Rigid-Rod Polymers and Model Compounds with Gold(I) Centers Bridged by Diisocyanides and Diacetylides

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Binuclear alkynyl(isocyanide)gold(I) complexes have been prepared by reaction of oligomeric precursors $[(AuC{\equiv}CRC{\equiv}CAu)_n]$ (R = C_6H_4, $C_6H_4C_6H_4$, 2,5-$C_6H_2Me_2$, $CH_2OC_6H_4C(Me)_2$-$C_6H_4OCH_2$) with 2,6-dimethylphenyl isocyanide (XyN≡C) to give [XyN≡CAuC≡CR-C≡CAuC≡NXy] or by reaction of $[(R'C{\equiv}CAu)_n]$ with a diisocyanide CNRNC to give [R′C≡CAuCNRCAuCNC≡CR′] (R = C_6H_4, 2-MeC_6H_3, C_6Me_4, 2,5-$Me_2C_6H_2$-2,5−$Me_2C_6H_2$, 2,5-$C_6H_2(t\text{-Bu})_2$; R′ = *t*-Bu or Ph). The products were characterized spectroscopically and, for R = 2,5-$C_6H_2(t\text{-Bu})_2$; and R′ = Ph, by an X-ray structure determination. The molecule has a rodlike structure, and there is a bowing of the isocyanide ligand, angle C−N≡C = 168(2)°, which allows the molecules to pack in zigzag chains with short intermolecular Au··Au contacts of 3.174(1) Å to give a loosely held polymeric structure. Analogous σ-bonded, conjugated rigid-rod polymeric complexes are prepared by reactions of the linear digold complexes $[(AuC{\equiv}CRC{\equiv}CAu)_n]$ (R = C_6H_4, $C_6H_4C_6H_4$, $C_6H_2Me_2$ and $CH_2OC_6H_4C(Me)_2C_6H_4OCH_2$) with appropriate diisocyanoarenes C≡NR′N≡C (R′ = C_6H_4, C_6H_3Me, C_6Me_4, $C_6H_2Me_2C_6H_2Me_2$, C_6H_2-*t*-Bu_2) to give $[(AuC{\equiv}CRC{\equiv}CAuC{\equiv}NR'N{\equiv}C)_x]$. These polymers are insoluble and are characterized by elemental analysis, IR and XPS methods; the IR, and XPS data indicate that the polymers contain the same functional groups as the binuclear model complexes. It is argued that the low solubility results in part from crosslinking due to interchain Au··Au contacts of the kind established crystallographically in the model binuclear complex.

Introduction

There has been great interest in the synthesis and properties of linear chain metal-containing polymers with extended backbone conjugation through $d_\pi-p_\pi$ or σ^*-p_π overlap leading toward potential applications as advanced materials.[1] In particular, polymeric species of the type $[ML_n(-C{\equiv}CRC{\equiv}C-)]_n$ (ML_n = d^6 to d^8 metal fragments; R = aromatic rings, disilanes, or disiloxanes) are attracting increasing attention because of their electrical conducting, nonlinear optical, and liquid crystalline properties.[2−7] One- and two-dimensional polymers with diisocyanoarenes linking metal centers are also known.[8,9] It is interesting to note that polymers of the type $[PcM(CNRNC)]_x$ (Pc = phthalocyanine; M = Fe, Ru) display semiconducting properties.[1,8] Novel rigid-rod Au-containing polymeric complexes where Au centers are bridged by isocyanoarylacetylides have recently been synthesized.[10] Cationic palladium complexes $[Pd(PBu_3)_2C{\equiv}CRC{\equiv}CPd(PBu_3)_2(L\text{-}L)]_n$ (L-L = bipyridyl derivatives) have also been reported to show electrical conducting properties.[11] In this regard, it would be interesting to synthesize and characterize novel rigid-rod metal-containing polymers in which the metal centers are connected consecutively with conjugated diisocyanides and conjugated diacetylides. The properties of the polymeric species could be easily

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altered by changing the properties of the individual ligands involved.

This report describes the synthesis and characterization of gold-containing polymers of the formula $(AuC{\equiv}NRN{\equiv}CAuC{\equiv}CR'C{\equiv}C-)_n$. Aryl diisocyanides and aryldiacetylides are chosen since they often form strong metal–ligand bonds, they have been used separately for the synthesis of interesting polymers, and their geometries are ideal for linear polymers. Gold(I) was chosen as the metal center since it tends to form simple two-coordinated linear complexes[12] and because gold alkynyl complexes of formula $[Au(C{\equiv}CR)(L)]$ (L = phosphine, arsine, stibine, isocyanide, and amine) are among the most stable organogold complexes and are known to have linear geometry.[13–16] Hence rigid-rod Au-containing polymers of the type $(AuC{\equiv}NRN{\equiv}CAuC{\equiv}C\text{-}R'\text{-}C{\equiv}C\text{-})_n$ were considered a logical target. They are related to the polymers $(AuC{\equiv}NRC{\equiv}C-)_n$ reported previously.[10]

Experimental Section

All chemicals were used as purchased from Aldrich Chemical Co. unless otherwise stated. Gold metal was purchased from Johnson Matthey Co. $[AuCl(SMe_2)]$,[17] $[AuC{\equiv}CPh]$, and $[AuC{\equiv}C\text{-}t\text{-}Bu)]$[18] were prepared by modified literature methods [**Caution**: *some gold acetylides are potentially explosive; they should be prepared in small quantities and not subjected to shock*!]. *p*-Diisocyanoarenes[19] (with the exception of 2,5-di-*tert*-butyl-1,4–diisocyanobenzene) were synthesized from *p*-diaminoarenes via the phase-transfer Hofmann carbylamine reaction[20] and were purified by column (neutral alumina) chromatography or sublimation. *p*-Diethynylarenes[21] were prepared from *p*-dibromoarenes and 2-methylbut-3-yn-2-ol using the procedure of Ames et al.[22] and were purified by sublimation. The catalyst CuI was prepared from the reaction of $CuSO_4$ and KI. $[PdCl_2(PPh_3)_2]$[23a] was prepared from the reaction of PPh_3 with $[PdCl_2(PhCN)_2]$.[23b]

NMR spectra were recorded by using a Varian XL 200 or Gemini 200 spectrometer. ^1H NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. IR spectra were recorded as Nujol mulls by using either one of a Bruker IFS32 spectrometer or a Perkin-Elmer FTIR. DSC analyses were carried out on a General V2.2A Dupont 9900 DSC thermal analyzer. Elemental analyses were performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario.

1,4-(NHCHO)$_2$-2,5-(*t*-Bu)$_2$-C$_6$H$_2$. 1,4-Diamino-2,5-di-*tert*-butylbenzene (10 g, 0.45 mmol) was added to 96% formic acid (ca. 100 mL). The mixture was warmed to 85 °C and allowed to stir for 10 h. The volume of the mixture was reduced under vacuum to leave an off white solid which was collected by filtration and subsequently washed with ether, pentane, and hexanes and dried. Yield: 10.9 g, 88%. NMR in acetone-d_6: $\delta(^1H) = 1.38$ [s, 18H, *t*-Bu]; 7 [s, 2H, Ph]; 8.42 [s, 2H, CHO]. MS: $m/z = 276$ amu; calcd for $C_{16}H_{24}N_2O_2$, $m/z = 276$.

