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(Isocyanoaryl)acetylides as Bridging Ligands in Rigid-Rod Polymers: Mononuclear and Oligonuclear Gold(I) Complexes

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The new ethynylaryl isocyanide ligands $4\text{-}C{\equiv}NC_6H_4C{\equiv}CH$ (**1a**) and $4\text{-}C{\equiv}N\text{-}3\text{-}MeC_6H_3\text{-}C{\equiv}CH$ (**1b**) have been prepared. They react with $[AuCl(SMe_2)]$ and with $[(AuC{\equiv}C\text{-}t\text{-}Bu)_x]$ to give the isocyanide complexes $[ClAu(4\text{-}C{\equiv}NArC{\equiv}CH)]$ (**2a**, Ar = C_6H_4; **2b**, Ar = $3\text{-}MeC_6H_3$) and $[t\text{-}BuC{\equiv}CAu(4\text{-}C{\equiv}NArC{\equiv}CH)]$ (**6a**, Ar = C_6H_4; **6b**, Ar = $3\text{-}MeC_6H_3$), respectively. The complex $[t\text{-}BuC{\equiv}CAuC{\equiv}NXy]$ (Xy = $2,6\text{-}Me_2C_6H_3$) reacts with the acidic alkyne $4\text{-}NO_2\text{-}C_6H_4C{\equiv}CH$ to give $t\text{-}BuC{\equiv}CH$ and $[4\text{-}NO_2C_6H_4C{\equiv}CAuC{\equiv}NXy]$. A similar reaction uses the more acidic alkyne in **6** to displace $t\text{-}BuC{\equiv}CH$ from **6** and so give the linear rigid-rod oligomers $[t\text{-}BuC{\equiv}C(AuC{\equiv}NArC{\equiv}C\text{-})_xH]$ (**7a**, Ar = C_6H_4; **7b**, Ar = $3\text{-}MeC_6H_3$). The complexes **2a** and **6b** have been characterized by X-ray structure determinations (**2a**, monoclinic, $P2_1/m$, a = 10.042(2) Å, b = 7.067(2) Å, c = 6.596(1) Å, β = 98.79(2)°, V = 462.6(1) Å^3, Z = 2, R = 0.0427, R_w = 0.0402; **6b**, monoclinic, $P2_1/n$, a = 14.225(4), b = 16.196(4), c = 6.747(2) Å, β = 93.86(3)°, V = 1551.0(8) Å^3, Z = 4, R = 0.0332, R_w = 0.0396), while the oligomers **7** have been characterized by elemental analysis and by comparison of the IR and XPS parameters with those of the model compounds **6**.

Introduction

There has been great interest in linear-chain metal-containing polymers with extended backbone conjugation through $d\pi\text{-}p\pi$ hybridization. These polymers exhibit interesting properties, with potential applications as advanced materials.[1] In particular, polymeric species of the type $[ML_n(\text{-}C{\equiv}CRC{\equiv}C\text{-})]_x$ (ML_n = d^6–d^8 metal fragments; R = aromatic rings, disilanes, disiloxanes) are attracting increasing attention because of their electrical conducting, nonlinear optical, and liquid crystalline properties.[2–7] Recently, polymers of the type $[ML_n(\mu\text{-}Ar\text{-})]_x$, in which metal centers are connected by bridging aromatic rings, have also been reported.[8] One- and two-dimensional polymers with diisocyanoarenes linking metal centers have been synthesized.[9,10] It is interesting to note that polymers of the type $[PcM(CNArNC)]_x$ (Pc = phthalocyanine, M = Fe, Ru) display semiconducting properties.[1,10]

The use of ligands with one σ and one coordinate bond to the metal centers in the backbone of polymers has received little attention, especially for organometallic polymers.[1c,11] In this context, we wish to report a synthetic route to the novel ethynylaryl isocyanides $HC{\equiv}CArN{\equiv}C$ and a study of their use in the synthesis of metal-containing oligomers, with backbone conjugation through $d\pi\text{-}p\pi$ hybridization. It is noted that the thermally unstable molecule ethynyl isocyanide, $HC{\equiv}CN{\equiv}C$, has recently been isolated and characterized.[12]

Gold(I) was chosen as the metal center, since it tends to form simple two-coordinated linear complexes[13] and

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because gold alkynyl complexes of formula Au(C$\equiv$CR)(L) (L = phosphine, arsine, stibine, isocyanide, amine) are among the most stable organogold complexes and are known to have linear geometry.[14–17] Examples of gold complexes with bidentate ligands containing both a two-electron and one-electron donor are the interesting cyclic (binuclear or trinuclear) derivatives prepared from pyrazoles, 2-pyridyllithium, imidazoles, ortho-metalated arylphosphines, or isocyanide precursors.[13,18] The extension to the synthesis of polymers appears simply to require a similar ligand with linear coordination; a 4-isocyano-1-ethynylarene is an obvious candidate. Hence, rigid-rod gold-containing polymers of the type [(AuCNC$_6$H$_4$C$\equiv$C)$_x$] and related derivatives, in which gold(I) centers are bridged by novel (isocyanoaryl)acetylide ligands, were considered a logical target. A preliminary report of this work has been communicated.[19]

Experimental Section

All chemicals were used as purchased from Aldrich Chemical Co., unless otherwise stated. The reagents [AuCl(SMe$_2$)],[20] [AuC$\equiv$C-*t*-Bu],[21] *p*-HC$\equiv$CC$_6$H$_4$NH$_2$,[22] *p*-HC$\equiv$CC$_6$H$_4$NO$_2$,[22] and [PdCl$_2$(PhCN)$_2$][23] were prepared by literature methods.

NMR spectra were recorded by using a Varian Gemini 200 spectrometer. ^{1}H NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. IR spectra were recorded by using a Bruker IFS32 spectrometer with Nujol mulls. Differential scanning calorimetry (DSC) analyses were carried out by using a Du Pont 9900 DSC thermal analyzer.

4-HC$\equiv$CC$_6$H$_4$NC (1a). A mixture of 4-HC$\equiv$CC$_6$H$_4$NH$_2$ (1.50 g, 12.8 mmol), CHCl$_3$ (1.60 g, 13.4 mmol), and [Et$_3$NCH$_2$Ph]Cl (0.40 g) in dichloromethane (20 mL) was slowly added to a solution of KOH (20 g) in water (20 mL). The mixture was stirred at room temperature for 3 h, and the dichloromethane was then removed with a rotary evaporator. The reaction mixture was extracted with ether to give a light yellow solution, and the solvent was then removed again using a rotary evaporator to give a pale yellow solid. Sublimation produced 0.92 g (57%) of a white needlelike solid. NMR (CDCl$_3$): δ(^{1}H) 3.18 (s, 1H, C$\equiv$CH), 7.31 (d, J = 8.6 Hz, 2H, Ar H), 7.49 (d, J = 8.6 Hz, 2H, Ar H); δ(^{13}C) 80.0, 81.8, 123.5, 126.4, 133.1, 166.0. IR (Nujol): 2120 [s, ν(N$\equiv$C)], 3305 [m, ν(C$\equiv$CH)] cm^{-1}. Anal. Calcd for C$_9$H$_5$N: C, 85.02; H, 3.96. Found: C, 84.56; H, 4.26.

