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Organometallic Polymers with Gold(I) Centers Bridged by Diphosphines and Diacetylides

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The new ligand, 4,4′-*i*-$Pr_2PC_6H_4C_6H_4P$-*i*-Pr_2 and new digold(I) diacetylides $[(AuC{\equiv}CArC{\equiv}CAu)_x]$, Ar = 1,4-$C_6H_4$, 4,4′-$C_6H_4$-$C_6H_4$, 1,4-$C_6H_2$-2,5-$Me_2$, have been synthesized. Model digold diacetylides were prepared in the following ways: reaction of [ClAu(μ-PP)AuCl], PP = 4,4′-*i*-$Pr_2PC_6H_4C_6H_4P$-*i*-Pr_2 or 1,4-$Ph_2PC_6H_4PPh_2$, with phenylacetylene and base or reaction of $[(AuC{\equiv}CPh)_x]$ with PP gave [PhC≡CAu(μ-PP)AuC≡CPh] while reaction of $[(AuC{\equiv}CArC{\equiv}CAu)_x]$ with PMe_3 gave $[Me_3PAuC{\equiv}C{-}Ar{-}C{\equiv}CAuPMe_3]$. The structure of [PhC≡CAu(μ-PP)AuC≡CPh], PP = 4,4′-*i*-$Pr_2PC_6H_4C_6H_4P$-*i*-Pr_2, was determined by single crystal X-ray diffraction [monoclinic, $P2_1/n$, a = 14.378(2) Å, b = 13.307(3) Å, c = 9.997(1) Å, β = 103.17(1)°, V = 1862.5 Å^3, Z = 2, R = 0.0354, R_w = 0.0333] and shown to adopt a conformation with (phenylethynyl)gold(I) units mutually *anti*. Polymers were prepared in ways similar to those of the model compounds. Thus, polymers $[(C{\equiv}CArC{\equiv}C{-}Au{-}PP{-}Au{-})_x]$, were prepared by reaction of $[(AuC{\equiv}CArC{\equiv}CAu)_x]$ with diphosphines, PP, or by reaction of [ClAu(μ-PP)AuCl] with HC≡C—Ar—C≡CH and base. The latter synthetic method gave polymers with AuCl end groups when PP = 4,4′-*i*-$Pr_2PC_6H_4C_6H_4P$-*i*-Pr_2 but only the derivatives [ClAu(μ-PP)AuC≡C—Ar—C≡CAu(μ-PP)AuCl] when PP = 1,4-$Ph_2PC_6H_4PPh_2$, the difference being attributed to the lower solubility of the phenylphosphine derivative. This work shows that kinked, linear polymers can be prepared successfully with diphosphine bridging ligands and that soluble polymers can be prepared if bulky alkyl substituents on phosphorus are present.

Introduction

There has been increasing interest in inorganic and organometallic polymers because of the expectation that these polymers might exhibit interesting properties either difficult or impossible to achieve with conventional organic polymers.[1] Among the known inorganic/organometallic polymers, the linear-chain metal-containing polymers, with extended conjugation in the polymer backbone, have excited particular interest.[2] For example, polymeric species in which metal centers are bridged by –C≡C—R—C≡C– (R = aromatic rings, disilanes, or disiloxanes),[3] CN—Ar—NC (Ar = aryl),[4] pyrazine, or bipyridine derivatives[5] are attracting great attention and are known to display electrical conducting, nonlinear optical or liquid crystalline properties.

We are interested in synthesis and characterization of new organometallic polymers with conjugated organic fragments in the polymer backbone.[6] One of the approaches to the target polymeric materials is to connect mononuclear or dinuclear complexes with appropriate bridging ligands. The properties of the polymeric species could be easily altered by changing the properties of the metals and/or ligands involved. This report describes the synthesis and characterization of dinuclear gold(I) complexes of diphosphines and diacetylides and their use in the preparation of polymeric gold(I) complexes.

The diphosphines chosen are 1,4-diphosphinobenzene or 4,4′-diphosphinobiphenyl derivatives because of their special geometry favoring bridging. Since phosphines form strong gold–ligand bonds, they should be capable of stabilizing coordination polymers. It is interesting to note that $PPh_2C_6H_4PPh_2$ has recently been used for the synthesis of polynuclear complexes[7] and coordination

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polymers of the formula $[\{\eta^6\text{-}1,4\text{-}(PPh_2)_2C_6H_4[Cr(CO)_2L]\text{-}Rh(CO)Cl\}_n]$ (L = CO, PPh_3).[8] The unusual Ru(I) polymers $(Ru_2(CO)_4(\mu\text{-}O_2CR)_2(\mu\text{-dppm}))_n$ (R = Me, Et; dppm = $Ph_2PCH_2PPh_2$) have also been reported.[9] Aryldiacetylides were chosen since they often form strong metal–ligand bonds, and they have been used for the synthesis of interesting linear polymers.[3]

Experimental Section

All chemicals were used as purchased from Aldrich Chemical Co. unless otherwise stated. $[AuCl(SMe_2)]$,[10] $[AuCl(PMe_3)]$,[11] and 1,4-bis(diphenylphosphino)benzene[12] were prepared by modified literature methods. New diethynylarenes[13] were prepared from the corresponding dibromoarenes and 2-methylbut-3-yn-2-ol using the procedure of Ames et al.[14] and were purified by sublimation. The catalyst CuI was freshly prepared from the reaction of $CuSO_4$ and KI. $[PdCl_2(PPh_3)_2]$[15] was prepared from the reaction of PPh_3 with $[PdCl_2(PhCN)_2]$.[16]

NMR spectra were recorded by using a Varian 200-MHz spectrometer. ^1H and ^{13}C NMR chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. Phosphorus chemical shifts were determined relative to the 85% H_3PO_4 as an external standard. IR spectra were recorded on a Bruker IFS32 spectrometer with Nujol mulls. Differential scanning calorimetry (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.