1,4-(NC)$_2$-2,5-(*t*-Bu)$_2$-C$_6$H$_2$. Phosgene (4 g, 41 mmol) (**Caution:** *a highly toxic gas*) was led into a suspension of 2,5-di-*tert*-butyl-1,4-diformylbenzene (5 g,18 mmol) in CH_2Cl_2 (150 mL) and diethylamine (11 mL). The mixture was stirred for 0.5 h until cessation of boiling resulting from the very exothermic reaction. A steady stream of ammonia was bubbled quickly into the mixture for ca. 5 min, after which time the resulting suspension was filtered. The filtrate was concentrated under vacuum, and the resulting light brown precipitate was dried. The product was purified by sublimation to yield a white crystalline solid. Yield: 3.69 g, 85%. NMR in $CDCl_3$: $\delta(^1H) = 1.47$ [s, 18H, *t*-Bu]; 7.38 [s, 2H, Ph]. IR (Nujol): $\upsilon(C{\equiv}N) = 2102\ cm^{-1}$. MS: $m/z = 240$ amu; calcd for $C_{16}H_{20}N_2$, $m/z = 240$.

[Au$_2$(C≡CC$_6$H$_4$C$_6$H$_4$C≡C)]$_n$. $AuCl(SMe_2)$(0.90 g, 3.06 mmol) was dissolved in the mixed solvents THF (200 mL)/MeOH (100 mL). To the solution was then added a solution of 4,4′-$HC{\equiv}CC_6H_4C_6H_4C{\equiv}CH$ (0.300 g, 1.48 mmol) and NaO_2CMe (0.60 g, 7.3 mmol) in THF (25 mL)/MeOH (25 mL). The resulting mixture was then stirred overnight (ca. 10 h) to produce a bright yellow precipitate. The solid was then collected by filtration, washed with THF, MeOH, water, MeOH and ether, and dried. Yield: 0.85 g, 97%. The solid is insoluble in common organic solvents. IR (Nujol): $\upsilon(C{\equiv}C) = 2000$ (w) cm^{-1}. Anal. Calcd for $C_{16}H_8Au_2$: C, 32.3; H, 1.4. Found: C, 32.7; H, 1.7.

[Au$_2$(C≡CC$_6$H$_2$Me$_2$C≡C)]$_x$. A solution of 4,4′-$(HC{\equiv}C)_2$-2,5-$Me_2C_6H_2$ (0.150 g, 0.973 mmol) and NaO_2CMe (0.40 g, 4.9 mmol) in THF (5 mL)/MeOH (20 mL) was added to a solution of $AuCl(SMe_2)$ (0.600 g, 2.04 mmol) in the mixed solvents THF (80 mL)/MeOH (20 mL). The resulting mixture was then stirred overnight (ca. 10 h) to produce a bright yellow precipitate. The solid was then collected by filtration, washed with THF, MeOH, water, MeOH, and ether, and dried. Yield: 0.85 g, 97%. The solid is insoluble in common organic solvents. IR (Nujol): $\upsilon(C{\equiv}C) = 2018$ (w), 1972 (w) cm^{-1}. Anal. Calcd for $C_{12}H_8Au_2$: C, 26.4; H, 1.5. Found: C, 26.0; H, 1.4.

[(2,6-Me$_2$C$_6$H$_3$NCAu)$_2$(μ-C≡CC$_6$H$_4$C$_6$H$_4$C≡C)]. A mixture of $Au_2(C{\equiv}CC_6H_4C_6H_4C{\equiv}C)$ (0.10 g, 0.17 mmol) and 2,6-$Me_2C_6H_3NC$ (50 mg, 0.38 mmol) in dichloromethane (100 mL) was stirred for 1 h to give a slightly cloudy solution. The solvent was removed completely, and the residue was washed with ether to give a pale yellow solid. The solid was collected by filtration, washed with ether, and dried. Yield: 0.13 g, 89%. NMR ($CDCl_3$) $\delta(^1H) = 2.46$ (s, 12H, Me), 7.15–7.57 (m, 14H, Ph). IR (Nujol): $\upsilon(N{\equiv}C) = 2211$ (s) cm^{-1}. Anal. Calcd for $C_{34}H_{26}Au_2N_2$: C, 47.7; H, 3.1. Found: C, 48.1; H, 3.4.

[(2,6-Me$_2$C$_6$H$_3$NCAu)$_2$(μ-C≡CC$_6$H$_2$Me$_2$C≡C)]. A mixture of $Au_2(C{\equiv}CC_6H_2Me_2C{\equiv}C)$ (0.10 g, 0.18 mmol) and 2,6-$Me_2C_6H_3$-NC (50 mg, 0.38 mmol) in dichloromethane (30 mL) was stirred for 1 h. The solvent was then removed completely, and the residue was washed with hexane to give a light yellow solid. The solid was collected by filtration, washed with ether, and dried. Yield: 0.13 g, 89%. NMR ($CDCl_3$): $\delta(^1H) = 2.41$ (s, 6H, Me), 2.44 (s, 12H, Me), 7.14–7.33 (m, 8H, Ph). IR (Nujol): 2220 (s), 2165 (sh), 2039 (br, w) cm^{-1}. Anal. Calcd for $C_{30}H_{26}Au_2N_2$: 44.5; H, 3.2. Found: C, 44.3; H, 3.0.

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[(*t*-BuC≡CAu)$_2$(*μ*-CNC$_6$H$_4$NC)]. A mixture of *t*-BuC≡CAu (0.10 g, 0.36 mmol) and CNC$_6$H$_4$NC (23 mg, 0.18 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 light yellow solid. The solid was collected by filtration, washed with hexane, and dried. Yield: 110 mg, 89%. NMR (CDCl$_3$): $\delta(^1H) = 1.27$ (s, 18H, Bu), 7.67 (s, 4H, Ph). IR (Nujol): 2211 (s), 2122 (sh), 2040 (br, w) cm^{-1}. Anal. Calcd for $C_{20}H_{22}Au_2N_2$: C, 35.1; H, 3.2. Found: C, 35.4; H, 3.0.

[(*t*-BuC≡CAu)$_2$(*μ*-CNC$_6$H$_3$MeNC)]. A mixture of *t*-BuC≡CAu (0.10 g, 0.36 mmol) and CNC$_6$H$_3$MeNC (26 mg, 0.18 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 light yellow solid. The solid was collected by filtration, washed with hexane, and dried. Yield: 113 mg, 90%. NMR (CDCl$_3$): $\delta(^1H) = 1.27$ (s, 18H, Bu), 2.48 (s, 3H, Me), 7.45−7.62 (m, 3H, Ph). IR (Nujol): 2207 (s), 2111 (sh), 2034 (br, w) cm^{-1}. Anal. Calcd for $C_{21}H_{24}Au_2N_2$: C, 36.1; H, 3.5. Found: C, 36.0; H, 3.3.