4-HC$\equiv$C-2-MeC$_6$H$_3$NH$_2$. A mixture of 4-I-2-MeC$_6$H$_3$NH$_2$ (5.0 g, 0.022 mol), HC$\equiv$CCMe$_2$OH (1.90 g, 0.023 mol), [PdCl$_2$(PhCN)$_2$] (0.10 g), PPh$_3$ (0.14 g), and CuI (0.05 g) in diethylamine (70 mL) was stirred at room temperature for 2 days. The solvent was then removed completely using a rotary evaporator, and water (5 mL) was added to the reaction mixture. The resulting mixture was extracted with ether, and the ether layer was passed through a column of neutral alumina. The ether was removed again to give a deep orange oil. Spectroscopic data for the oil are consistent with the composition 4-(HOCMe$_2$C$\equiv$C)-2-MeC$_6$H$_3$NH$_2$. NMR (CDCl$_3$): δ(^{1}H) 1.54 (s, 6H, CMe$_2$), 2.04 (s, 3H, ArMe) 3.1 (br, 1H, OH), 3.76 (br, 2H, NH$_2$), 6.61 (d, J = 7.9 Hz, 1H, Ar H), 7.01–7.06 (m, 2H, Ar H); δ(^{13}C) 18.0, 32.6, 83.6, 92.6, 112.9, 115.6, 123.0, 131.5, 134.7, 145.8. IR: 2215 [s, ν(C$\equiv$C)], 3248, 3366, 3438 [m, ν(OH and NH)] cm^{-1}. The oily compound was redissolved in toluene (80 mL). To the solution was added KOH (1.4 g, 25 mmol), and the resulting mixture was refluxed overnight. Some black insoluble material was then removed by filtration to give an orange solution. The solvent was removed using a rotary evaporator to give an orange oily residue. Sublimation yielded 2.1 g (74%) of colorless crystals. NMR (CDCl$_3$): δ(^{1}H) 2.10 (s, 3H, Me), 2.95 (s, 1H, C$\equiv$CH), 3.75 (br, 2H, NH$_2$), 6.55 (d, J = 8.6 Hz, 1H, Ar H), 7.15–7.19 (m, 2H, Ar H); δ(^{13}C) 17.2, 74.8, 84.9, 83.6, 111.0, 114.5, 122.3, 131.3, 134.4, 146.2. IR (Nujol): 2099 [s, ν(C$\equiv$C)], 3314 [m, ν(C$\equiv$CH)], 3490–3212 [w, ν(NH)] cm^{-1}. Anal. Calcd for C$_9$H$_9$N: C, 82.41; H, 6.92. Found: C, 82.48; H, 7.13.

4-HC$\equiv$C-2-MeC$_6$H$_3$NC (1b). A mixture of 4-HC$\equiv$C-2-MeC$_6$H$_3$NH$_2$ (0.50 g, 3.8 mmol), CHCl$_3$ (0.45 g, 4.0 mmol), and [Et$_3$NCH$_2$Ph]Cl (0.12 g) in dichloromethane (10 mL) was slowly added to a solution of KOH (6 g) in water (6 mL). The mixture was stirred at room temperature for 3 h, and then the dichloromethane was removed with a rotary evaporator. The reaction mixture was extracted with ether to give a light yellow solution, and the solvent was then removed again with a rotary evaporator to give a pale yellow solid. Sublimation produced 0.32 g (59%) of white needlelike solid. NMR (CDCl$_3$): δ(^{1}H) 2.39 (s, 3H, Me), 3.15 (s, 1H, C$\equiv$CH), 7.24–7.39 (m, 3H, Ar H); δ(^{13}C) 18.4, 79.4, 82.1, 123.2, 126.4, 130.3, 134.0, 135.0, 166.0. IR (Nujol): 2114 [m, ν(N$\equiv$C)], 3235 [m, ν(CCH)] cm^{-1}. Anal. Calcd for C$_{10}$H$_7$N: C, 85.08; H, 5.00. Found: C, 84.72; H, 5.22.

[AuCl(4-CNC$_6$H$_4$C$\equiv$CH)] (2a). A mixture of [AuCl(SMe$_2$)] (0.10 g, 0.34 mmol) and 4-CNC$_6$H$_4$C$\equiv$CH (43 mg, 0.34 mmol) in dichloromethane (15 mL) was stirred at room temperature for 15 min. To the reaction mixture was then added hexane (15 mL) to give a white precipitate. The precipitate was collected by filtration, washed with hexane, and dried. Yield: 105 mg, 86%. The isolated solid has low solubility in halogenated solvents. Suitable crystals were produced by layering a CH$_2$Cl$_2$ solution of 4-CNC$_6$H$_4$C$\equiv$CH over a CH$_2$Cl$_2$ solution of [AuCl(SMe$_2$)] followed by slow diffusion. NMR (CDCl$_3$): δ(^{1}H) 3.31 (s, 1H, C$\equiv$CH), 7.48 (d, J = 8.8 Hz, 2H, Ar H), 7.60 (d, J = 8.8 Hz, 2H, Ar H). IR (Nujol): 2234 [s, ν(N$\equiv$C)], 3279 [m, ν(C$\equiv$CH)] cm^{-1}. Anal. Calcd for C$_9$H$_5$AuClN: C: 30.06; H, 1.40. Found: C, 29.87; H, 1.37.

[AuCl(4-CN-3-MeC$_6$H$_3$C$\equiv$CH)] (2b). A mixture of [AuCl(SMe$_2$)] (0.20 g, 0.68 mmol) and 4-CN-3-MeC$_6$H$_3$C$\equiv$CH (0.10 g, 0.71 mmol) in dichloromethane (10 mL) was set aside. The solvent evaporated at room temperature in air over a period of 2 days to give a pale yellow crystalline solid, which was washed with hexane, collected by filtration, and dried to give 0.24 g (94%) of light yellow microcrystals. NMR (CDCl$_3$): δ(^{1}H) 2.43 (s, 3H, Me), 3.26 (s, 1H, C$\equiv$CH), 7.40–7.47 (m, 3H, Ar H). IR (Nujol): 2216 [s, ν(N$\equiv$C)], 3260 [m, ν(C$\equiv$CH)] cm^{-1}. Anal. Calcd for C$_{10}$H$_7$AuClN: C, 32.16; H, 1.89. Found: C, 32.53; H, 1.70.

[(AuC$\equiv$CC$_6$H$_4$-4-NO$_2$)$_x$] (3). A mixture of 4-HC$\equiv$CC$_6$H$_4$NO$_2$ (0.150 g, 1.02 mmol), NaO$_2$CMe (0.30 g, 3.7 mmol), and [AuCl(SMe$_2$)] (0.30 g, 1.0 mol) in the mixed solvent THF (60 mL)/MeOH (30 mL) was stirred at room temperature for 2 h to give a white precipitate. The solid was then collected by filtration, washed with MeOH, water, MeOH, and ether, and dried. Yield: 0.15 g, 43%. The solid is insoluble in common organic solvents. IR (Nujol): 2016 [m, ν(C$\equiv$C)] cm^{-1}. Anal. Calcd for C$_8$H$_4$AuN$_2$: C, 28.01; H, 1.18. Found: C, 27.99; H, 1.08.