$4,4'\text{-}(i\text{-}Pr)_2P\text{–}C_6H_4\text{–}C_6H_4\text{–}P(i\text{-}Pr)_2$. To a solution of $4,4'\text{-}Br\text{–}C_6H_4\text{–}C_6H_4\text{–}Br$ (10.0 g, 32 mmol) in THF (60 mL) cooled at −78 °C was added BuLi in hexane (30 mL, 2.5 M, 75 mmol). The mixture was warmed to room temperature and then cooled to −78 °C again. To the reaction mixture was then added $(i\text{-}Pr)_2PCl$ (8 mL, 7.68 g, 76.8 mmol). The reaction mixture was warmed to room temperature and stirred for an additional 1 h to give a clear solution. The solvent was removed completely, and the residue was hydrolyzed with degassed water. The reaction mixture was then extracted with benzene, and the benzene solution was passed through a column of neutral alumina to give a clear solution. The benzene was removed again to give a colorless oil. The oil was redissolved in ether (30 mL), and to the ether solution was added concentrated HCl (7 mL) to give a white precipitate. The clear ether layer was pipetted away, the residue was further washed with ether, and the ether was removed again. To the reaction flask was then added ether (80 mL) and KOH until the aqueous solution became basic. The ether solution was separated from the water layer, and the water layer was further extracted with ether. The ether solutions were combined, and the evaporation of ether produced a white solid. The solid was washed with a small amount of MeOH and then dried under vacuum to give a white solid. NMR in $CDCl_3$: $\delta(^{31}P) = 7.7$ [s]; $\delta(^1H) = 0.95$ [dd, $J = 11.2, 6.9$ Hz, 12H, CH_3], 1.11 [dd, $J = 15.2, 7.1$ Hz, 12H, CH_3], 2.14 [m, 4H, CH], 7.5–7.6 [m, 8H, Ph]; $\delta(^{13}C) = 18.7$ [d, $J = 8.2$ Hz, CH_3], 19.8 [d, $J = 18.1$ Hz, CH], 22.7 [d, $J = 11.0$ Hz, CH_3], 126.3 [d, $J = 5.6$ Hz, 3-Ph], 135.0 [d, $J = 18.5$ Hz, 2-Ph], 140.9 [s, 1-Ph]. Anal. Calcd for $C_{24}H_{36}P_2$: C, 74.58; H, 9.39. Found: C, 74.49; H, 9.23.

$[\{Au_2(C\equiv C—C_6H_4—C_6H_4—C\equiv C)\}_n]$. A solution of $4,4'\text{-}HC\equiv C—C_6H_4—C_6H_4—C\equiv CH$ (0.300 g, 1.48 mmol) and NaO_2CMe (0.60 g, 7.3 mmol) in THF (25 mL)/MeOH (25 mL) was added to a solution of $[AuCl(SMe_2)]$ (0.90 g, 3.06 mmol) in THF (200 mL)/MeOH (100 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): 2000 cm^{-1} [w, $\nu(C\equiv C)$]. Anal. Calcd for $C_{16}H_8Au_2$: C, 32.34; H, 1.36. Found: C, 32.67; H, 1.66.

$[\{Au_2(C\equiv C—C_6H_2Me_2—C\equiv C)\}_n]$. A solution of $1,4\text{-}(HC\equiv C)_2 2,5\text{-}Me_2C_6H_2$ (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 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: 0.48 g, 96%. The solid is insoluble in common organic solvents. IR (Nujol): 2018 cm^{-1} [w, $\nu(C\equiv C)$]. Anal. Calcd for $C_{12}H_8Au_2$: C, 26.39; H, 1.48. Found: C, 25.99; H, 1.44.

$[\{Au_2(C\equiv C—C_6H_4—C\equiv C)\}_n]$. A solution of NaO_2CMe (0.40 g, 4.9 mmol) in THF (5 mL)/MeOH (20 mL) was added to a solution containing $1,4\text{-}HC\equiv C—C_6H_4—C\equiv CH$ (96.5 mg, 0.765 mmol) and $[AuCl(SMe_2)]$ (0.45 g, 1.53 mmol) in 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: 0.36 g, 96%. The solid is insoluble in common organic solvents. IR (Nujol): 2004 cm^{-1} [w, $\nu(C\equiv C)$]. Anal. Calcd for $C_{10}H_4Au_2$: C, 23.18; H, 0.78. Found: C, 23.20; H, 0.78.

