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Rigid-Rod Compounds: Monomeric and Oligomeric Complexes with Gold(I) Centers Bridged by (Isocyanoaryl)acetylides

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Summary: The new ligands $4\text{-CNC}_6\text{H}_4\text{CCH}$ *(**1a**) and* $3\text{-Me-4-CNC}_6\text{H}_3\text{CCH}$ *(**1b**), which contain 4-isocyano-1-ethynylbenzene units designed to act as bridging ligands in rigid-rod, conjugated organometallic polymers, have been prepared. They react with* $[\text{AuCl(SMe}_2)]$ *and with* $[(\text{AuCC-}t\text{-Bu})_4]$ *to give the corresponding isocyanide complexes* $[\text{ClAuC}{\equiv}\text{N—Ar—C}{\equiv}\text{CH}]$ *(**2**) and* $[t\text{-BuC}{\equiv}\text{CAuC}{\equiv}\text{N—Ar—C}{\equiv}\text{CH}]$ *(**5**) (Ar =* C_6H_4*, Me-*C_6H_3*), respectively. The structures of **2a** and **5b** have been determined by single-crystal X-ray diffraction studies. Complexes **5**, when heated in benzene solution, eliminate t-BuCCH to give the rigid-rod, conjugated oligomers* $[t\text{-BuC}{\equiv}\text{C(AuC}{\equiv}\text{N—Ar—C}{\equiv}\text{C)}_x\text{H]}$ *(**6a**, Ar =* C_6H_4*; **6b**, R =* MeC_6H_3*).*

There has been great interest in the synthesis and properties of linear-chain metal-containing polymers, with extended backbone conjugation through dπ–pπ hybridization leading toward potential applications as advanced materials.[1] In particular, polymeric species of the type $[\text{ML}_n(\text{-C}{\equiv}\text{C—R—C}{\equiv}\text{C-})]_x$ (ML_n = d^6 to 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] One- and two-dimensional polymers with diisocyanoarenes linking metal centers have been synthesized,[8,9] and it is interesting to note that polymers of the type $[\text{PcM(CN—Ar—NC)}]_x$ (Pc = phthalocyanine, M = Fe, Ru) display semiconducting properties.[1,9] Whereas the diacetylides and diisocyanides are ideal ligands for polymeric linking of ML_n^{2+} and ML_n^{0} fragments, respectively, related ligands with one σ and one coordinate bond to the metal centers in the backbone of polymers, suitable for polymeric linking of ML_n^{+} fragments, have not received much attention. There are examples in polymers with well-known ligands such as CN^- and SCN^- bridging metal centers,[1c,10] but there appear to be no such polymers with designed organometallic ligands. In this context, we wish to report a synthetic route to new linear ethynylaryl isocyanide ligands[11] and their use in the synthesis of gold(I) oligomers, $(\text{Au—C}{\equiv}\text{N—Ar—C}{\equiv}\text{C-})_x$, with extended backbone conjugation through dπ–pπ hybridization. Gold(I) was chosen as the metal center because it tends to form simple two-coordinated linear complexes.[12-14]

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 $[\text{PdCl}_2(\text{PPh}_3)_2]$. The protecting group was then removed as acetone by treatment with KOH in refluxing toluene.[15] The isocyanides were prepared by the phase-transfer Hofmann carbylamine reaction[16] and could be easily purified by sublimation.[17] They are colorless solids which become light yellow on storage at room temperature[18] but which are stable if stored at 0 °C. The new compounds are readily characterized by their spectroscopic data.[19]

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(19) Spectroscopic data are as follows. **1a**: NMR in CDCl_3 $\delta(^1\text{H})$ = 3.18 [s, 1H, $\text{C}{\equiv}\text{CH}$], 7.31 [d, J = 8.6 Hz, 2H, Ph], 7.49 [d, J = 8.6 Hz, 2H, Ph], $\delta(^{13}\text{C})$ = 80.0, 81.8 [$C{\equiv}C$], 123.5 [$C\text{—C}{\equiv}\text{C}$], 126.4 [$\text{HC}C\text{C}{\equiv}\text{C}$], 130.5 [br, w, C—NC], 133.1 [$\text{H}C\text{CNC}$], 166.0 [$\text{N}{\equiv}C$]; IR (Nujol) 2120 [s, $\nu(\text{N}{\equiv}\text{C})$], 3305 [m, ν(CC-H)] cm^{-1}. Anal. Calcd for $\text{C}_9\text{H}_5\text{N}$: C, 85.0; H. 4.0. Found: C, 84.6; H, 4.3. **1b**: NMR in CDCl_3 $\delta(^1\text{H})$ = 2.39 [s, 3H, Me], 3.15 [s, 1H, $\text{C}{\equiv}\text{CH}$], 7.24–7.39 [m, 3H, Ph]; $\delta(^{13}\text{C})$ = 18.4, 79.4, 82.1, 123.2, 126.4, 130.3, 134.0, 135.0, 167.5 [note: C—NC resonance not resolved]; IR (Nujol) 2114 [m, $\nu(\text{N}{\equiv}\text{C})$], 3235 [m, $\nu(\text{C}{\equiv}\text{C—H})$] cm^{-1}. Anal. Calcd for $\text{C}_{10}\text{H}_7\text{N}$: C, 85.08; H, 5.00. Found: C, 84.7; H, 5.2.