[*t*-BuC$\equiv$CAuCNC$_6$H$_3$-2,6-Me$_2$] (4). A mixture of *t*-BuC$\equiv$CAu (0.10 g, 0.36 mmol) and CNC$_6$H$_3$-2,6-Me$_2$ (50 mg, 0.38 mmol) in dichloromethane (10 mL) was stirred for 30 min. The solvent was then removed completely, and the residue was washed with hexane to give a white solid. The solid was collected by filtration, washed with hexane, and dried. Yield: 0.11 g, 75%. The

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compound is partially soluble in hexane. NMR ($CDCl_3$): $\delta(^1H)$ 1.28 (s, 9H, Bu), 2.37 (s, 6H, Me), 7.10–7.30 (m, 3H, Ar H). IR (Nujol): 2193 [s, $\nu(N{\equiv}C)$] cm^{-1}. Anal. Calcd for $C_{15}H_{18}AuN$: C, 44.02; H, 4.43. Found: C, 44.36; H, 4.37.

[(2,6-$Me_2C_6H_3NC$)$AuC{\equiv}CC_6H_4$-4-NO_2] (5). A mixture of $AuC{\equiv}CC_6H_4$-4-NO_2 (0.20 g, 0.58 mmol) and CNC_6H_3-2,6-Me_2 (0.10 g, 0.76 mmol) in dichloromethane (30 mL) was stirred for 1 h. The insoluble material was removed by filtration. CH_2Cl_2 was then removed completely, and the residue was washed with hexane to give a yellowish solid. The solid was collected by filtration, washed with hexane, and dried. Yield: 0.24 g, 87%. NMR ($CDCl_3$): $\delta(^1H)$ 2.43 (s, 6H, Me), 7.15 (d, J = 7.4 Hz, 2H, Ar H), 7.33 (dd, J = 8.6, 6.8 Hz, 1H, Ar H), 7.54 (d, J = 9.0 Hz, 2H, Ar H), 8.10 (d, J = 9.0 Hz, 2H, Ar H). IR (Nujol): 2199 [s, $\nu(N{\equiv}C)$], 2120 [m, $\nu(C{\equiv}C)$] cm^{-1}. Anal. Calcd for $C_{17}H_{13}AuN_2O_2$: C, 43.05; H, 2.76. Found: C, 43.12; H, 2.83.

[t-$BuC{\equiv}CAu$(4-$CNC_6H_4C{\equiv}CH$)] (6a). A mixture of t-$BuC{\equiv}CAu$ (0.10 g, 0.36 mmol) and CNC_6H_4-4-$C{\equiv}CH$ (0.046 g, 0.36 mmol) in dichloromethane (15 mL) was stirred for 30 min. The solvent was then removed completely, and the residue was washed with hexane to give a white solid. The solid was collected by filtration, washed with hexane, and dried. Yield: 110 mg, 75%. NMR ($CDCl_3$): $\delta(^1H)$ 1.28 (s, 9H, Bu), 3.30 (s, 1H, $C{\equiv}CH$), 7.44 (d, J = 8.8 Hz, 2H, Ar H), 7.57 (d, J = 8.8 Hz, 2H, Ar H). IR (Nujol): 3295 [s, ν(CH)], 2215 (s), 2114 (sh) [$\nu(N{\equiv}C)$], 2042 [br, w, $\nu(C{\equiv}C)$] cm^{-1}. Anal. Calcd for $C_{15}H_{14}AuN$: C, 44.46; H, 3.48. Found: C, 44.16; H, 3.41.

[t-$BuC{\equiv}CAu$(4-CN-3-$MeC_6H_3C{\equiv}CH$)] (6b). A mixture of t-$BuC{\equiv}CAu$ (0.19 g, 0.68 mmol) and 4-CN-3-$MeC_6H_3C{\equiv}CH$ (0.10 g, 0.71 mmol) in dichloromethane (5 mL) was stirred for 30 min. The solvent was then removed completely, and the residue was washed with hexane to give a white solid. The solid was collected by filtration, washed with hexane, and dried. Yield: 0.25 g, 88%. X-ray-quality crystals were produced by slow evaporation of solvents from a saturated solution of the compound in CH_2Cl_2/hexane at ca. 0 °C. NMR ($CDCl_3$): $\delta(^1H)$ 1.27 (s, 9H, Bu), 2.37 (s, 3H, Me), 3.24 (s, 1H, $C{\equiv}CH$), 7.42 (br, 2H, Ar H), 7.42 (br, 1H, Ar H). IR (Nujol): 3227 [m, ν(CCH)], 2201 [s, $\nu(N{\equiv}C)$], 2105, 2030 [br, w, $\nu(C{\equiv}C)$] cm^{-1}. Anal. Calcd for $C_{16}H_{16}AuN$: C, 45.84; H, 3.85. Found: C, 45.52; H, 3.73.

[t-$BuC{\equiv}C$($AuCNC_6H_4$-4-$C{\equiv}C$)$_x$H] (7a). A solution of t-$BuC{\equiv}CAu$(CNC_6H_4-4-$C{\equiv}CH$) (0.050 g, 0.12 mmol) in benzene (5 mL) was heated at 80 °C for 5 h to give a brown precipitate. The brown solid was then collected by filtration, washed with benzene and ether, and dried to give 30 mg of brown solid. The solid is insoluble in common organic solvents. IR (Nujol): 3295 [vw, ν(CCH)], 2209 [s, $\nu(N{\equiv}C)$], 2120, 2034 [br, w, $\nu(C{\equiv}C)$] cm^{-1}. Anal. Calcd for t-$BuC{\equiv}C$($AuCNC_6H_4C{\equiv}C$)$_{3.4}$H: C: 37.23; H, 2.01. Found: C, 36.91; H, 2.16.

[t-$BuC{\equiv}C$(Au-4-CN-3-$MeC_6H_3C{\equiv}C$)$_x$H] (7b). A solution of [t-$BuC{\equiv}CAu$-4-CN-3-$MeC_6H_3C{\equiv}CH$] (0.10 g, 0.24 mmol) in benzene (10 mL) was refluxed overnight (ca. 10 h) to give a brown powder. The powder was collected by filtration, washed with benzene and ether, and dried to give 50 mg of brown solid. The solid is insoluble in common organic solvents. IR (Nujol): 3300 [vw, ν(CCH)], 2205 [s, $\nu(N{\equiv}C)$], 2118 [sh, $\nu(C{\equiv}C)$] cm^{-1}. Anal. Calcd for [t-$BuC{\equiv}C$(Au-4-CN-3-$MeC_6H_3C{\equiv}C$)$_{5.0}$H]: C, 38.04; H, 2.27. Found: C, 37.86; H, 2.74.

X-ray Structure Determinations for [AuCl(4-$C{\equiv}NC_6H_4C{\equiv}CH$)] and [$t$-$BuC{\equiv}CAu$-4-CN-3-$MeC_6H_3C{\equiv}CH$]. Compounds **2a** and **6b** were examined by similar experimental procedures. An overview is given below, followed by details specific to each analysis. Crystallographic data are summarized in Table I.