$[ClAuPPh_2C_6H_4PPh_2AuCl]$. $1,4\text{-}PPh_2C_6H_4PPh_2$ (0.45 g, 1.0 mmol) was added to a solution of $[AuCl(SMe_2)]$ (0.60 g, 2.0 mmol) in dichloromethane (40 mL). The reaction mixture was stirred at room temperature for $^1/_2$ h to give a cloudy reaction mixture. The volume of the reaction solution was reduced to ca. 10 mL. To the reaction mixture was then added MeOH (30 mL) to give a white precipitate. The precipitate was collected by filtration, washed with MeOH and ether, and dried. Yield: 0.81 g, 88%. NMR in $CDCl_3$: $\delta(^{31}P) = 30.9$ (the chemical shift for the free ligand is −8.0 ppm); $\delta(^1H) = 7.48–7.88$ [m, Ph]. Anal. Calcd for $C_{30}H_{24}Au_2Cl_2P_2$: C, 39.54; H, 2.65. Found: C, 39.51; H, 2.71.

$[ClAuP(i\text{-}Pr)_2C_6H_4\text{–}C_6H_4P(i\text{-}Pr)_2AuCl]$. A mixture of $(i\text{-}Pr)_2PC_6H_4\text{–}C_6H_4P(i\text{-}Pr)_2$ (0.394 g, 1.02 mmol) and $[AuCl(SMe_2)]$ (0.600 g, 2.04 mmol) in dichloromethane (30 mL) was stirred at room temperature for $^1/_2$ h to give a clear solution. The solvent of the reaction mixture was removed completely. To the reaction flask was then added MeOH (30 mL) to give a white precipitate. The precipitate was collected by filtration, washed with MeOH and ether, and dried. Yield: 0.75 g, 86%. NMR in $CDCl_3$: $\delta(^{31}P) = 56.8$ [s]; $\delta(^1H) = 1.07–1.35$ [m, 24H, CH_3], 2.54 [m, 4H, CH], 7.68–7.88 [m, 8H, Ph]. Anal. Calcd for $C_{24}H_{36}Au_2Cl_2P_2$: C, 33.86; H, 4.26. Found: C, 33.82; H, 4.48.

$[(PMe_3)AuC\equiv C—C_6H_4—C_6H_4—C\equiv CAu(PMe_3)]$, Method A. A solution of PMe_3 (0.70 mmol) in THF (5 mL) was added to a suspension of $[\{AuC\equiv C—C_6H_4—C_6H_4—C\equiv CAu\}_x]$ (0.20 g, 0.34 mmol) in dichloromethane (20 mL). The resulting mixture was stirred at room temperature for $^1/_2$ h to give a slightly purple solution. The solution was filtered to give a colorless solution. The solvent was removed completely, and the residue was washed with hexane to give a white solid. The solid was collected by filtration, washed with hexane and ether, and dried. Yield: 0.20 g, 79%. NMR in $CDCl_3$: $\delta(^{31}P) = -2.24$ [s]; $\delta(^1H) = 1.50$ [d, $J = 10.1$ Hz, 18H, CH_3], 7.4–7.5 [m, 8H, Ph]. IR (Nujol): 2106.5 cm^{-1} [m, $\nu(C\equiv C)$]. Anal. Calcd for $C_{22}H_{26}Au_2P_2$: C, 35.40; H, 3.51. Found: C, 35.78; H, 3.90.

$[(PMe_3)AuC\equiv C—C_6H_4—C_6H_4—C\equiv CAu(PMe_3)]$, Method B. A mixture of $[AuCl(PMe_3)]$ (0.10 g, 0.32 mmol), $HC\equiv C—C_6H_4—C_6H_4—C\equiv CH$ (33 mg, 0.16 mmol) and KOH (0.10 g, 1.8 mmol) in THF (20 mL)/MeOH (20 mL) was stirred at room

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temperature overnight to give a white precipitate. The solvent was then removed completely, and the residue was washed with MeOH to give a white solid. The solid was collected by filtration, washed with MeOH, water, MeOH, and ether, and dried. Yield: 93 mg, 78%. The product displayed spectral properties identical to those from method A.

$[(PMe_3)AuC{\equiv}C{-}C_6H_4{-}C{\equiv}CAu(PMe_3)]$. A mixture of $[AuCl(PMe_3)]$ (0.10 g, 0.32 mmol), $HC{\equiv}C{-}C_6H_4{-}C{\equiv}CH$ (20 mg, 0.16 mmol), and KOH (0.10 g, 1.8 mmol) in THF (20 mL)/MeOH (20 mL) was stirred at room temperature for 3 h to give a white precipitate. The solvents were then removed completely, and the residue was washed with MeOH to give a white solid. The solid was collected by filtration, washed with MeOH, water, MeOH, and ether, and dried. Yield: 90 mg, 83%. NMR in $CDCl_3$: $\delta(^{31}P) = -1.32$ [s]; $\delta(^{1}H) = 1.52$ [d, $J = 10.2$ Hz, 18H, CH_3], 7.20 [s, 4H, Ph]. IR (Nujol): 2110 [m], 2034 cm^{-1} [w]. Anal. Calcd for $C_{16}H_{22}Au_2P_2$: C, 28.67; H, 3.31. Found: C, 28.61; H, 3.28.