[(*t*-BuC≡CAu)$_2$(*μ*-CNC$_6$Me$_4$NC)]. A mixture of *t*-BuC≡CAu (0.10 g, 0.36 mmol) and CNC$_6$Me$_4$NC (33 mg, 0.18 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 light yellow solid. The solid was collected by filtration, washed with hexane, and dried. Yield: 110 mg, 83%. NMR (CDCl$_3$): $\delta(^1H) = 1.28$ (s, 18H, Bu), 2.36 (s, 12H, Me). IR (Nujol): 2205 (s), 2124 (sh), 2045 (br, w) cm^{-1}. Anal. Calcd for $C_{24}H_{30}Au_2N_2$: C, 38.9; H, 4.1. Found: C, 38.8; H, 4.0.

[(*t*-BuC≡CAu)$_2$(*μ*-CN-2,2′,6,6′-Me$_2$C$_6$H$_2$Me$_2$C$_6$H$_2$NC)]. A mixture of *t*-BuC≡CAu (0.10 g, 0.36 mmol) and CN-2,2′,6,6′-Me$_2$C$_6$H$_2$Me$_2$C$_6$H$_2$NC (47 mg, 0.18 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 light yellow solid. The solid was collected by filtration, washed with hexane, and dried. Yield: 126 mg, 86%. NMR (CDCl$_3$): $\delta(^1H) = 1.28$ (s, 18H, Bu), 2.45 (s, 12H, Me), 7.30 (br, 4H, Ph). IR (Nujol): 2193 (s), 2119 (sh), 2025 (br, w) cm^{-1}. Anal. Calcd for $C_{30}H_{34}Au_2N_2$: C, 44.1; H, 4.2. Found: C, 43.4; H, 3.8.

[(ClAu)$_2$(*μ*-CNC$_6$H$_2$(*t*-Bu)$_2$NC)]. AuCl(SMe$_2$) (0.0912 g, 0.310 mmol) was dissolved in dichloromethane (50 mL). To the solution was then added *p*-CNC$_6$H$_2$(*t*-Bu)$_2$NC (0.0385 g, 0.160 mmol). The resulting mixture was stirred overnight to give a cloudy solution. The solvent was removed completely, and the residue washed with ether to give a white solid. The solid was collected by filtration, washed with ether, and pentane and dried. Yield: 207 mg, 95%. IR (Nujol):: ν(NC) = 2202 cm^{-1}. Anal. Calcd for $C_{16}H_{20}Au_2N_2Cl_2$: C, 27.3; H, 2.9; N, 4.0. Found: C, 27.5; H, 2.9; N, 3.9.

[(*t*-BuC≡CAu)$_2$(*μ*-CNC$_6$H$_2$(*t*-Bu)$_2$NC)]. A mixture of *t*-BuC≡CAu (0.0948 g, 0.341 mmol) and CNC$_6$H$_2$(*t*-Bu)$_2$NC (45 mg, 0.188 mmol) in dichloromethane (60 mL) was stirred for 30 min. The solvent was then removed completely, and the residue was washed with hexane to give a light yellow solid. The solid was collected by filtration, washed with hexane, and dried. Yield: 249 mg, 92%. ^{1}H NMR (CDCl$_3$): δ 1.280 (s, 18H, *t*-Bu), 1.415 (s, 18H, *t*-Bu), 7.495 (s, 2H, Ph). IR (Nujol): 2202 (s) cm^{-1}. Anal. Calcd for $C_{28}H_{38}Au_2N_2$: C, 42.2; H, 4.8, N, 3.5. Found: C, 42.6; H, 4.3; N, 3.3.

[(PhC≡CAu)$_2$(*μ*-CNC$_6$H$_2$(*t*-Bu)$_2$NC)]. A mixture of PhC≡CAu (0.0892 g, 0.299 mmol) and CNC$_6$H$_2$(*t*-Bu)$_2$NC (36.5 mg, 0.152 mmol) in dichloromethane (50 mL) was stirred for 30 min. The solvent was then removed completely, and the residue was washed with hexane to give a light yellow solid. The solid was collected by filtration, washed with pentane and hexane and dried. Yield: 225 mg, 90%. ^{1}H NMR (CDCl$_3$): δ 1.463 (s, 18H, Bu), 7.30 (m, 5H, Ph). IR (Nujol): 2204 (s) cm^{-1}. Anal. Calcd for $C_{32}H_{30}Au_2N_2$: C, 45.9; H, 3.6, N, 3.3. Found: C, 45.3; H, 4.0; N, 3.5.

[(AuC≡CC$_6$H$_4$C$_6$H$_4$C≡CAuCNC$_6$H$_4$NC)$_x$]. A mixture of Au$_2$(C≡CC$_6$H$_4$C$_6$H$_4$C≡C) (0.10 g, 0.17 mmol) and CNC$_6$H$_4$NC (22 mg, 0.17 mmol) in dichloromethane (60 mL) was stirred for 36 h to give a yellow precipitate. The solid was collected by filtration, washed with dichloromethane, THF, and ether, and dried. Yield: 0.11 g, 90%. The solid is insoluble in common organic solvents. IR (Nujol): 2205 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{12}Au_2N_2$: C, 39.9; H, 1.7. Found: C, 40.5; H, 2.1.

[(AuC≡CC$_6$H$_4$C$_6$H$_4$C≡CAuCNC$_6$H$_3$MeNC)$_x$]. A mixture of Au$_2$(C≡CC$_6$H$_4$C$_6$H$_4$C≡C) (0.10 g, 0.17 mmol) and CNC$_6$H$_3$MeNC (25 mg, 0.18 mmol) in dichloromethane (50 mL) was stirred for 48 h to give a yellow precipitate. The solid was collected by filtration, washed with dichloromethane and ether, and dried. Yield: 0.ll g, 88%. The solid is insoluble in common organic solvents. IR (Nujol): 2201 (s), 2121 (sh) cm^{-1}. Anal. Calcd for $C_{25}H_{14}Au_2N_2$: C, 40.8; H, 1.9. Found: C, 40.7; H, 2.3.

[(AuC≡CC$_6$H$_4$C$_6$H$_4$C≡CAuCNC$_6$Me$_4$NC)$_x$]. A mixture of Au$_2$(C≡CC$_6$H$_4$C$_6$H$_4$C≡C) (0.10 g, 0.17 mmol) and CNC$_6$Me$_4$NC (32 mg, 0.17 mmol) in dichloromethane (60 mL) was stirred for 48 h to give a yellow precipitate. The solid was collected by filtration, washed with dichloromethane and ether, and dried. Yield: 0.l2 g, 91%. The solid is insoluble in common organic solvents. IR (Nujol): 2209 (s), 2113 (sh), 2021 (w) cm^{-1}. Anal. Calcd for $C_{28}H_{20}Au_2N_2$: C, 43.2; H, 2.6. Found: C, 43.9; H, 2.9.