Crystal densities were determined by the neutral buoyancy method in mixtures of bromoform and 1,2-dibromoethane for **2a** and 1,2-dibromoethane and carbon tetrachloride for **6b**. All diffraction measurements were carried out on an Enraf-Nonius CAD4F diffractometer at ambient temperatures (295 K) using incident-beam monochromated Mo Kα radiation. Photo and automatic indexing routines, followed by least-squares fits (of 21 reflections ($13.6 \le \theta \le 19.5°$) for **2a** and 22 reflections ($12.0 \le \theta \le 13.8°$) for **6b**), gave cell constants and orientation matrices.[24] Intensity data were recorded in the θ–2θ scan mode at variable scan speeds (1.5–3.3 deg min^{-1} for **2a** and 1.0–4.1 deg min^{-1} for **6b**), so chosen as to optimize counting statistics within a maximum time per data point of 60 s. Background estimates were made by extending the scan by 25% on each side for **2a**, whereas static background measurements were made at the end points of the width 0.9 + 0.35 tan θ for **6b**. Three standard reflections were monitored every 120 min of X-ray exposure time. No significant decay was observed for both **2a** and **6b**. Lorentz, polarization, and background radiation corrections were applied using the Structure Determination Package running on a PDP11/23+ computer.[25] Both structures were solved and partially refined using the NRCVAX crystal structure programs running on a SUN3/80 workstation.[26] Absorption corrections were then applied to the data using the program AGNOST[27] for **2a** and ABSCOR[28] for **6b**. p values of 0.05 for **2a** and 0.06 for **6b** were applied to the data.[29] The final full-matrix least-squares refinements on F were done using the SHELX76 software[30] running on the SUN3/80 workstation with absorption-corrected data. Scattering factors for neutral non-hydrogen atoms were taken from ref 31a. All the hydrogen atoms were located successfully by difference Fourier methods and were placed in calculated positions (C–H = 0.90 H Å); they were included for the structure factor calculations only.

Table I. Crystallographic Data and Summary of X-ray Structure Determination for 2a and 6b

	2a	**6b**
compd, fw	C_9H_5AuClN, 359.57	$C_{16}H_{16}NAu$, 419.28
cryst syst, space gp	monoclinic, $P2_1/m$	monoclinic, $P2_1/n$
cell dimens		
a (Å)	10.042(2)	14.225(4)
b (Å)	7.067(2)	16.196(4)
c (Å)	6.596(1)	6.747(2)
β (deg)	98.79(2)	93.86(3)
cell vol (Å^3), Z	462.6(1), 2	1551.0(8), 4
obsd, calcd density (g cm^{-3})	2.58(2), 2.581	1.80(3), 1.795
F(000)	323.9	791.8
radiation, wavelength (Å)	Mo Kα, 0.710 73	Mo Kα, 0.710 73
abs coeff (cm^{-1})	161.2	91.0
R, R_w	0.0427, 0.0402	0.0332, 0.0396

Complex 2a. A light yellow crystal of suitable quality was mounted in air on a glass fiber with epoxy cement. For a primitive cell, the systematic absences ($0k0$, $k \ne 2n$) suggest[31b] two possible space groups, $P2_1$ (No. 4) and $P2_1/m$ (No. 11). With Z = 2, the space group $P2_1$ was tried first and the structure was solved using the NRCVAX package[26] and refined to R_F = 0.045 and R_w = 0.032. At this stage the bond angles and the esd's were abnormal. The program MISSYM[32] suggested an extra mirror plane in the molecule. Therefore, the structure was again solved in the space group $P2_1/m$ and successfully refined. The final full-matrix least-squares refinements were done using the SHELX76 software with absorption-corrected data. With the use of 1035 observations having $I \ge 3\sigma(I)$, and weights of the form $w = k/\sigma^2(F_o) + gF^2$ where g = 0.0001, refinement of 71 variables converged at agreement factors R = 0.0427 and R_w = 0.0402. The top six

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Table II. Atomic Positional ($\times 10^4$) and Thermal ($\times 10^3$) Parameters for 2a

atom	x	y	z	U_{eq} (Å^2)[a]
Au	4695.7(5)	2500	–4818.9(7)	53.0(2)
Cl	3389(4)	2500	–7919(5)	72(1)
C(1)	5771(14)	2500	–2148(20)	57(4)
N(1)	6389(1)	2500	–516(15)	58(3)
C(2)	7116(12)	2500	1430(17)	49(3)
C(3)	7477(9)	4183(13)	2394(12)	59(2)
C(4)	8209(9)	4180(14)	4322(13)	60(2)
C(5)	8556(13)	2500	5315(17)	53(3)
C(6)	9343(14)	2500	7376(18)	60(4)
C(7)	9967(17)	2500	9022(19)	79(5)

[a] The isotropic equivalent displacement parameter is defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j a_i \cdot a_j$.

Table III. Atomic Positional ($\times 10^4$) and Thermal ($\times 10^3$) Parameters for 6b

atom	x	y	z	U_{eq} (Å^2)[a]
Au	1081.6(3)	4495.2(2)	178.8(6)	47.3(1)
N	–209(6)	3238(5)	–2175(13)	51(2)
C(1)	248(7)	3692(6)	–1185(15)	54(2)
C(2)	–722(4)	2805(4)	–3598(8)	44(2)
C(3)	–1005(4)	2003(4)	–3196(8)	56(3)
C(4)	–1493(4)	1540(4)	–4669(8)	60(3)
C(5)	–1699(4)	1880(4)	–6542(8)	50(2)
C(6)	–1417(4)	2682(4)	–6944(8)	52(2)
C(7)	–928(4)	3145(4)	–5471(8)	50(2)
C(8)	–2139(9)	1374(8)	–8111(18)	68(4)*
C(9)	–2507(11)	986(9)	–9375(20)	86(5)*
C(10)	–644(10)	4033(7)	–5849(17)	71(4)*
C(11)	2025(7)	5262(6)	1348(15)	49(2)
C(12)	2670(8)	5693(6)	1970(16)	56(3)
C(13)	3520(9)	6147(8)	2659(18)	67(3)
C(14)	4399(11)	5670(11)	2380(42)	151(10)*
C(15)	3519(13)	6388(16)	4823(29)	165(10)*
C(16)	3549(15)	6940(12)	1698(48)	206(13)*

[a] Parameters marked with an asterisk were assigned anisotropic thermal parameters, given as the isotropic equivalent displacement parameter defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij}a^*_i a^*_j a_i \cdot a_j$.

peaks in the final difference Fourier synthesis had electron density in the range 2.31–0.80 e Å^{-3}; of these, the top three and the sixth peak were associated with the gold atom at distances of 0.11–0.89 Å. The other two were found near the chlorine atom (0.43 and 1.0 Å).

Complex 6b. The systematic absences ($h0l$, $h + l \neq 2n$; $0k0$, $k \neq 2n$) suggested the space group $P2_1/n$, and the correctness of the choice of the space group was confirmed by the successful refinement of the structure. In the final cycle two bad reflections (–9,7,6 and 15,1,3) were omitted and the refinements converged at R = 0.0332 and R_w = 0.0396 for 1821 ($I \geq 3\sigma(I)$) observations and 98 variables. In the final difference Fourier synthesis, there were four peaks with electron density in the range 0.804–0.518 e Å^{-3}. Of these, two were associated with the Au atom at distances of 1.00 and 2.03 Å and the other two were around C(13) and C(12) at distances of 0.60 and 0.65 Å, respectively. The positional and U(equiv) thermal parameters for **2a** and **6b** are given in Tables II and III.