$[(PMe_3)AuC{\equiv}C{-}C_6H_2Me_2{-}C{\equiv}CAu(PMe_3)]$. A mixture of $[AuCl(PMe_3)]$ (0.10 g, 0.32 mmol), $HC{\equiv}C{-}C_6H_2Me_2{-}C{\equiv}CH$ (24 mg, 0.16 mmol), and KOH (0.10 g, 1.8 mmol) in THF (20 mL)/MeOH (20 mL) was stirred at room temperature overnight to give a white precipitate. The solvents were then removed completely, and the residue was washed with MeOH to give a white solid. The solid was collected by filtration, washed with MeOH, water, MeOH, and ether, and dried. Yield: 94 mg, 84%. NMR in $CDCl_3$: $\delta(^{31}P) = -1.29$ [s]; $\delta(^{1}H) = 1.50$ [d, $J = 10.5$ Hz, 18H, $P{-}CH_3$], 2.37 [s, 6H, $Ph{-}CH_3$], 7.24 [s, 2H, Ph]. IR (Nujol): 2106.5 [m], 2037 cm^{-1} [w]. Anal. Calcd for $C_{18}H_{26}Au_2P_2$: C, 30.96; H, 3.75. Found: C, 30.71; H, 3.70.

$[PhC{\equiv}CAuPPh_2C_6H_4PPh_2AuC{\equiv}CPh]$. A mixture of $[ClAuPPh_2C_6H_4PPh_2AuCl]$ (0.10 g, 0.11 mmol), $PhC{\equiv}CH$ (0.10 g, 0.98 mmol), and KOH (0.10 g, 1.8 mmol) in THF (20 mL)/MeOH (20 mL) was stirred at room temperature for 8 h to give a cloudy reaction mixture. The solvents were then removed completely, and the residue was washed with MeOH to give a white solid. The solid was collected by filtration, washed with MeOH and ether, and dried. Yield: 90 mg, 79%. NMR in $CDCl_3$: $\delta(^{31}P) = 39.8$ [s]; $\delta(^{1}H) = 7.20$–7.61 [m, Ph]. IR (Nujol): no bands due to $\nu(C{\equiv}C)$ between 2000 and 2200 cm^{-1} were observed. Anal. Calcd for $C_{46}H_{34}Au_2P_2$: C, 52.99; H, 3.29. Found: C, 52.43; H, 3.20.

$[PhC{\equiv}CAuP(i\text{-}Pr)_2C_4H_4{-}C_6H_4P(i\text{-}Pr)_2AuC{\equiv}CPh]$. A mixture of $[ClAuP(i\text{-}Pr)_2C_6H_4{-}C_6H_4P(i\text{-}Pr)_2AuCl]$ (0.20 g, 0.235 mmol), $PhC{\equiv}CH$ (0.10 g, 0.98 mmol), and KOH (0.15 g, 2.7 mmol) in THF (20 mL)/MeOH (20 mL) was stirred at room temperature for 10 h to give a cloudy reaction mixture. The solvents were then removed completely, and the residue was extracted with chloroform. The chloroform of the extract was removed, and the residue was washed with MeOH to give a white solid. The solid was collected by filtration, washed with MeOH and dried. Yield: 0.18 g, 78%. NMR in $CDCl_3$: $\delta(^{31}P) = 60.5$ [s]; $\delta(^{1}H) = 1.08$–1.37 [m, 24H, CH_3], 2.59 [m, 4H, CH], 7.21–7.90 [m, 18H, Ph]. IR (Nujol): 2112 cm^{-1} [w]. Anal. Calcd for $C_{40}H_{46}Au_2P_2$: C, 48.94; H, 4.65. Found: C, 48.34; H, 4.72.

$[Au{-}C{\equiv}C{-}C_6H_4{-}C_6H_4{-}C{\equiv}C{-}AuP(i\text{-}Pr)_2C_6H_4{-}C_6H_4P(i\text{-}Pr)_2]_x$, Method A. A mixture of $[ClAuP(i\text{-}Pr)_2C_6H_4{-}C_6H_4P(i\text{-}Pr)_2AuCl]$ (0.20 g, 0.235 mmol), $HC{\equiv}C{-}C_6H_4{-}C_6H_4{-}C{\equiv}CH$ (48 mg, 0.237 mmol), and KOH (0.15 g, 2.7 mmol) in THF (20 mL)/MeOH (20 mL) was stirred at room temperature overnight to give a yellow precipitate. The precipitate was collected by filtration, washed with MeOH, water, MeOH, and ether, and dried. Yield: 0.20 g, 87%. NMR in $CDCl_3$: $\delta(^{31}P) = 60.3$ [s], 56.7 [s]; $\delta(^{1}H) = 1.07$–1.38 [m, 24H, CH_3], 2.60 [m, 4H, CH], 7.36–8.38 [m, 16H, Ph]. IR (Nujol): 2035 cm^{-1} [w]. Anal. Calcd for $C_{40}H_{44}Au_2P_2$: C, 48.99; H, 4.52. Found: C, 48.30; H, 4.34.