[(AuC≡CC$_6$H$_4$C$_6$H$_4$C≡CAuCN-2,2′,6,6′-Me$_2$C$_6$H$_2$Me$_2$C$_6$H$_2$NC)$_x$]. A mixture of Au$_2$(C≡CC$_6$H$_4$C$_6$H$_4$C≡C) (0.10 g, 0.17 mmol) and CN-2,2′,6,6′-Me$_2$C$_6$H$_2$Me$_2$C$_6$H$_2$NC (45 mg, 0.17 mmol) in dichloromethane (60 mL) was stirred for 48 h to give a yellow precipitate. The solid was collected by filtration, washed with THF, dichloromethane and ether, and dried. Yield: 0.l3 g, 89%. The solid is insoluble in common organic solvents. IR (Nujol): 2195 (s), 2121 (sh), 2020 (br, w) cm^{-1}. Anal. Calcd for $C_{34}H_{24}Au_2N_2$: C, 47.8; H, 2.8, N, 3.3. Found: C, 46.8; H, 2.4; N, 3.0.

[(AuC≡CC$_6$H$_2$Me$_2$C≡CAuCNC$_6$H$_4$NC)$_x$]. A mixture of Au$_2$(C≡CC$_6$H$_2$Me$_2$C≡C) (0.10 g, 0.18 mmol) and CNC$_6$H$_4$NC (24 mg, 0.19 mmol) in dichloromethane (60 mL) was stirred for 36 h to give a yellow precipitate. The solid was collected by filtration, washed with dichloromethane, THF, and ether, and dried. Yield: 113 mg, 93%. The solid is insoluble in common organic solvents. IR (Nujol): 2207 (s), 2120 (sh), 2010 cm^{-1}. Anal. Calcd for $C_{20}H_{12}Au_2N_2$: C, 35.6; H, 1.4. Found: C, 34.9; H, 1.5.

[(AuC≡CC$_6$H$_2$Me$_2$C≡CAuCNC$_6$H$_3$MeNC)$_x$]. A mixture of Au$_2$(C≡CC$_6$H$_2$Me$_2$C≡C) (0.10 g, 0.18 mmol) and CNC$_6$H$_3$MeNC (27 mg, 0.19 mmol) in dichloromethane (60 mL) was stirred for 48 h to give a yellow precipitate. The solid was collected by filtration, washed with dichloromethane and ether, and dried. Yield: 116 mg, 92%. The solid is insoluble in common organic solvents. IR (Nujol): 2205 (s), 2122 (sh) cm^{-1}. Anal. Calcd for $C_{21}H_{14}Au_2N_2$: C, 36.6; H, 2.0. Found: C, 36.3; H, 2.2.

[(AuC≡CC$_6$H$_2$Me$_2$C≡CAuCNC$_6$Me$_4$NC)$_x$]. A mixture of Au$_2$(C≡CC$_6$H$_2$Me$_2$C≡C) (0.10 g, 0.18 mmol) and CNC$_6$Me$_4$NC (35 mg, 0.19 mmol) in dichloromethane (60 mL) was stirred for 48 h to give a yellow precipitate. The solid was collected by filtration, washed with dichloromethane and ether, and dried. Yield: 0.l2 g, 91%. The solid is insoluble in common organic solvents. IR (Nujol): 2207 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{20}Au_2N_2$: C, 39.5; H, 2.8. Found: C, 39.0; H, 2.8.

[(AuC≡CC$_6$H$_2$Me$_2$AuCN-2,2′,6,6′-Me$_2$C$_6$H$_2$Me$_2$-C$_6$H$_2$NC)$_x$]. A mixture of Au$_2$(C≡CC$_6$H$_2$Me$_2$C≡C) (0.10 g, 0.18 mmol) and CN-2,2′,6,6′-Me$_2$C$_6$H$_2$Me$_2$C$_6$H$_2$NC (50 mg, 0.19 mmol) in dichloromethane (60 mL) was stirred for 48 h to give a yellow precipitate. The solid was collected by filtration, washed with THF, dichloromethane and ether, and dried. Yield: 0.l3 g, 90%. The solid is insoluble in common organic solvents. IR (Nujol): 2195 (s), 2121 (sh), 2020 (w) cm^{-1}. Anal. Calcd for $C_{30}H_{24}Au_2N_2$: C, 44.7; H, 3.0. Found: C, 44.4; H, 2.8.

Table 1. Crystal Data and Structure Refinement for 3f

$C_{32}H_{30}Au_2N_2$	fw = 836.51
T = 223(2) K	space group $P4_2/n$ (No. 86)
λ = 0.710 73 Å	ρ(obsd) = 1.94(2) Mg/m^3
a = 16.734(2) Å	ρ(calc) = 1.906 Mg/m^3
c = 10.160(2) Å	μ = 10.074 mm^{-1}
V = 2845.0(8) Å^3	$R_1{}^a$ = 0.0467
Z = 4	w$R_2{}^b$ = 0.0926

^{a} $R_1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. ^{b} $wR_2 = [\{\sum w(|F_o^2| - |F_c^2|)^2\})/\sum w|F_o^2|^2]^{0.5}$.

[(AuC≡CC$_6$H$_4$C≡CAuCNC$_6$H$_2$(*t*-Bu)$_2$NC)$_x$]. A mixture of Au_2(C≡CC$_6$H$_4$C≡C) (0.0986 g, 0.191 mmol) and CNC$_6$H$_2$(*t*-Bu)$_2$NC (47 mg, 0.195 mmol) in dichloromethane (60 mL) was stirred for 48 h to give a yellow precipitate. The solid was collected by filtration, washed with THF, dichloromethane and ether, and dried. Yield: 0.1298 g, 90%. The solid is insoluble in common organic solvents. IR (Nujol): 2200 (s), 2121 (sh), 2020 (w) cm^{-1}. Anal. Calcd for $C_{26}H_{24}Au_2N_2$: C, 41.2; H, 3.2; N, 3.7. Found: C, 41.2; H, 3.4; N, 3.7.

[(AuC≡CC$_6$H$_2$Me$_2$C≡CAuCNC$_6$H$_2$(*t*-Bu)$_2$NC)$_x$]. A mixture of Au_2(C≡CC$_6$H$_2$Me$_2$C≡C) (0.0923 g, 0.169 mmol) and CNC$_6$H$_2$(*t*-Bu)$_2$NC (41.4 mg, 0.172 mmol) in dichloromethane (60 mL) was stirred for 48 h to give a yellow precipitate. The solid was collected by filtration, washed with THF, dichloromethane and ether, and dried. Yield: 0.1178 g, 89%. The solid is insoluble in common organic solvents. IR (Nujol): 2198 (s), 2121 (sh), 2020 (w) cm^{-1}. Anal. Calcd for $C_{28}H_{28}Au_2N_2$: C, 42.7; H, 3.6; N, 3.6. Found: C, 42.7; H, 3.8; N, 3.5.