Results and Discussion

Synthesis of Ligands. The route for synthesis of ethynylaryl isocyanides is shown in Scheme I. The (aminoaryl)alkynols were produced by condensation of aminoaryl iodide with 2-methylbut-3-yn-2-ol as the protected acetylene in diethylamine in the presence of CuI and [PdCl$_2$(PPh$_3$)$_2$]. The protecting group was then removed as acetone by treatment with KOH in refluxing toluene. Such a procedure has been previously applied in the synthesis of ethynyl-*N*-heteroarenes.[33] The isocyanides were prepared by the phase-transfer Hofmann carbylamine reaction[34] and could be purified easily by sublimation. Attempts to prepare corresponding formamides from the reaction of NH$_2$ArC≡CH with HCO$_2$H or HCO$_2$Et failed since the reaction produced a complex mixture. Synthesis of the isocyanides by dehydration methods[35] is therefore not feasible.

The new isocyanides are colorless solid compounds which are soluble in common organic solvents. The compounds appear to be unstable when stored at room temperature for a long period of time, as indicated by a color change from colorless to light yellow, most likely due to thermally induced polymerization of the N≡C group.[36] Thus, the isocyanides should be stored cold. The new compounds are readily characterized by spectroscopic (IR, ^{1}H and ^{13}C NMR) data, as reported in the Experimental Section.

Gold(I) Chloride Complexes and Attempts To Convert Them to Gold-Containing Polymers. Monomeric gold alkynyl complexes [RC≡CAuL] can be prepared by either the reactions of [AuX(L)] with organolithium or Grignard reagents (eq 1)[37] or addition of L to polymeric [(AuC≡CR)$_x$] (eq 2).[21] The phosphine complexes [Au(C≡CR′)(PR$_3$)] could also be conveniently prepared by the reaction of [AuCl(PR$_3$)] with R′C≡CH in the presence of strong bases (eq 3).[15,38] The gold complexes [(AuC≡CR)$_x$] could be prepared by the reaction of Au(I) halide with RC≡CH in the presence of the weak base sodium acetate.[21]

$$\mathrm{X{-}Au{-}L + RC{\equiv}CM \rightarrow RC{\equiv}C{-}Au{-}L + MX} \quad (1)$$

$$\mathrm{(Au{-}C{\equiv}CR)X + L \rightarrow RC{\equiv}C{-}Au{-}L + MX} \quad (2)$$

$$\mathrm{Cl{-}Au{-}PR_3 + HC{\equiv}CR' + B \rightarrow R'C{\equiv}C{-}Au{-}PR_3 + BH^+Cl^-} \quad (3)$$

We therefore attempted to prepare the target polymeric compounds by treatment of gold(I) isocyanide complexes [ClAuCNArC≡CH] with appropriate bases. The complexes [AuCl(CNArC≡CH)] (Ar = C$_6$H$_4$, C$_6$H$_3$Me) are produced from the rapid, quantitative reaction of 1 equiv of [AuCl(SMe$_2$)] with CNArC≡CH (eq 4).

The pale yellow isocyanide complexes were characterized by elemental analysis and ^{1}H NMR and IR spectroscopy. The ^{1}H NMR spectra of [AuCl(C≡NArC≡CH)] display characteristic resonances for the terminal C≡CH (at 3.31 ppm for Ar = C$_6$H$_4$ and 3.26 ppm for Ar = C$_6$H$_3$Me) and for other protons of the ligands. In the IR spectra, strong bands due to ν(N≡C) were observed at 2234 cm^{-1} for the phenyl isocyanide complex and at 2216 cm^{-1} for the tolyl isocyanide complex. For comparison the CN stretching frequencies are at 2120 cm^{-1} for the phenyl isocyanide and at 2115 cm^{-1} for the tolyl isocyanide. The increase (ca. 100 cm^{-1}) in the CN stretching frequency of coordinated isocyanide is well documented and is partly attributed to the σ donation of the antibonding carbon lone pair (in the

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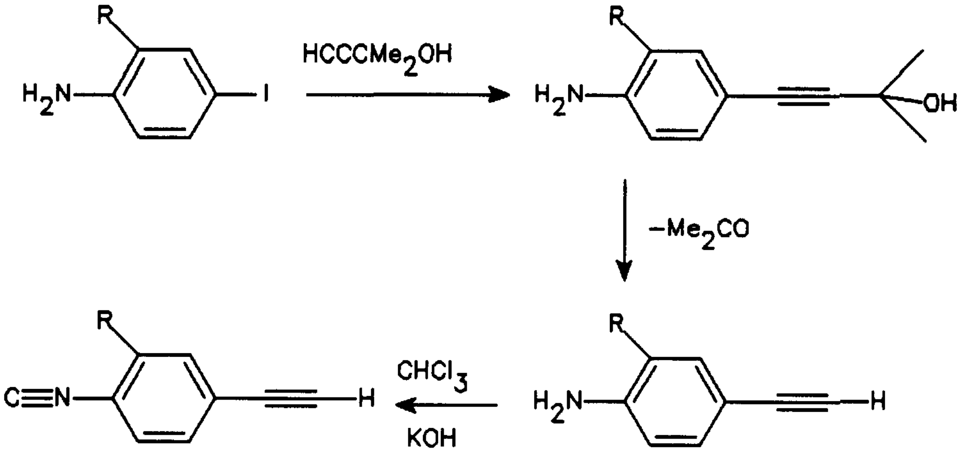
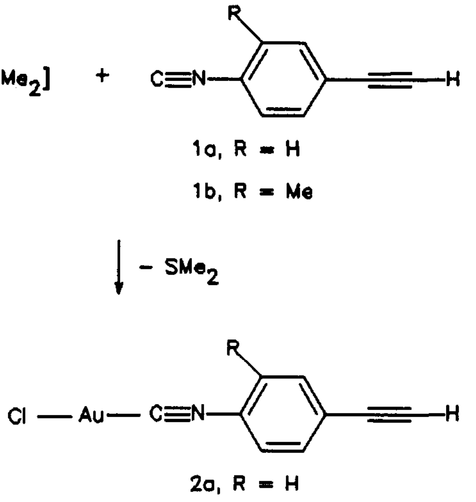
Scheme I



1a, R = H
1b, R = Me



(4)

2a, R = H
2b, R = Me

$7a_1$ orbital) to Au upon complexation.[39] The ν(CCH) bands were observed at 3279 cm^{-1} for Ar = C_6H_4 and 3260 cm^{-1} for Ar = C_6H_3Me. An X-ray structure determination on [AuCl(CNC_6H_4C≡CH)] confirmed that the complex has a linear geometry, as expected (see below).

Unfortunately, attempts to obtain polymers by treatment of [AuCl(C≡NArC≡CH)], or an equimolar mixture of [AuCl(SMe$_2$)] and C≡NArC≡CH, with various bases were unsuccessful. Decomposition occurred when strong bases such as NaOMe, LiBu, LiMe, LiN(CHMe$_2$)$_2$, and Na were used, apparently because the bases attacked the coordinated isocyanides and destroyed the complexes. Reactions of isocyanides coordinated to gold have been noted previously.[13,40] Surprisingly, no reaction occurred when a mixture of [AuCl(C≡NArC≡CH)] and excess Proton Sponge, which is a strong base (pK_a = 12.3)[41] and has been used to remove protons from metal hydride complexes,[42] was refluxed in tetrahydrofuran. It has been reported previously that even weak bases such as sodium acetate[21] are effective in the formation of gold acetylide complexes.