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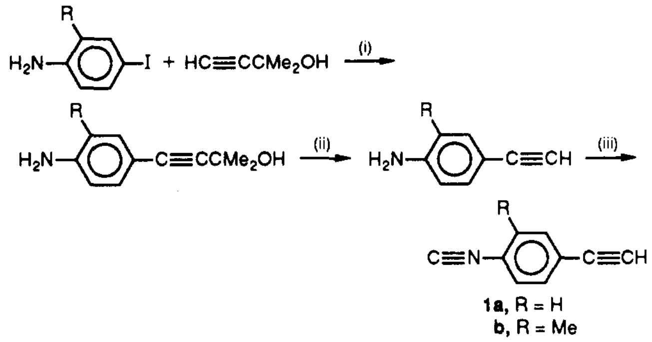
Scheme I[a]



[a] Reagents: (i) Et_2NH, $-[Et_2NH_2]I$; CuI/$[PdCl_2(PPh_3)_2]$ catalyst; (ii) KOH, $-Me_2CO$; (iii) KOH/$CHCl_3$, $[Et_3NCH_2Ph]Cl$ phase-transfer catalyst.

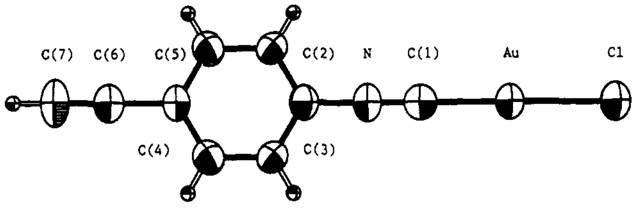
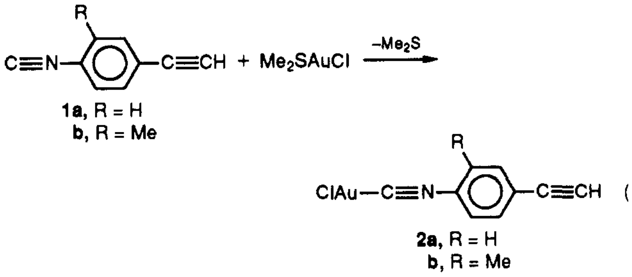


Figure 1. View of the structure of $[ClAuCNC_6H_4CCH]$ (**2a**). Parameters are as follows: Au–Cl = 2.254(3), Au–C(1) = 1.92(1) Å; C(1)–Au–Cl = 178.6(4), N(1)–C(1)–Au = 178(1), C(2)–N(1)–C(1) = 179.6(9)°.

Alkynylgold phosphine complexes $[Au(C{\equiv}CR')(PR_3)]$ can be prepared by the reaction of $[AuCl(PR_3)]$ with $R'C{\equiv}CH$ in the presence of a base such as sodium alkoxide.[13b,20] By analogy, the chlorogold(I) derivatives **2** were prepared (eq 1, Figure 1)[21] and attempts were made to convert them to polymers by elimination of HCl on reaction with bases. However, strong bases such as NaOMe, *n*-BuLi, MeLi, $LiN(CHMe_2)_2$, and Na caused decomposition of **2**, probably by attack at the isocyanide group, while milder bases such as Proton Sponge[22] and sodium acetate failed to react.



(1)

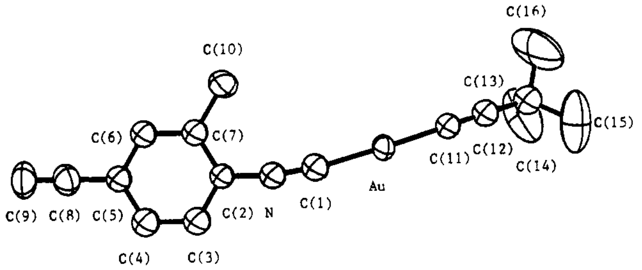
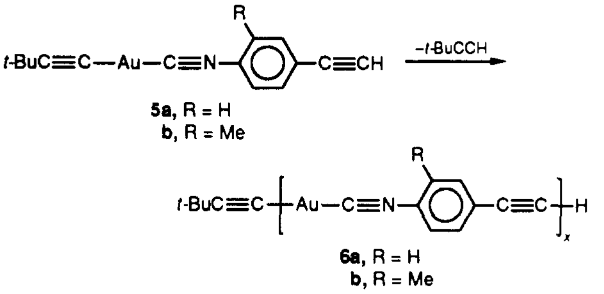