$[Au{-}C{\equiv}C{-}C_6H_4{-}C_6H_4{-}C{\equiv}C{-}AuP(i\text{-}Pr)_2C_6H_4{-}C_6H_4P(i\text{-}Pr)_2]_x$, Method B. A mixture of $P(i\text{-}Pr)_2C_6H_4{-}C_6H_4P(i\text{-}Pr)_2$ (50.0 mg, 0.129 mmol) and $[\{AuC{\equiv}C{-}C_6H_4{-}C_6H_4{-}C{\equiv}CAu\}_x]$ (76.9 mg, 0.129 mmol) in dichloromethane (70 mL) was stirred at room temperature for 8 h to give a slightly cloudy solution. The insoluble material was removed by filtration. The solvent was removed from the filtrate by using a rotary evaporator and the residue was washed with MeOH to give a pale-yellow powder. The powder was collected by filtration, washed with MeOH and ether, and dried. Yield: 87 mg, 70%. NMR in $CDCl_3$: $\delta(^{31}P) = 60.5$ [s]; $\delta(^{1}H) = 1.12$–1.37 [m, 24H, CH_3], 2.62 [m, 4H, CH], 7.48–7.90 [m, 16H, Ph]. IR (Nujol): 2112 cm^{-1} [w]. Anal. Calcd for $C_{40}H_{44}Au_2P_2$: C, 48.99; H, 4.52. Found: C, 49.55; H, 5.06.

$[ClAuPPh_2C_6H_4PPh_2Au{-}C{\equiv}C{-}C_6H_4{-}C_6H_4{-}C{\equiv}C{-}AuPPh_2C_6H_4PPh_2AuCl]$. A mixture of $[ClAuPPh_2C_6H_4PPh_2AuCl]$ (0.150 g, 0.165 mmol), $HC{\equiv}C{-}C_6H_4{-}C_6H_4{-}C{\equiv}CH$ (33.0 mg, 0.163 mmol), and KOH (0.20 g, 3.6 mmol) in THF (20 mL)/MeOH (20 mL) was stirred at room temperature overnight to give a yellow precipitate. The precipitate was collected by filtration, washed with MeOH, water, MeOH, and ether, and dried. Yield: 155 mg, 91%. NMR in $CDCl_3$: $\delta(^{31}P) = 40.0$ [s], 30.7 [s]; $\delta(^{1}H) = 7.34$–7.53. IR (Nujol): 2108 cm^{-1} [w]. Anal. Calcd for $C_{76}H_{56}Au_4Cl_2P_4$: C, 46.77; H, 2.89; Cl, 3.63. Found: C, 46.63; H, 2.87; Cl, 3.21.

$[\{Au{-}C{\equiv}C{-}C_6H_4{-}C_6H_4{-}C{\equiv}C{-}AuPPh_2C_6H_4PPh_2\}_x]$. A mixture of $PPh_2C_6H_4PPh_2$ (50 mg, 0.112 mmol) and $[\{AuC{\equiv}C{-}C_6H_4{-}C_6H_4{-}C{\equiv}CAu\}_x]$ (66.5 mg, 0.112 mmol) in dichloromethane (70 mL) was stirred at room temperature overnight to give an off-white precipitate. The precipitate was collected by filtration, washed with MeOH and ether, and dried. Yield: 102 mg, 88%. The product is insoluble in common organic solvents. IR (Nujol): 2113 cm^{-1} [w]. Anal. Calcd for $C_{48}H_{32}Au_2P_2$: C, 53.09; H, 3.10. Found: C, 52.42; H, 3.24.

$[Au{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}AuP(i\text{-}Pr)_2C_6H_4{-}C_6H_4(i\text{-}Pr)_2]_x$, Method A. A mixture of $[ClAuP(i\text{-}Pr)_2C_6H_4{-}C_6H_4P(i\text{-}Pr)_2AuCl]$ (0.20 g, 0.235 mmol), $HC{\equiv}C{-}C_6H_4{-}C{\equiv}CH$ (30 mg, 0.238 mmol), and KOH (0.15 g, 2.6 mmol) in THF (25 mL)/MeOH (25 mL) was stirred at room temperature overnight to give a yellow precipitate. The precipitate was collected by filtration, washed with MeOH, water, MeOH, and ether, and dried. Yield: 0.18 g, 85%. NMR in $CDCl_3$: $\delta(^{31}P) = 60.5$, 56.7 [s]; $\delta(^{1}H) = 1.07$–1.37 [m, 24H, CH_3], 2.60 [m, 4H, CH], 7.40 [s, 4H, C_6H_4], 7.69–7.90 [m, 8H, Ph—Ph]. IR (Nujol): 2099 cm^{-1} [w]. Anal. Calcd for $C_{34}H_{40}Au_2P_2$: C, 45.15; H, 4.46. Calcd for $(C_{34}H_{40}Au_2P_2)_{20}{\cdot}C_{24}H_{36}Au_2Cl_2P_2$: C, 44.6; H, 4.45; Cl, 0.4. Found: C, 44.32; H, 4.32; Cl, 0.3.

$[Au{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}AuP(i\text{-}Pr)_2C_6H_4{-}C_6H_4(i\text{-}Pr)_2]_x$, Method B. A mixture of $P(i\text{-}Pr)_2C_6H_4{-}C_6H_4P(i\text{-}Pr)_2$ (50.0 mg, 0.129 mmol) and $[\{AuC{\equiv}C{-}C_6H_4{-}C{\equiv}CAu\}_x]$ (67.0 mg, 0.129 mmol) in dichloromethane (70 mL) was stirred at room temperature overnight to give a slightly cloudy solution. The insoluble material was removed by filtration. The solvent of the filtration was removed on a rotary evaporator, and the residue was washed with MeOH to give a pale-yellow powder. The powder was collected by filtration, washed with MeOH and ether, and dried. Yield: 82 mg, 70%. NMR in $CDCl_3$: $\delta(^{31}P) = 60.8$ [s]; $\delta(^{1}H) = 1.07$–1.36 [m, 24H, CH_3], 2.56 [m, 4H, CH], 7.41 [s, 4H, C_6H_4], 7.69–7.90 [m, 8H, Ph—Ph]. IR (Nujol): 2110 cm^{-1} [w]. Anal. Calcd for $C_{34}H_{40}Au_2P_2$: C, 45.15; H, 4.46. Found: C, 46.02; H, 4.69.