Preparation of Complexes [*t*-BuC≡CAu(CNArC≡CH)] and Their Use in the Synthesis of Polymers. It is known that a displacement reaction takes place readily when RH is more acidic than R′H (eq 5). With

$$\text{R—H} + \text{R}'\text{—Au—L} \rightarrow \text{R}'\text{—H} + \text{R—Au—L} \quad (5)$$

this process, for example, several gold complexes have been prepared by the reaction of [QAuL] (Q = imidazole) or [Q′(AuL)$_2$] (Q′ = pyrazolone, L = tertiary phosphines) with some acidic reagents HZ, where HZ = terminal acetylene, imide, thiol, and dithio acid.[43] Similarly, methane and gold acetylide complexes were produced from the reaction of terminal acetylenes with methylgold complexes, as exemplified in eq 6.[44]

$$\begin{aligned}&\text{AuMe(PMe}_2\text{Ph)} + \text{CF}_3\text{C}{\equiv}\text{CH} \rightarrow \\ &\qquad\qquad \text{Au(C}{\equiv}\text{CCF}_3\text{)(PMe}_2\text{Ph)} + \text{CH}_4 \quad (6)\end{aligned}$$

The complex acetylene [*t*-BuC≡CAu(CNArC≡CH)] should be more acidic than *t*-BuC≡CH (the 4-isocyanoaryl substituent is more electron withdrawing than *t*-Bu, and the coordination of the isocyanide substituent to gold(I) will enhance the acidity); therefore, it should eliminate *t*-BuC≡CH with the formation of the desired polymer. To test the feasibility of this proposed polymerization process, the compounds [*t*-BuC≡CAuCNXy] (Xy = *o*-xylyl) and [4-NO$_2$C$_6$H$_4$C≡CAuCNXy] were prepared by reactions of C≡NXy with [(*t*-BuC≡CAu)$_x$] and [(4-NO$_2$C$_6$H$_4$C≡CAu)$_x$] and were characterized by elemental analysis and ^{1}H NMR and IR spectroscopy (see Experimental Section for details). Reaction of [*t*-BuC≡CAuCNXy] and 4-NO$_2$C$_6$H$_4$C≡CH was then carried out and was shown to occur quantitatively to give [4-NO$_2$C$_6$H$_4$-C≡CAuC≡NXy] and *t*-BuC≡CH, as monitored by ^{1}H NMR (eq 7). It is interesting to note that no reaction is observed under similar conditions if [*t*-BuC≡CAuCNXy]

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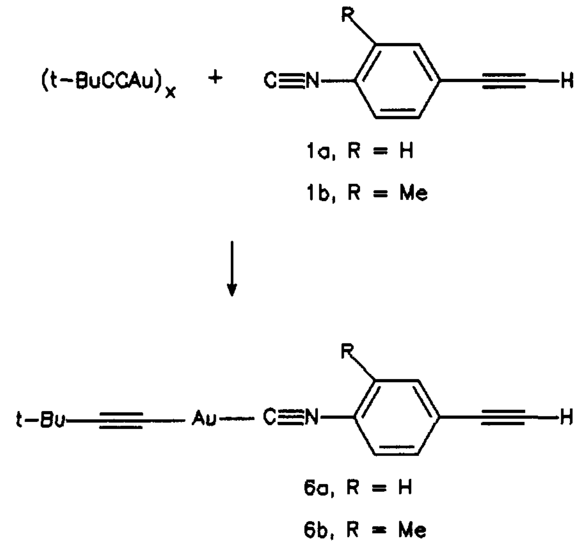
$$[t\text{-BuC}{\equiv}\text{CAuC}{\equiv}\text{NXy}] + [4\text{-NO}_2\text{C}_6\text{H}_4\text{C}{\equiv}\text{CH}] \rightarrow [4\text{-NO}_2\text{C}_6\text{H}_4\text{C}{\equiv}\text{CAuC}{\equiv}\text{NXy}] + t\text{-BuC}{\equiv}\text{CH} \quad (7)$$

is mixed with the less acidic PhC≡CH or if [4-$\mathrm{NO_2C_6H_4}$-C≡CAuCNXy] is mixed with t-BuC≡CH.

The mononuclear gold acetylide complexes [t-BuC≡CAu(CNArC≡CH)] could be synthesized by the reaction of 1 equiv of [(t-Bu-C≡CAu)$_x$] with the respective isocyanide ligands (eq 8). The reaction is quantitative and rapid at room temperature.



(8)

The ^{1}H NMR spectra display resonances for the t-Bu group around 1.27 ppm, the terminal C≡CH at 3.30 ppm for Ar = $\mathrm{C_6H_4}$ and 3.24 ppm for Ar = $\mathrm{C_6H_3Me}$, and resonances due to other protons of the isocyanide ligands. The strong IR bands for ν(CN) stretching were observed at 2215 cm^{-1} for Ar = $\mathrm{C_6H_4}$ and 2201 cm^{-1} for Ar = $\mathrm{C_6H_3Me}$. As expected, the CN stretching frequencies of the isocyanide ligands are about 90 cm^{-1} higher than those for the free isocyanides. In addition to the strong bands for ν(CN), there is also one weak shoulder around 2110 cm^{-1} and a very broad and weak band around 2035 cm^{-1} in the IR spectra. These bands could be assigned to the C≡C stretching. The ν(C≡CH) bands were observed at 3295 cm^{-1} for Ar = $\mathrm{C_6H_4}$ and 3227 cm^{-1} for Ar = $\mathrm{C_6H_3Me}$. An X-ray diffraction study on [Au(C≡C-t-Bu)($\mathrm{CNC_6H_3}$-(Me)C≡CH)] confirmed that the complex has the expected linear geometry.

The pure acetylide complexes are air-stable white solids and are very soluble in halogenated and aromatic hydrocarbons. However, they are thermally unstable. Thus, the color of the solid changed when the isolated solids were stored at room temperature for a long period of time or the samples were evacuated under vacuum at room temperature for a few hours. In fact, a brown solid was formed when a benzene solution of [t-BuC≡C-AuCNArC≡CH] was heated at 80 °C. The brown solid is insoluble in common organic solvents. t-BuC≡CH was detected when the heating process was monitored by ^{1}H NMR. Elemental analysis and IR data for the brown solid indicated that its composition is [t-BuC≡C(AuCN-ArC≡C)$_x$H]. The chemical transformation for the process is illustrated in Scheme II.

For example, when a solution of [t-BuC≡CAuCN-$\mathrm{C_6H_4}$C≡CH] in benzene was heated at 80 °C for 5 h, a brown precipitate which was analyzed as [t-BuC≡C(Au-$\mathrm{CNC_6H_4}$C≡C)$_{3.4}$H] was obtained. A strong IR band due to ν(CN) was observed at 2209 cm^{-1}. The CN stretching frequency of the isocyanide ligand is about 90 cm^{-1} higher than that for the free isocyanide. In addition to the strong band for ν(CN), there is also a weak shoulder around 2120 cm^{-1} and a very broad and weak band around 2034 cm^{-1} in the IR spectrum. These bands could be assigned to ν(C≡C). In fact, the IR features are very similar to those of the monomer, except that the intensity for the ν(CCH) band for the brown solid was significantly decreased; this IR band was hardly observable at 3295 cm^{-1} for the brown solid compared to the sharp, well-resolved, medium-intensity band at the same position for the monomer.