[(AuC≡CC$_6$H$_4$C$_6$H$_4$C≡CAuCNC$_6$H$_2$(*t*-Bu)$_2$NC)$_x$]. A mixture of Au_2(C≡CC$_6$H$_4$C$_6$H$_4$C≡C) (0.0916 g, 0.177 mmol) and CNC$_6$H$_2$(*t*-Bu)$_2$NC (43.5 mg, 0.181 mmol) in dichloromethane (55 mL) was stirred for 48 h to give a yellow precipitate. The solid was collected by filtration, washed with THF, dichloromethane, and ether, and dried. Yield: 0.13 g, 88%. The solid is insoluble in common organic solvents. IR (Nujol): 2196 (s), 2121 (sh), 2020 (w) cm^{-1}. Anal. Calcd for $C_{32}H_{28}Au_2N_2$: C, 46.1; H, 3.4; N, 3.4. Found: C, 46.2; H, 3.3; N, 3.3.

[(AuC≡CCH$_2$OC$_6$H$_4$C(Me)$_2$-C$_6$H$_4$OCH$_2$C≡CAuCNC$_6$H$_2$(*t*-Bu)$_2$NC)$_x$]. A mixture of Au_2(C≡CCH$_2$OC$_6$H$_4$C(Me)$_2$OCH$_2$C≡C) (0.1083 g, 0.156 mmol) and CNC$_6$H$_2$(*t*-Bu)$_2$NC (39.2 mg, 0.163 mmol) in CH_2Cl_2 (50 mL) was stirred for 48 h to give a yellow precipitate. The solid was collected by filtration, washed with THF, dichloromethane and ether, and dried. Yield: 0.14 g, 95%. The solid is insoluble in common organic solvents. IR (Nujol): 2195 (s), 2121 (sh), 2029 (w) cm^{-1}. Anal. Calcd for $C_{37}H_{38}Au_2N_2O_2$: C, 47.7; H, 4.1; N, 3.0. Found: C, 47.9; H, 4.0; N, 2.8.

Crystallographic Analysis for (PhC≡CAu)$_2$(CNC$_6$H$_2$-(*t*-Bu)$_2$NC). Crystallographic data are summarized in Table 1. Pale-yellow, rodlike crystals were grown by diffusion of CH$_3$-CN into a solution of the complex in CH_2Cl_2 at 4 °C. The density (1.94 g mL^{-1}) was determined by the neutral buoyancy method using a mixture of carbon tetrachloride and bromoform. The diffraction experiments were carried out on an Enraf Nonius CAD4F diffractometer using the CAD4 EXPRESS software package[24a] and graphite-monochromated Mo Kα radiation. Data collection was performed at −50 °C on a crystal of size 0.11 × 0.11 × 0.37 mm mounted in air. The cell constants were obtained by centering 24 high-angle reflections (25.7 ≤ 2θ ≤ 26.3°), and Laue symmetry 4/m was confirmed by merging equivalent reflections. The tetragonal space group $P4_2/n$ with Z = 4 was unambiguously assigned on the basis of systematic absences (hk0, $h + k$ odd; 00l, l odd; h00, h = odd). During data collection three standards were monitored every 2 h, and showed no appreciable decay. In total 3193 reflections were collected in the 2θ range 2.35−24.99° (−19 ≤ h ≤ 1, −1 ≤ k ≤ 19, −12 ≤ l ≤ 1) in ω scan mode at variable scan speeds (2−30 deg/min). Moving background measurements were made at 25% extensions of the scan range. The data were processed (XCAD4) and corrected for absorption by the Gaussian integration method SHELX-76.[24b] The minimum and the maximum transmission factors are 0.0181 and 0.1044. respectively. Solution and initial refinements were done using the SHELXTL-PC[24c] programs. The molecule occupies Wyckoff position d and lies upon a center of symmetry. Final refinements were carried out using SHELXL-93.[24d] Anisotropic thermal parameters were assigned and refined for the Au, N, and C atoms of the diisocyanide ligand. All other phenyl rings were constrained to have 2-fold symmetry. All 15 hydrogen atoms in the molecule were placed in the calculated positions, and they were included in structure factor calculations. A common thermal parameter was assigned for all hydrogen atoms and refined in the least-squares cycles. In the final full-matrix refinements on F^2, the model converged at R_1 = 0.0467, wR_2 = 0.1348, and Goof = 1.011 for 1040 observations with $F_o \geq 4\sigma(F_o)$, 143 parameters, and 8 restraints. The maximum shift/esd = 0.076 for U12 of C(2) and the maximum shift = 0.004 Å for H(14A). The electron density in the final difference Fourier synthesis ranges from 0.89 to −0.59 e Å^{-3}; the top seven peaks were associated with gold at distances of 0.95−1.27 Å. The positional and U(equiv) thermal parameters are given in Table 2, and hydrogen atom parameters are available as Supporting Information, Table S1.

Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters, U(eq) (Å^2 × 10^3), for 3f

atom	x	y	z	U(eq)
Au(1)	1685(1)	2014(1)	872(1)	72(1)
C(1)	2111(10)	965(11)	1340(14)	70(5)
C(2)	2398(10)	330(12)	1599(16)	79(5)
C(3)	2748(9)	−462(10)	1878(16)	72(5)
C(4)	3031(10)	−954(10)	900(18)	111(6)
C(5)	3360(11)	−1682(12)	1159(22)	126(8)
C(6)	3386(12)	−1912(13)	2411(20)	130(8)
C(7)	3195(13)	−1437(14)	3442(22)	151(9)
C(8)	2861(12)	−707(12)	3157(20)	121(7)
C(9)	1166(10)	3034(10)	345(16)	69(5)
N(1)	882(8)	3608(8)	62(13)	66(4)
C(10)	437(8)	4337(8)	−43(13)	50(4)
C(11)	48(8)	4557(9)	1092(12)	53(4)
C(12)	412(8)	4776(8)	−1206(12)	49(4)
C(13)	845(10)	4576(10)	−2477(15)	72(5)
C(14)	465(11)	3834(12)	−3013(16)	127(8)
C(15)	755(13)	5215(12)	−3493(16)	35(9)
C(16)	1719(10)	4435(13)	−2283(17)	37(9)

Results and Discussion

Synthesis of Precursors and the Model Reactions. Monomeric alkynyl(isocyanide)gold(I) complexes of the type RC≡CAuCNR′ can be prepared by either the reactions of [AuX(CNR′)] with alkynyllithium or Grignard reagents (eq 1, M = Li or MgX)[25] or the reaction of (AuC≡CR)$_x$ with CNR′ (eq 2).[18] Thus it is expected that polymeric compounds can be similarly produced from the reaction of a linear dinuclear gold(I) diisocyanide complex XAuCNR′NCAuX with a difunctionalized linear organolithium or Grignard reagent (eq 3) or the reaction of a linear dinuclear gold(I) diacetylide complex (AuC≡CRC≡CAu)$_x$ with a linear diisocyanide (eq 4).