$[ClAuPPh_2C_6H_4PPh_2Au{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}AuPPh_2C_6H_4PPh_2AuCl]$. A mixture of $[ClAuPPh_2C_6H_4\text{-}PPh_2AuCl]$ (0.150 g, 0.165 mmol), $HC{\equiv}C{-}C_6H_4{-}C{\equiv}CH$ (20.0 mg, 0.158 mmol) and KOH (0.20 g, 3.6 mmol) in THF (20 mL)/MeOH (20 mL) was stirred at room temperature overnight to give a yellow precipitate. The precipitate was collected by filtration, washed with MeOH, water, MeOH, and ether, and dried. Yield: 140 mg, 92%. NMR in $CDCl_3$: $\delta(^{31}P) = 40.1$ [s], 30.7 [s]; $\delta(^{1}H) = 7.34$–7.53. IR (Nujol): 2129 cm^{-1} [w]. Anal. Calcd for $C_{70}H_{52}Au_4Cl_2P_4$: C, 44.82; H, 2.79; Cl, 3.78. Found: C, 44.39; H, 2.65; Cl, 3.29.

$[Au{-}C{\equiv}C{-}C_6H_4{-}C{\equiv}C{-}AuPPh_2C_6H_4PPh_2]_x$. A mixture of $PPh_2C_6H_4PPh_2$ (50 mg, 0.112 mmol) and $[\{AuC{\equiv}C{-}C_6H_4{-}C{\equiv}CAu\}_x]$ (58.0 mg, 0.112 mmol) in dichloromethane (70 mL) was stirred at room temperature overnight to give an off-white precipitate. The precipitate was collected by filtration, washed with MeOH and ether, and dried. Yield: 94 mg, 87%. The product is insoluble in common organic solvents. IR

(Nujol): 2118 cm^{-1} [w]. Anal. Calcd for $C_{40}H_{28}Au_2P_2$: C, 49.81; H, 2.93. Found: C, 49.65; H, 3.02.

[Au—C≡C—$C_6H_2Me_2$—C≡C—AuP(*i*-Pr)$_2$$C_6H_4$—$C_6H_4$P(*i*-Pr)$_2$]$_x$, Method A. A mixture of [ClAuP(*i*-Pr)$_2$$C_6H_4$—$C_6H_4$P(*i*-Pr)$_2$AuCl] (0.20 g, 0.235 mmol), HC≡C—C_6H_4—C≡CH (37 mg, 0.240 mmol), and KOH (0.15 g, 2.6 mmol) in THF (20 mL)/MeOH (20 mL) was stirred at room temperature overnight to give a yellow precipitate. The precipitate was collected by filtration, washed with MeOH, water, MeOH, and ether, and dried. Yield: 0.186 g, 85%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 60.5 [s], 56.7 [s]; $\delta(^{1}H)$ = 1.07–1.36 [m, 24H, CH_3], 2.45 [s, 6H, $C_6H_2Me_2$], 2.47 [m, 4H, CH], 7.34 [s, 2H, $C_6H_2Me_2$], 7.69–7.90 [m, 8H, Ph—Ph]. IR (Nujol): 2093 cm^{-1} [w]. Anal. Calcd for $C_{36}H_{44}Au_2P_2$: C, 46.36; H, 4.76. Calcd for $(C_{36}H_{44}Au_2P_2)_{20}{\cdot}C_{24}H_{36}Au_2Cl_2P_2$: C, 45.8; H, 4.7; Cl, 0.4. Found: C, 45.57; H, 4.50; Cl, 0.3.

[Au—C≡C—$C_6H_2Me_2$—C≡C—AuP(*i*-Pr)$_2$$C_6H_4$—$C_6H_4$P(*i*-Pr)$_2$]$_x$, Method B. A mixture of P(*i*-Pr)$_2$$C_6H_4$—$C_6H_4$P(*i*-Pr)$_2$ (50.0 mg, 0.129 mmol) and [{AuC≡C—$C_6H_2Me_2$—C≡CAu}$_x$] (70.0 mg, 0.129 mmol) in dichloromethane (70 mL) was stirred at room temperature overnight to give a slightly cloudy solution. The insoluble material was removed by filtration. The solvent of the filtration was removed on a rotary evaporator, and the residue was washed with MeOH to give a pale-yellow powder. The powder was collected by filtration, washed with MeOH and ether, and dried. Yield: 82 mg, 68%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 60.4 [s]; $\delta(^{1}H)$ = 1.07–1.37 [m, 24H, CH_3], 2.45 [s, 6H, $C_6H_2Me_2$], 2.47 [m, 4H, CH], 7.34 [s, 2H, $C_6H_2Me_2$], 7.70–7.90 [m, 8H, Ph—Ph]. IR (Nujol): 2098 cm^{-1} [w]. Anal. Calcd for $C_{36}H_{44}Au_2P_2$: C, 46.36; H, 4.76. Found: C, 45.90; H, 4.66.