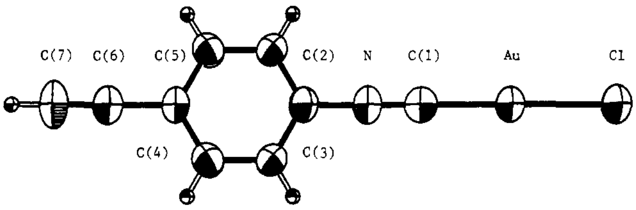


Figure 1. View of the structure of [ClAu-4-C≡N$\mathrm{C_6H_4}$-C≡CH] (**2a**).

Under similar conditions a brown solid which was analyzed as [t-BuC≡C(Au$\mathrm{CNC_6H_3Me}$C≡C)$_{6.0}$H] was obtained from [t-BuC≡CAu$\mathrm{CNC_6H_3}$(Me)C≡CH] and was characterized in a similar way (Experimental Section).

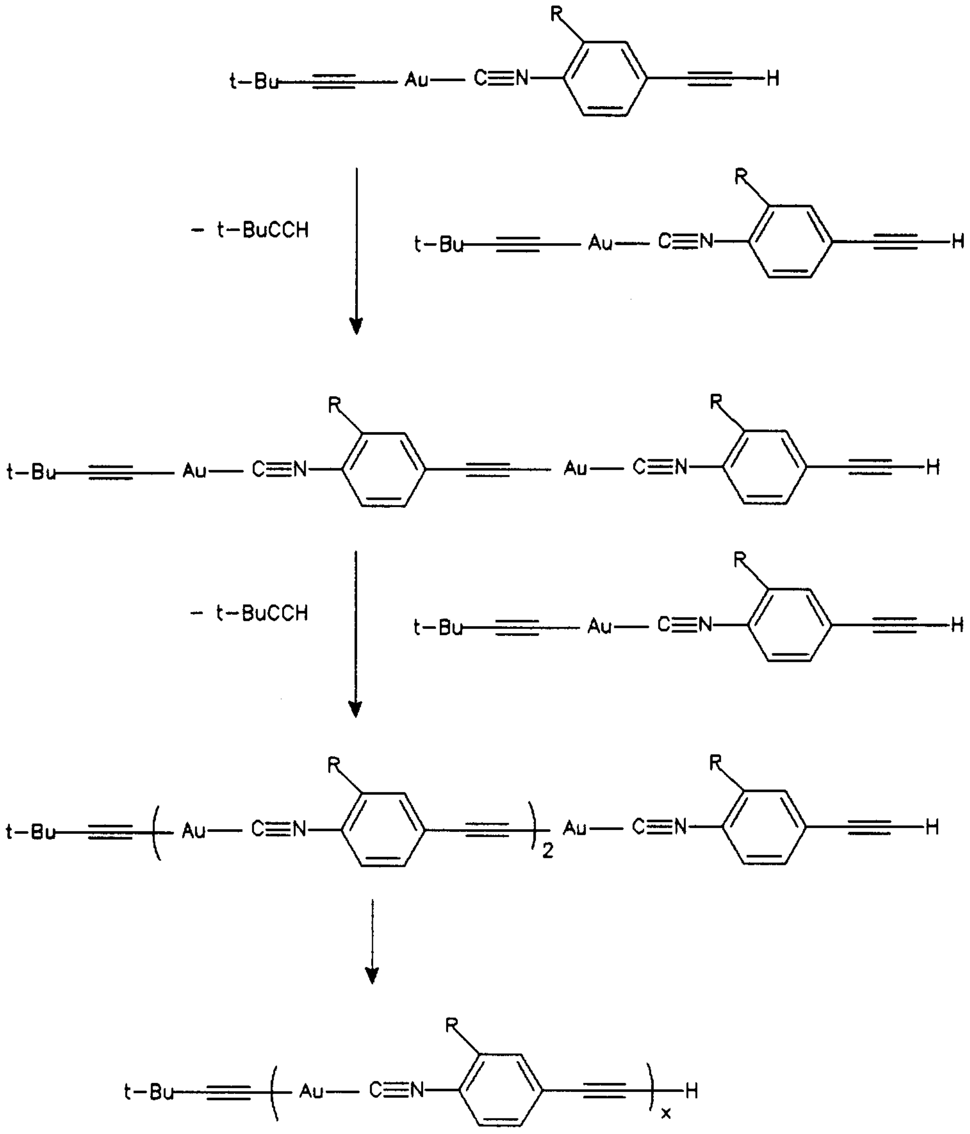
The brown solids [t-BuC≡C(AuCNArC≡C)$_x$H] could be dissolved in the presence of excess tertiary phosphines $\mathrm{PR_3}$ ($\mathrm{PR_3}$ = $\mathrm{PMe_3}$, P(OMe)$_3$) in organic solvents such as chloroform, acetone, and benzene owing to the formation of [t-BuC≡CAu$\mathrm{PR_3}$], [CNArC≡CAu$\mathrm{PR_3}$], and CNAr-C≡CH. When the solvent was evaporated, $\mathrm{PR_3}$ was also removed and re-formation of the insoluble polymers occurred; the $\mathrm{PR_3}$ for isocyanide substitution is evidently reversible.

The brown polymeric compounds and the monomeric complexes display almost identical XPS parameters. For example, the bonding energies for Au 4f and N 1s were observed at 85.1 and 400.1, 85.0 and 400.1, and 85.2 and 400.3 eV, respectively, for monomeric [t-BuC≡CAu-$\mathrm{CNC_6H_4}$C≡CH] and oligomeric [t-BuC≡C(Au$\mathrm{CNC_6H_4}$C≡C)$_x$H] and [t-BuC≡C(Au$\mathrm{CNC_6H_3Me}$C≡C)$_x$H]. These data confirm that the polymeric compounds and the monomeric complexes adopt similar structures with similar bonding. The thermal properties of the polymeric compounds and the precursor monomeric complexes have been studied using differential scanning calorimetry (DSC). The monomeric complexes [t-BuC≡CAuCNAr-C≡CH] melted at 149 °C for Ar = $\mathrm{C_6H_4}$ and at 159 °C for Ar = $\mathrm{C_6H_3Me}$ and decomposed immediately after melting. The polymeric samples displayed an endothermic transition over a wide temperature range (30–150 °C) and then decomposed, leaving a residue of metallic gold.

Since all the ligands are linear and the geometry around Au is also linear, these polymers must have a linear rigid-rod structure. The insolubility makes it impossible to determine the molecular weight of the polymers.