In order to produce a high polymer, the polymerization reaction must be of high yield (essentially no side

(24) (a) CAD4 Express, Enraf-Nonius X-Ray Instruments Inc. **19**90. (b) Sheldrick, G. M. SHELX-76, University of Cambridge, England, 1976. (c) Sheldrick, G. M. SHELXTL-PC 4.2, Siemens Analytical X-Ray Instruments Inc., Madison, 1990. (d) Sheldrick, G. M., SHELXL-93, Institut für Anorg. Chemie, Göttingen, Germany, 1993.

(25) Puddephatt, R. J.; Treurnicht, I. *J. Organomet. Chem.* **1987**, *319*, 129.

$$\mathrm{AuX(CNR') + RC{\equiv}CM \rightarrow RC{\equiv}CAuCNR' + MX} \quad (1)$$

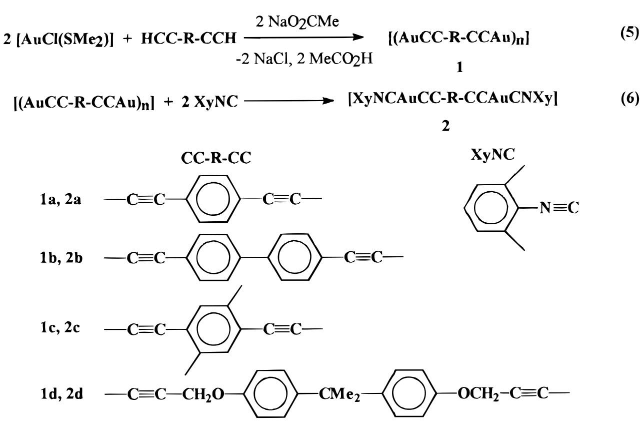
$$\mathrm{(AuC{\equiv}CR)_x + CNR' \rightarrow RC{\equiv}CAuCNR'} \quad (2)$$

$$n\mathrm{XAuCNR'NCAuX} + n\mathrm{MC{\equiv}CRC{\equiv}CM} \rightarrow 2n\mathrm{MX} + \mathrm{(AuCNR'NCAuC{\equiv}CRC{\equiv}C{-})}_n \quad (3)$$

$$n\mathrm{AuC{\equiv}CRC{\equiv}CAu} + n\mathrm{CNR'NC} \rightarrow \mathrm{(AuCNR'NCAuC{\equiv}CRC{\equiv}C{-})}_n \quad (4)$$

reactions and fast). Thus reaction 4 is an ideal reaction for preparation of polymers since such reactions are usually very fast and quantitative and no side products are produced. Besides the delicate reaction conditions, side reactions might occur in reaction 3 since coordinated isocyanides are very reactive toward nucleophilic reagents and reactions of isocyanides coordinated to gold(I) are well-known.[12,26] The possibility of using reaction 3 to prepare polymers has therefore not been investigated in detail in this study.

The yellow complexes $(AuC{\equiv}CRC{\equiv}CAu)_x$, **1**, (R = C_6H_4, $C_6H_4C_6H_4$, 2,5-$C_6H_2Me_2$, $CH_2OC_6H_4C(Me)_2C_6H_4$-OCH_2) are produced from the essentially quantitative reaction of 2 equiv of $[AuCl(SMe_2)]$ with the appropriate diethynylarenes in the presence of sodium acetate as a base in the mixed solvents THF/MeOH (eq 5). These



complexes are stable yellow powders which are insoluble in common organic solvents. The $\upsilon(C{\equiv}C)$ bands in the infrared spectra were observed as weak bands around 2000 cm^{-1}. These digold complexes are similar in appearance to phenylethynylgold(I), which is proposed to be a coordination polymer. The digold diacetylides are likely also polymeric in nature. To our knowledge, similar dinuclear gold acetylide complexes are rare,[7] although the explosive gold(I) acetylide Au_2C_2 was reported in 1900.[27]

The diacetylide complexes react readily with 2,6-dimethylphenyl isocyanide (XyN≡C) to give the dinuclear isocyanide complexes **2** in high yield (eq 6). The pale yellow isocyanide complexes were characterized by elemental analysis, ^1H NMR, and IR spectroscopy. The ^1H NMR spectra display characteristic resonances for the aromatic protons in the region 7.1−7.6 ppm and for the methyls on the aromatic rings in the region 2.41−2.45 ppm. The strong bands due to $\nu(N{\equiv}C)$ were observed at 2211 cm^{-1} for **2b** and at 2220 cm^{-1} for **2c**. For comparison the $\nu(N{\equiv}C)$ stretching frequency is at 2116 cm^{-1} for the free ligand. The increase (ca. 100 cm^{-1}) in the CN stretching frequency of coordinated isocyanide is attributed to the σ donation of the antibonding carbon lone pair (in the $7a_1$ orbital) to gold upon complexation.[28] The very weak bands which appeared between 2000−2170 cm^{-1} are likely to be due to $\nu(C{\equiv}C)$.

(26) Fehlhammer, W. P.; Finck, W. *J. Organomet. Chem.* **1991**, *414*, 261.
(27) (a) Matthews, J. A.; Watters, L. L. *J. Am. Chem. Soc.* **1990**, *22*, 108. (b) Vicente, J.; Chicote, M.-T.; Abrisqueta, M.-D. *J. Chem. Soc., Dalton Trans.* **1995**, 497.

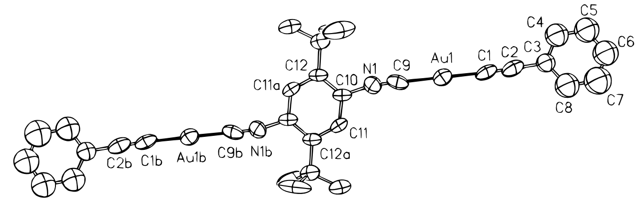
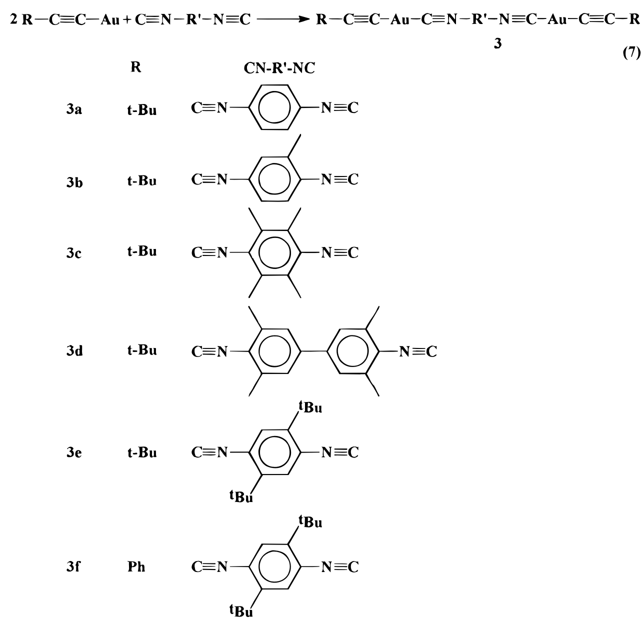


Figure 1. View of the molecule $[Au_2(C{\equiv}CPh)_2(\mu\text{-}C{\equiv}N\text{-}(t\text{-}Bu)_2C_6H_2N{\equiv}C)]$, **3f**, with the atom-labeling scheme.