[ClAuPPh$_2$$C_6H_4PPh_2$Au—C≡C—$C_6H_2Me_2$—C≡C—AuPPh$_2$$C_6H_4PPh_2$AuCl]. A mixture of [ClAuPPh$_2$$C_6H_4PPh_2$AuCl] (0.150 g, 0.165 mmol), HC≡C—$C_6H_2Me_2$—C≡CH (25.0 mg, 0.158 mmol), and KOH (0.20 g, 3.6 mmol) in THF (20 mL)/MeOH (20 mL) was stirred at room temperature overnight to give a yellow precipitate. The precipitate was collected by filtration, washed with MeOH, water, MeOH, and ether, and dried. Yield: 142 mg, 88%. NMR in $CDCl_3$: $\delta(^{31}P)$ = 40.1 [s], 30.7 [s]; $\delta(^{1}H)$ = 2.40 [s, 6H, $C_6H_2Me_2$], 7.34–7.56 [br, 12H, Ph]. IR (Nujol): no bands assignable to ν(C≡C) were observed. Anal. Calcd for $C_{72}H_{56}Au_4Cl_2P_4$: C, 45.42; H, 2.96; Cl, 3.72. Found: C. 44.68; H, 2.85; Cl, 3.04.

[Au—C≡C—$C_6H_2Me_2$—C≡C—AuPPh$_2$$C_6H_4PPh_2$]$_x$. A mixture of PPh$_2$$C_6H_4PPh_2$ (50 mg, 0.112 mmol) and [{AuC≡C—$C_6H_2Me_2$—C≡CAu}$_x$] (61.2 mg, 0.112 mmol) in dichloromethane (70 mL) was stirred at room temperature overnight to give an off-white precipitate. The precipitate was collected by filtration, washed with MeOH and ether, and dried. Yield: 97 mg, 87%. The product is insoluble in common organic solvents. IR (Nujol): 2112 cm^{-1} [w]. Anal. Calcd for $C_{42}H_{32}Au_2P_2$: C, 50.82; H, 3.25. Found: C, 49.83; H, 3.16.

Crystallographic Analysis of [PhC≡CAuP(*i*-Pr)$_2$$C_6H_4$—$C_6H_4$P(*i*-Pr)$_2$AuC≡CPh]. A colorless crystal (dimensions 0.13 × 0.24 × 0.30 mm) was mounted in air on a glass fiber with epoxy cement. The data collection was carried out at 23 °C on an Enraf-Nonius CAD4F diffractometer using graphite monochromated Mo Kα radiation.[17] The cell constants and the orientation matrix were obtained from photoindexing and automatic indexing routines followed by least-squares fits of 21 accurately centered reflections ($25.0 \leq 2\theta \leq 41.7°$). Intensity data were recorded in the θ–2θ mode, at variable scan speeds (0.97–4.1° min^{-1}) and a scan width of $(0.85 + 0.35 \tan\theta)°$, with a maximum time per datum of 60 s. Static background measurements were made at the end points of the width $(0.95 + \tan\theta)°$. Three standard reflections were monitored every 180 min and showed a random decay of 1.3% over the total period of 40.4 h. In all, 4061 data in the range 2θ = 0–50° and 56 standards were recorded. Data processing was carried out by using the NRCVAX Crystal Structure programs[18] running on a SUN 3/80 workstation. An empirical absorption correction was applied,[19] based upon the ψ scans of nine reflections with θ ranging from 3.7 to 16.3°. Equivalent reflections averaged (R_f = 0.023) to give 3265 data for structure solution and refinement. The cell parameters and the systematic absences[20a] indicated a monoclinic space group, $P2_1/n$ with $Z = 2$ and, this imposes the presence of an inversion center in the molecule. The correctness of the choice of this space group was confirmed by successful solution and refinement of the structure. The structure was solved by SHELXS-86[21] and subsequent difference Fourier techniques. Refinement was by full-matrix least-squares techniques on F, using the SHELX-76 software[22] running on a SUN 3/80 workstation. Scattering factors for neutral, non-hydrogen atoms were taken from ref 20b. The benzene rings were treated as regular hexagons with C–C = 1.395 Å. The hydrogen atoms were placed in the ideal positions (C–H = 0.95 Å) and were included in the least-squares cycles for the structure factor calculations only. Anisotropic thermal parameters were assigned for all the non-hydrogen atoms with the exception of phenyl ring carbons and were refined in the least-squares cycles. In the final least-squares cycle the refinement of 117 variables and 2308 ($I \geq 3\sigma(I)$) data converged at agreement factors R = 0.0354 and R_w = 0.0333 using the weighting scheme, $w = k/\sigma^2(F_o) + gF^2$ where k = 2.3324 and g = 0.000 178. The extinction parameter was refined to 3.4(5) × 10^{-4}. The top five peaks in the final difference Fourier synthesis have electron densities in the range 0.672–0.791 e Å^{-3}; of these the top three were associated with the Au atom at distances of 0.99–1.09 Å. The largest shift/error in the final cycle was −0.035. The experimental details and crystal data, the positional and U_{eq} thermal parameters are given in Tables I and II, respectively. Selected bond lengths and angles are listed in Table III. Tables of aniostropic thermal parameters and calculated hydrogen atom positional parameters are given as supplementary material.