Figure 2. View of the structure of $[t\text{-}BuCCAuCNC_6H_3MeCCH]$ (**5b**). Parameters are as follows: Au–C(1) = 1.95(1), Au–C(11) = 1.96(1) Å; C(11)–Au–C(1) = 173.6(4), N–C(1)–Au = 173.0(9), C(2)–N–C(1) = 169.8(9), C(12)–C(11)–Au = 174(1)°. Note the greater distortion from linearity of **5b** compared to **2a**.

$$\underset{\mathbf{3}}{t\text{-BuC}{\equiv}\text{C—Au—C}{\equiv}\text{NXy}} \xrightarrow[-t\text{-BuCCH}]{4\text{-}O_2NC_6H_4CCH} \underset{\mathbf{4}}{4\text{-}O_2NC_6H_4C{\equiv}\text{C—Au—C}{\equiv}\text{NXy}} \quad (2)$$



(3)

A successful route to the desired polymers was discovered based on the facts that complexes $[t\text{-}BuC{\equiv}CAuL]$ can be prepared by reaction of $[(AuC{\equiv}C\text{-}t\text{-}Bu)_4]$ with ligands L[23] and that a more acidic hydrocarbon RH will displace a less acidic hydrocarbon R′H from [R′AuL].[24] Thus, the complex acetylene *t*-Bu—C≡C—Au-(CN—Ar—C≡CH) should be more acidic than *t*-BuCCH (the 4-isocyanoaryl substituent is more electron-withdrawing than *t*-Bu and coordination of the isocyanide substituent to gold(I) will enhance the acidity) and so it should eliminate *t*-BuCCH with formation of the desired polymer. Since there was no direct analogy for the alkyne elimination step, the reaction of eq 2 (Xy = 2,6-dimethylphenyl) was carried out and was shown to occur quantitatively as monitored by ^1H NMR. The complexes **5** were prepared by reaction of $[(AuC{\equiv}C\text{-}t\text{-}Bu)_4]$ with the corresponding ligand **1** and were readily characterized.[25] The structure of **5b** is shown in Figure 2 and demonstrates that the alkynylgold isocyanide unit has the desired rodlike structure.[25] The pure acetylide complexes are air-stable

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(21) **2a**: NMR in $CDCl_3$ $\delta(^1H)$ = 3.31 [s, 1H, C≡CH], 7.48 [d, *J* = 8.8 Hz, 2H, Ph], 7.60 [d, *J* = 8.8 Hz, 2H, Ph]; IR (Nujol) 2234 [s, ν(N≡C)], 3279 [m, ν(C≡C—H)] cm^{-1}. Anal. Calcd for C_9H_5AuClN: 30.1; H, 1.4. Found: C, 29.9; H, 1.4. **2b**: NMR in $CDCl_3$ $\delta(^1H)$ = 2.43 [s, 3H, Me]; 3.26 [s, 1H, C≡CH]; 7.40–7.47 [m, 3H, Ph]; IR (Nujol) 2216.5 [s, ν(N≡C)], 3260 [m, ν(C≡C—H)] cm^{-1}. Crystal data for **2a**: AuC_9H_5ClN, M_n = 359.57, monoclinic, space group $P2_1/m$, a = 10.042(2) Å, b = 7.067(2) Å, c = 6.596(2) Å, β = 98.79(2)°, V = 462.6(1) $Å^3$, D_c = 2.58 g cm^{-3}, Z = 2, μ = 161.2 cm^{-1}, $F(000)$ = 323.9. Data were collected on an Enraf-Nonius CAD4F diffractometer with Mo Kα radiation (λ = 0.710 73 Å) with graphite monochromator: R = 0.0427, R_w = 0.0402 for 1035 observed reflections ($I \geq 3\sigma(I)$).