Linear dinuclear complexes could also be prepared easily from the reaction of mononuclear gold acetylide complex and a diisocyanide as illustrated by the reaction of 2 equiv of either *t*-BuC≡CAu or PhC≡CAu with para-substituted diisocyanoarenes to give **3** (eq 7). The



reaction is also essentially quantitative and appears to be complete in a few minutes. The ^1H NMR spectra of **3** display resonances assignable to the alkynyl group at around 1.27 ppm, R = t-Bu, or 7.35 ppm, R = Ph, and the expected resonances of the diisocyanide ligands. The strong IR bands due to $\nu(N{\equiv}C)$ were observed between 2194 and 2211 cm^{-1}. As expected the CN stretching frequencies of the diisocyanide ligands are about 90 cm^{-1} higher than that for the free ones. In addition to the strong bands for $\upsilon(CN)$, there are also weak shoulders around 2120 cm^{-1} and a very broad and weak band around 2040 cm^{-1} in the IR spectra. These bands could be assigned to $\upsilon(C{\equiv}C)$. The structure of one binuclear complex is described below.

Description of the Structure of PhC≡CAu-CNC_6H_2(*t*-Bu)$_2$CAuCNC≡CPh. The molecular structure of $[PhC{\equiv}CAuC{\equiv}N\text{-}C_6H_2(t\text{-}Bu)_2\text{-}N{\equiv}CAuC{\equiv}CPh]$, **3f**, is shown in Figure 1, and selected bond lengths and

(28) Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1975**, *14*, 247.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 3f[a]

Au(1)−Au(1)[1]	3.1745(13)	Au(1)−C(1)	1.95(2)
Au(1)−C(9)	1.99(2)	C(1)−C(2)	1.20(2)
C(2)−C(3)	1.48(2)	C(3)−C(4)	1.38(2)
C(3)−C(8)	1.38(2)	C(4)−C(5)	1.36(2)
C(5)−C(6)	1.33(2)	C(6)−C(7)	1.35(2)
C(7)−C(8)	1.38(2)	C(9)−N(1)	1.11(2)
N(1)−C(10)	1.43(2)	C(10)−C(11)	1.37(2)
C(10)−C(12)	1.39(2)	C(11)−C(12)[2]	1.36(2)
C(12)−C(11)[2]	1.36(2)	C(12)−C(13)	1.52(2)
C(13)−C(16)	1.49(2)	C(13)−C(14)	1.50(2)
C(13)−C(15)	1.49(2)		
C(9)−Au(1)−C(1)	175.0(6)	C(9)−Au(1)−Au(1)[1]	86.3(5)
C(1)−Au(1)−Au(1)[1]	98.5(5)	C(2)−C(1)−Au(1)	178((2)
C(1)−C(2)−C(3)	178((2)	C(2)−C(3)−C(4)	122((2)
C(2)−C(3)−C(8)	120((2)	C(4)−C(3)−C(8)	117((2)
C(5)−C(4)−C(3)	122((2)	C(4)−C(5)−C(6)	117((2)
C(5)−C(6)−C(7)	124((3)	C(8)−C(7)−C(6)	117((2)
C(7)−C(8)−C(3)	121((2)	N(1)−C(9)−Au(1)	179((1)
C(9)−N(1)−C(10)	168((2)	C(11)−C(10)−C(12)	124((1)
C(11)−C(10)−N(1)	114((1)	C(12)−C(10)−N(1)	122((1)
C(12)[2]−C(11)−C(10)	124((1)	C(11)[2]−C(12)−C(10)	112((1)
C(11)[2]−C(12)−C(13)	122((1)	C(10)−C(12)−C(13)	126((1)
C(16)−C(13)−C(12)	113((1)	C(16)−C(13)−C(14)	109((2)
C(12)−C(13)−C(14)	107((1)	C(16)−C(13)−C(15)	108((2)
C(12)−C(13)−C(15)	112((1)	C(14)−C(13)−C(15)	107((2)

[a] Symmetry transformations used to generate equivalent atoms: (1) $-x + 1/2$, $-y + 1/2$, z; (2) $-x$, $-y + 1$, $-z$.

angles are presented in Table 3. The molecule has the predicted rodlike structure and possesses a center of symmetry at the center of the diisocyanide ligand. The angles which are expected to be 180° in an ideal linear complex, namely C(1)−Au(1)−C(9), Au(1)−C(9)−N(1), C(9)−N(1)−C(10), Au(1)−C(1)−C(2), and C(1)−C(2)−C(3), are 175.0(6), 179(1), 168(2), 178(2), and 178(2)°, respectively. The only large deviation from the ideal value is the C(9)−N(1)−C(10) angle of 168(2)°. Similar bowing of the isocyanide ligand has been reported for other coordinated isocyanides,[10,29] but the distortion is greater than in the other known gold(I) isocyanide complexes in which the angle C−N≡C ranges from 170 to 180°.[10,29] Overall, the ligand appears well suited to act as a linear bridge in the the desired rigid-rod polymers. Other features of the molecule are normal; for example, the Au−C distances in the Au−CN or Au−C≡C units of 1.99(2) and 1.95(2) Å, respectively, fall in the usual ranges for such groups.[10,12−16]

The most interesting feature of the structure of **3f** is the packing of the molecules in the lattice. This is shown in two perspectives in Figure 2. It can be seen that the rodlike molecules are packed in zigzag chains to give what may be considered a loosely held polymeric structure. The attractive forces between neighboring molecules appear to be due to short Au··Au contacts[10,12] and π-stacking of aryl groups.[30] This occurs despite the presence of bulky *tert*-butyl groups on the diisocyanide ligand. The intermolecular gold−gold contacts of 3.174(1) Å fall within the normal range of ca. 2.75−3.40 Å for Au··Au bonds between neighboring gold(I) centers,

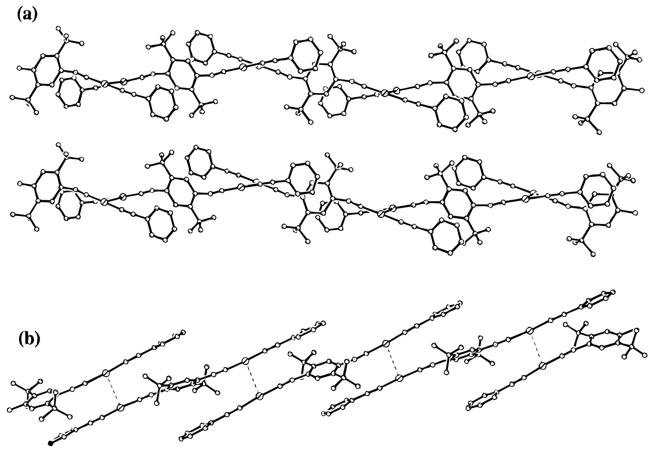


Figure 2. Two views of the packing of the molecules of **3f**, showing the zigzag chain structure with (a) π-stacking of aryl groups and (b) short intermolecular Au··Au contacts.

and this value is significantly shorter than that of 3.252(1) Å found in a related diphosphine complex.[31] The bowing of the isocyanide ligands appears to allow a closer Au··Au contact than would otherwise be possible, and this may account for the significant distortion from linearity observed.[10,12] The evidence for π-stacking is less clear-cut. The dihedral angle between nearest aryl groups of the phenylethynyl and diisocyanoarene groups is 20.8°, the distance between the ring centroids is 4.35 Å, and the closest intermolecular C··C contact is C(4A)··C(12) = 3.905 Å. Any bonding interactions at such distances are presumed to be weak.[30] If the Au··Au interactions are strong enough to allow easy electron migration (it is not obvious if this is so), crystals of the complex may be expected to have some electrical conductivity along the chain direction in the solid state, but studies require larger crystals than have yet been grown.

