot of compound **19** with labeling scheme (50% probability levels). Selected bond lengths (Å) and angles (deg): Au−C1 1.997(8), Au−P 2.271(2), C1−C2 1.187(11), C2−C3 1.509(13), C1−Au−P 178.0(2), C(2)−C(1)−Au 175.0(8), C1−C2−C3 179.3(9).

CH_2OH (2119 cm^{-1}), CH_2Br (2118 cm^{-1}), ^tBu (2109 cm^{-1}), $SiMe_3$ (2036 cm^{-1}), H (1974 cm^{-1}, Raman)) ≥ $[Au(C{\equiv}CR)_2]^-$ (2125−1971 cm^{-1}), except in the case of the neutral complex **31** (R = H and L = $C(NH^tBu)(NEt_2)$) whose value (1932 cm^{-1}) is lower than those of the alkyne (1974 cm^{-1}) and that of the anionic complex **1** (1962 cm^{-1}). When the anionic complexes are ordered according to $\nu_{C\equiv C}$, the same series observed for the free alkynes is obtained ($CH_2X > {}^tBu > SiMe_3 > H$). The same occurs with the neutral complexes. In this case, although the nature of the neutral ligand causes little differences in $\nu_{C\equiv C}$ (2−10 cm^{-1}), the order $^tBuNC > PR_3 > NHEt_2 > C(NH^tBu)(NEt_2)$ is observed. In the anionic ethynyl complexes **1**, and **7**−**9**, $\nu_{C\equiv C}$ decreases in the series Cl (1982 cm^{-1}) ≅ Br (1980 cm^{-1}) > I (1964 cm^{-1}) ≅ $C{\equiv}CH$ (1962 cm^{-1}). A similar result was observed in phenylethynylgold(I) complexes.[52] All of these IR data are difficult to rationalize because $\nu_{C\equiv C}$ depends on the force constants of the ≡C−X bonds, the mass of the substituents, and potential $p\pi{-}d\pi$ bonding.[66,67] The ethynyl complexes **1**, **7**−**9**, **12**, **13,** and **31** show one weak ν_{CH} band in the 3266−3272 region in their IR spectra and a medium band at around 300 cm^{-1} (except **1**) (325 (**7**), 323 (**8, 9**), 298 (**12**), 297 (**13**)) that we tentatively assign to some vibration mode of the Au−C bond. In the case of **7**, this band could also involve ν(Au−Cl). The hydroxypropargyl complexes **6** and **16** show a medium ν_{OH} band at 3416 and 3470 cm^{-1}, respectively, which in the free ligand is at 3444 cm^{-1}. The CN^tBu complexes **24**−**26** show the ν_{CN} band in the 2224−2230 cm^{-1} region, intermediate between that of the free ligand at 2143 cm^{-1} and that of $[AuCl(CN^tBu)]$ at 2252 cm^{-1}, implying that in our complexes the isocyanide ligand acts preferentially as a σ donor.[68] Complexes with diethylamine (**10, 11**) or carbene ligands (**27**−**31**) show the corresponding ν_{NH} bands in the 3154−3156 or 3204−3360 cm^{-1} range, respectively. The carbene complexes also show a strong band in the 1538−1562 cm^{-1} region, assignable to asymmetric stretching of the N−C−N moiety.

NMR Spectroscopy. The electronic effect of the $AuPR_3$ group on the resonance of the acetylenic proton in complexes **12** (1.83 ppm) and **13** (1.81 ppm) is similar to that of H in C_2H_2 (1.80 ppm). Probably, the shielding effect arising from the substitution of the proton by the less electronegative $AuPR_3$ group is compensated by the π-acceptor ability of the $AuPR_3$ group, which reduces the paramagnetic anisotropy of the C≡C bond. The anionic nature of complex **1** is probably responsible for the high-field shift of the proton (1.37 ppm). The δ(H) in the anionic halocomplexes **7**−**9** (1.63−1.65 ppm) and the neutral carbene complex **31** (1.58 ppm) are similar and intermediate between **1** and **12**, **13**.

The ^{13}C resonance corresponding to the carbon bonded to gold (C_α) in RC≡CAuL complexes depends mainly on R, with $\delta(C_\alpha)$ values (in ppm) for Me_3Si (154.48−126.56) > H (142.64−126.3) > ^tBu (120.89) when L is the same ligand. In the anionic complexes the order is $ClCH_2$ (130.68) > $HOCH_2$ (127.29) ≅ H (127.09) > ^tBu (117.35). The influence of L on the shielding of the C_α nucleus is less marked, the order of $\delta(C_\alpha)$ in the ^tBu, Me_3Si, and the dinuclear 1,5-nonadiyndiyl complexes being $PCy_3 > PAr_3 > C(NH^tBu)(NEt_2) > {}^tBuNC > Et_2NH$. In the case of the ethynyl complexes with L = $C(NH^tBu)(NEt_2)$ (**31**) and $P(C_6H_4OMe\text{-}4)_3$ (**13**), the order is reversed. Therefore, it seems that shielding of C_α is greater for a “σ-only” donor ligand such as Et_2NH than for π-acceptor ligands such as PR_3, carbene, and isocyanide, as expected.

The ^{13}C resonance corresponding to the carbon in the β position with respect to gold (C_β) is practically independent of the nature of L in the neutral $Me_3SiC{\equiv}C$ derivatives (110−108), whereas in the case of neutral $^tBuC{\equiv}C$ derivatives, the values of $\delta(C_\beta)$ are in the range 114.5−102.41 for π-acceptor ligands while a high-field shift is found for L = Et_2NH (90.46). In the ethynyl complexes, the values of $\delta(C_\beta)$ follow the order PAr_3 (90) > $C(NH^tBu)(NEt_2)$ (77).

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Supporting Information Available: X-ray crystallographic files, in CIF format, for compounds **6**, **14**, **15**, **17**, and **19** are available on the Internet only. Access information is given on any current masthead page.

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