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(25) **5a**: NMR in $CDCl_3$ $\delta(^1H)$ = 1.28 [s, 9H, Bu], 3.30 [s, 1H, C≡CH], 7.44 [d, *J* = 8.8 Hz, 2H, Ph], 7.57 [d, *J* = 8.8 Hz, 2H, Ph]; IR (Nujol) 3295 (m), 2215 (s), 2114 (sh), 2042 (br, w) cm^{-1}. Anal. Calcd for $C_{15}H_{14}AuN$: C, 44.5; H, 3.5. Found: C, 43.1; H, 3.4 (the percentages for C and H are low apparently owing to partial loss of Bu—C≡CH when the sample was stored at room temperature; heating **5a** gives BuCCH more rapidly as shown by TGA and MS). **5b**: NMR in $CDCl_3$ $\delta(^1H)$ = 1.27 [s, 9H, Bu], 2.37 [s, 3H, Me], 3.24 [s, 1H, C≡CH], 7.37 [br, 2H, Ph], 7.42 [br, 1H, Ph]; IR (Nujol) 3227 (m), 2201 (s), 2105 (sh), 2030 (br, w) cm^{-1}. Anal. Calcd for $C_{16}H_{16}AuN$: c, 45.8; H, 3.85. Found: C, 45.5; H, 3.7. Crystal data for **5b**: $AuC_{16}H_{16}N$, M_n = 419.29, monoclinic, space group $P2_1/n$, a = 14.225(4) Å, b = 16.196(4) Å, c = 6.747(2) Å, β = 93.86(3)°, V = 1551.0(8) $Å^3$, D_c = 1.80 g cm^{-3}, Z = 4, μ = 91.0 cm^{-1}, $F(000)$ = 791.8. For 1821 ($I \geq 3\sigma(I)$) observed reflections, R = 0.0332 and R_w = 0.0396 (λ(Mo Kα) = 0.710 73 Å).

white solids and are very soluble in halogenated and aromatic hydrocarbons. However, they are thermally unstable. Decomposition occurred slowly in the solid state with an accompanying color change to brown, and a brown solid was precipitated in high yield when a benzene solution was heated at 80 °C. This solid, of structure **6** (eq 3), is insoluble in common organic solvents, and so direct molecular weight determination was not possible. t-BuC≡CH was detected when the reaction of eq 3 was monitored by ^{1}H NMR. The molecular weights are probably low, and the products are oligomers only. Thus, when **5a** or **5b** in benzene was heated at 80 °C for 5–10 h, a brown precipitate which was analyzed as t-Bu—C≡C—(Au—CN—C_6H_4—C≡C)$_{3.75}$—H or t-Bu—C≡C—(Au—CN—C_6H_3Me—C≡C)$_{5.0}$—H was obtained.[26] The strong IR band for ν(CN) shifted slightly from 2215 cm^{-1} in **5a** to 2209 cm^{-1} in **6a**, both frequencies being consistent with coordination to gold(I).[27] The medium-intensity band at 3295 cm^{-1}, due to the acetylenic ν(C—H) for **5a**, was present only as a very weak band, also at 3295 cm^{-1}, in **6a**. The XPS binding energies, calibrated to C(1s) = 284.9 eV, were very similar for **5a** [E_b; Au(4$f_{7/2}$) 85.1; N(1s) 400.1 eV] and **6a** [E_b; Au(4$f_{7/2}$) 85.0; N(1s) 400.1 eV], indicating similar coordination environments.

The brown solids t-Bu—C≡C—(Au—CN—Ar—C≡C)$_x$—H could be dissolved in the presence of excess tertiary phosphines PR_3 (PR_3 = PMe_3, $P(OMe)_3$) in organic solvents such as chloroform, acetone, and benzene with the formation of t-Bu—C≡C—Au—PR_3, CN—Ar—C≡CAu—PR_3 and CN—Ar—C≡CH, with a color change to yellow as the conjugation is lost. When excess PR_3 was removed, re-formation of insoluble brown oligomers occurred.

This work establishes the value of the (isocyanoaryl)-acetylides as bridging units in rigid-rod complexes. Further derivatization is required to give higher solubility and longer chain lengths in the oligomeric products.

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Supplementary Material Available: Tables of crystallographic data and a summary of the structure determination, atomic positional parameters, bond distances and angles, anisotropic thermal parameters, and calculated hydrogen parameters (11 pages). Ordering information is given on any current masthead page.

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(26) **6a**: IR (Nujol) 3295 (vw), 2209 (s), 2120 (sh), 2034 (br, w) cm^{-1}. Anal. Calcd for t-Bu—C≡C—(Au—CN—C_6H_4—C≡C)$_{3.75}$—H: C, 37.23; H, 2.01. Found: C, 36.91; H, 2.16. **6b**: IR (Nujol) 3300 (vw), 2205 (s), 2118 (sh) cm^{-1}. Anal. Calcd for t-Bu—C≡C—(Au—CN—C_6H_3Me—C≡C)$_{5.02}$—H: C, 38.0; H, 2.3. Found: C, 37.6; H, 2.5.

(27) See for example: Puddephatt, R. J.; Treurnicht, I. *J. Organomet. Chem.* 1987, *319*, 129.