Synthesis of Polymers. Reactions of the linear digold complexes AuC≡CRC≡CAu (R = C_6H_4, $C_6H_4C_6H_4$, $C_6H_2Me_2$, and $CH_2OC_6H_4C(Me)_2C_6H_4OCH_2$) with appropriate para-substituted diisocyanoarenes in dichloromethane produced a series of polymers **4**, as illustrated in eq 8. All the products are air-stable yellow powders which are insoluble in common organic solvents.

The polymers **4** are characterized primarily by elemental analysis and IR spectroscopy. In particular, the polymeric species display IR spectral properties similar to those of the model complexes. The values of ν(N≡C) of the diisocyanide ligands are observed around 2200 cm^{-1} and are about 90 cm^{-1} higher than that for the free ones. Since all the ligands are linear and the geometry around Au is also linear, these polymers presumably have a linear structure. The insolubility makes it impossible to determine the molecular weights of the polymers. The Au··Au interaction established for the model complex, even with bulkiest *t*-butyl substituents, suggests that the polymers of this type, regardless of the organic substituents present, will also have interchain Au··Au contacts. This leads to virtual crosslinking and so may account in part for the low solubility of the polymers in common organic solvents. Although individual Au··Au attractions are expected to

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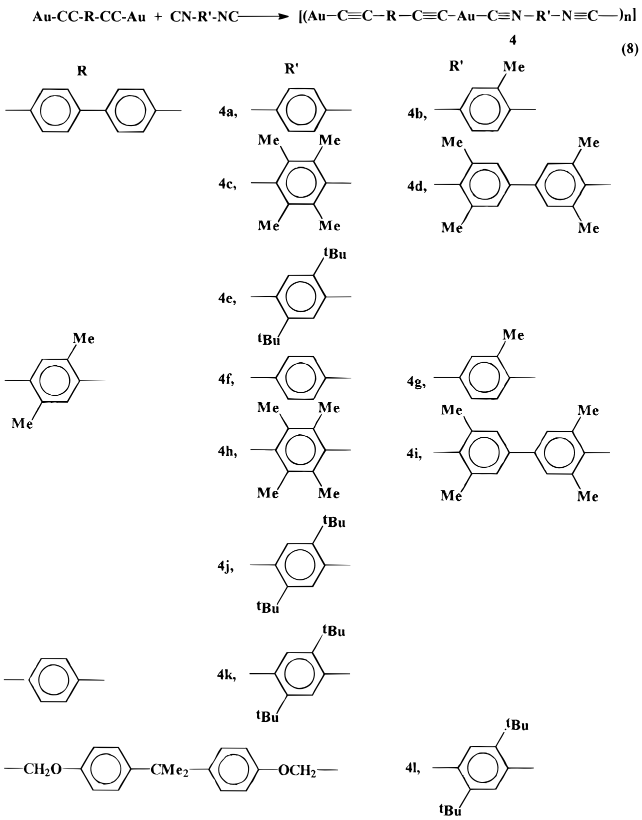

be weak, the combination of many such attractions between polymer chains could lead to low solubility, though it should be emphasized that at present this is a speculative interpretation and that the gold(I) polymers might be insoluble without such effects. Even the polymer [(AuC≡$CC_6H_2Me_2C$≡$CAuCNC_6H_2$(*t*-Bu)$_2$NC-Au)$_x$], **4j**, which contains several bulky organic groups, is poorly soluble. Clearly it will be a challenge to obtain more soluble polymers. The use of extremely bulky substituents on the aryl spacer groups might give sufficient solubility, but there are synthetic problems to overcome.

The yellow polymeric compounds, **4**, and the dinuclear model complexes, **2** and **3**, display almost identical XPS parameters. Table 4 contains the binding energies for Au 4f for several of the compounds described above. These data are in close agreement with XPS values for a variety of simple gold−isocyanide compounds[32,33] and confirm that the model compounds and corresponding polymers have the same core structures, namely linear with one alkynyl and one isocyanide ligand at each gold(I) center.

Table 4. Gold 4f(7/2) Binding Energies in Alkynylgold(I) Complexes and Polymers

compound	binding energy, eV
PhC≡$CAuCNC_6H_2$(*t*-Bu)$_2$CAuCNC≡CPh, **3f**	85.1
(AuC≡C-$(C_6H_4)_2$C≡$CAuCNC_6H_3$MeNC−)$_x$, **4b**	85.3
(AuC≡C-$(C_6H_4)_2$C≡$CAuCNC_6Me_4$NC−)$_x$, **4c**	85.7
(AuC≡$CC_6H_2Me_2C$≡$CAuCNC_6H_3$MeNC−)$_x$, **4g**	85.3
(AuC≡$CC_6H_2Me_2C$≡$CAuCNC_6Me_4$NC−)$_x$, **4h**	85.1
(AuC≡$CC_6H_2Me_2C$≡$CAuCNC_6H_2$(*t*Bu)$_2$NC−)$_x$, **4j**	85.2
(AuC≡CC_6H_4C≡$CAuCNC_6H_2$(*t*-Bu)$_2$NC−)$_x$, **4k**	85.2

The thermal properties of the polymeric compounds, **4**, have been studied using differential scanning calorimetry, DSC. Without exception, all of the compounds display significant endothermic transition over a wide temperature range 30−170 °C and decomposed around 200 °C before melting.

Conclusions

It is shown that binuclear rigid rod complexes of gold(I) can form infinite chain structures by formation of internuclear Au··Au bonding interactions. In principle, such a structure should be capable of acting as a one-dimensional conductor in single-crystal form. Routes to rigid rod polymers with alternating diisocyanide and diacetylide ligands bridging between gold(I) centers have also been developed. However, despite efforts to introduce organic substituents, including *t*-butyl groups, as solubility enhancing units, all the polymers prepared proved to be insoluble. Crosslinking by way of interchain Au··Au bonding, as established in the model complex **3f**, is thought to be at least partly responsible for the poor solubility.

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Supporting Information Available: Tables of anisotropic thermal parameters and hydrogen parameters (2 pages). Ordering information is given on any current masthead page.

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