Structures of [AuCl($\mathrm{CNC_6H_4}$C≡CH)] and [Au-(C≡C-t-Bu)($\mathrm{CNC_6H_3}$(Me)C≡CH)]. The molecular structure of [AuCl($\mathrm{CNC_6H_4}$C≡CH)] is shown in Figure 1, and selected bond distances and angles are given in Table IV. The Au–Cl distance in chlorogold(I) complexes, Cl–Au–L, is sensitive to the trans influence of L. The value of 2.254(3) Å in **2a** can be compared to analogous

Scheme II



7a, R = H

7b, R = Me

Table IV. Bond Distances (Å) and Angles (deg) for 2a

Au–Cl	2.254(3)	Au–C(1)	1.921(13)
C(1)–N(1)	1.157(16)	N(1)–C(2)	1.376(15)
C(2)–C(3)	1.371(10)	C(3)–C(4)	1.368(11)
C(4)–C(5)	1.375(11)	C(5)–C(6)	1.464(16)
C(6)–C(7)	1.168(14)	C(7)–H7	0.902(9)
C(1)–Au–Cl	178.6(4)	N(1)–C(1)–Au	178.2(13)
C(2)–N(1)–C(1)	179.6(9)	C(3)–C(2)–N(1)	119.8(5)
C(4)–C(3)–C(2)	119.8(8)	C(5)–C(4)–C(3)	120.3(8)
C(6)–C(5)–C(4)	120.3(5)	C(7)–C(6)–C(5)	179.8(6)

values of *d*(Au–Cl) in Cl–Au–L of 2.256(8) Å (L = piperidine), 2.261(6) Å (L = CO), 2.281(2) Å (L = Cl$^-$), and 2.279(3) Å (L = PPh$_3$).[13] The isocyanide ligand exerts only a low trans influence, similar to piperidine and CO. The angles Cl–Au–C(1), Au–C(1)–N, C(1)–N–C(2), and C(5)–C(6)–C(7) are 178.6(4), 178.2(13), 179.6(9), and 179.8°, respectively. Obviously, all are close to linear and so confirm that the ligand is well suited to act as a linear bridge.

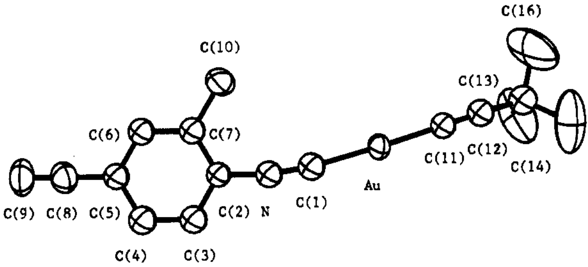
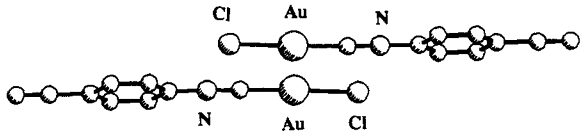


Figure 2. View of the structure of [*t*-BuC≡CAu-4-C≡N-3-MeC$_6$H$_3$C≡CH] (**6b**).

The molecular structure of [*t*-BuC≡CAuC≡NC$_6$H$_3$(Me)C≡CH] is shown in Figure 2, and selected bond distances and angles are given in Table V. In this case, the angles C(11)–Au–C(1), Au–C(1)–N, C(1)–N–C(2), Au–C(11)–C(12), C(11)–C(12)–C(13), and C(5)–C(8)–C(9) are 173.6(4), 173.0(9), 169.8(9), 174(1), 174(1), and 178(1)°, respectively. While these are close to linear, the distortion from the ideal angle of 180° in each case is greater than for [AuCl(CNC$_6$H$_4$C≡CH)] (**2a**) and, in most cases, considerably greater. The overall result is that the molecules of complex **6b** have a bowed, rather than strictly linear, geometry.



(a) Complex 2a

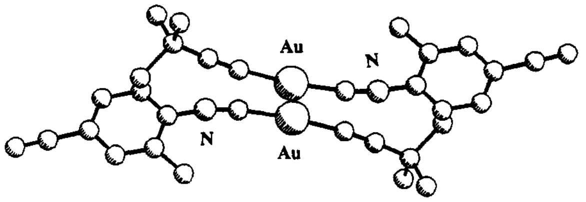


Figure 3. Orientation of neighboring molecules in the structures of (a) **2a** and (b) **6b**. Note the distortion from linearity in **6b** due to steric interactions between *t*-Bu and aryl substituents.

Table V. Bond Distances (Å) and Angles (deg) for 6b

Au–C(1)	1.949(10)	Au–C(11)	1.955(10)
C(1)–N	1.163(12)	N–C(2)	1.361(9)
C(5)–C(8)	1.447(13)	C(7)–C(10)	1.520(12)
C(8)–C(9)	1.156(16)	C(11)–C(12)	1.206(15)
C(12)–C(13)	1.463(16)	C(13)–C(14)	1.493(19)
C(13)–C(15)	1.511(19)	C(13)–C(16)	1.442(22)
C(11)–Au–C(1)	173.6(4)	N–C(1)–Au	173.0(9)
C(2)–N–C(1)	169.8(9)	C(3)–C(2)–N	119.5(4)
C(7)–C(2)–N	120.5(4)	C(8)C(5)–C(4)	119.6(5)
C(8)–C(5)–C(6)	120.2(5)	C(10)–C(7)–C(2)	119.0(5)
C(10)–C(7)–C(6)	121.0(5)	C(9)–C(8)–C(5)	178.2(14)
C(12)–C(11)–Au	173.6(10)	C(13)–C(12)–C(11)	173.9(12)
C(14)–C(13)–C(12)	112.4(11)	C(15)–C(13)–C(12)	112.5(12)
C(15)–C(13)–C(14)	108.1(16)	C(16)–C(13)–C(12)	110.6(12)
C(16)–C(13)–C(14)	110.8(16)	C(16)–C(13)–C(15)	101.9(17)

Figure 3 shows how nearest neighbors of **2a** and **6b** are arranged in the respective lattices. For complex **2a**, the nearest intermolecular gold···gold contact is 3.60 Å, which is slightly longer than the normal range of ca. 2.75–3.40 Å for such weak intermolecular bonds between gold(I) centers.[13] If there is gold–gold bonding, it must be very weak. The nearest neighbors of **6b** are arranged in a similar way, with the shortest intermolecular gold···gold distance being 3.479(2) Å. Although this is at the long end of the range for a bonding interaction,[13] the packing of the molecules does suggest some weak intermolecular gold–gold bonding. Thus, the distortion of the molecule from linear geometry appears to be due to the attraction of the neighboring gold atoms counterbalanced by steric repulsion between the *tert*-butyl and aryl substituents on the neighboring molecules, as illustrated in Figure 3. Neighboring molecules of **6b** are therefore bowed in opposite directions to allow a short Au···Au contact while the *tert*-butyl and aryl substituents on the neighboring molecules are bent away from each other. Although a similar bowing could occur in the oligomeric complexes **7**, the distortion is unlikely to be great enough to allow the formation of small cyclic oligomers and the "rigid-rod" description is still reasonable. To our knowledge, complex **6b** is the first gold complex containing both an acetylide and an isocyanide ligand to be characterized by X-ray diffraction.

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Supplementary Material Available: Tables of calculated positional and thermal parameters for hydrogen atoms and root-mean-square amplitudes of anisotropic displacement parameters for **2a** and **6b**, weighted least-squares planes and torsion angles for **2a**, and anisotropic thermal parameters for **6b** (3 pages). Ordering information is given on any current masthead page.

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