Results and Discussion

Ligand Synthesis. The ligand (*i*-Pr)$_2$PC_6H_4–C_6H_4P(*i*-Pr)$_2$ was prepared by the reaction of 2 equiv of ClP(*i*-Pr)$_2$ with LiC_6H_4–C_6H_4Li generated in situ by treatment of BrC_6H_4–C_6H_4Br with BuLi (eq 1). The ligand can be

$$\mathrm{BrC_6H_4{-}C_6H_4Br} \xrightarrow[\text{2. ClP}(i\text{-Pr})_2]{\text{1. BuLi}} (i\text{-Pr})_2\mathrm{PC_6H_4{-}C_6H_4P}(i\text{-Pr})_2 \tag{1}$$

purified by protonation and deprotonation and column chromatography. The procedure is similar to that for the preparation of analogous compound PPh$_2$$C_6H_4$–$C_6H_4PPh_2$[23] and α,ω-bis(diphenylphosphino)polyether.[24] The ^{31}P NMR spectrum of the new ligand displays one singlet at 7.7 ppm, while two sets of methyl signals and one set of P–CH and aromatic ring signals were observed in both the ^{1}H and ^{13}C NMR spectra (see data in Experimental Section). The inequivalence of the methyl groups of each Me_2CH–P

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Table I. Summary of X-ray Structure Determination

compd, fw	$C_{40}H_{47}Au_2P_2$, 982.69
cryst syst, space group	monoclinic $P2_1/n$
cell dimens	
a (Å)	14.378(2)
b (Å)	13.307(3)
c (Å)	9.997(1)
β (deg)	103.17(1)
cell vol (Å^3), Z	1862.5(3), 2
density (g·cm^{-3}) (obsd, calcd)	1.75(5), 1.752
$F(000)$	948
diffractometer, monochromator	Enraf-Nonius CAD4F; graphite
radiation, wavelength (Å)	Mo Kα, 0.710 73
abs coeff (cm^{-1})	76.7
transm max, min	0.202, 0.119
no. of observ, variables	2308 ($I \geq 3\sigma(I)$), 117
final model; R and R_w	0.0354, 0.0333

Table II. Atomic Positional (×10^4) and Thermal (×10^3) Parameters

atom	x	y	z	U_{eq} (Å^2)
Au	2720.8(2)	2893.0(2)	6367.1(4)	42.1(1)*
P	1239(2)	2437(2)	6616.2	35(1)*
C(1)	4058(7)	3316(7)	6400(9)	50(3)*
C(2)	4860(7)	3580(7)	6572(10)	50(3)*
C(3)	259(6)	2519(7)	5079(9)	52(3)*
C(4)	−708(6)	2224(7)	5345(11)	71(4)*
C(5)	221(8)	3542(7)	4422(11)	87(4)*
C(6)	1244(6)	1142(6)	7240(9)	43(3)*
C(7)	2015(6)	1018(6)	8555(9)	57(3)*
C(8)	1394(6)	418(6)	6141(9)	56(3)*
C(11)	872(4)	3260(3)	7882(5)	34(2)
C(12)	297(4)	2928(3)	8745(5)	45(2)
C(13)	−33(4)	3610(3)	9591(5)	56(2)
C(14)	212(4)	4624(3)	9574(5)	31(2)
C(15)	786(4)	4956(3)	8712(5)	44(2)
C(16)	1116(4)	4274(3)	7865(5)	45(2)
C(21)	5840(4)	3933(4)	6839(6)	50(2)
C(22)	6052(4)	4934(4)	6621(6)	65(3)
C(23)	7000(4)	5258(4)	6914(6)	89(4)
C(24)	7735(4)	4580(4)	7426(6)	86(4)
C(25)	7523(4)	3579(4)	7644(6)	94(4)
C(26)	6575(4)	3256(4)	7351(6)	76(3)

[a] Values marked with an asterisk refer to atoms that were assigned anisotropic thermal parameters given as the isotropic equivalent displacement parameter defined as $U_{eq} = {}^1/_3\sum_i\sum_j U_{ij} \cdot a^*_i \cdot a^*_j \cdot \mathbf{a}_i \cdot \mathbf{a}_j$.

Table III. Selected Bond Distances (Å) and Angles (deg)

Au–P	2.282(2)	Au–C(1)	1.997(9)
P–C(3)	1.837(9)	P–C(6)	1.832(8)
P–C(11)	1.840(5)	C(1)–C(2)	1.179(11)
C(2)–C(21)	1.451(11)	C(3)–C(4)	1.526(12)
C(3)–C(5)	1.506(12)	C(6)–C(7)	1.523(11)
C(6)–C(8)	1.513(11)	C(14)–C(14)′	1.528(9)
C(1)–Au–P	172.9(3)	C(3)–P–Au	116.8(3)
C(6)–P–Au	110.8(3)	C(11)–P–Au	109.8(2)
C(6)–P–C(3)	106.5(4)	C(11)–P–C(3)	104.7(3)
C(11)–P–C(6)	107.8(3)	C(2)–C(1)–Au	172.7(9)
C(21)–C(2)–C(1)	177.2(9)	C(4)–C(3)–P	113.3(7)
C(5)–C(3)–P	111.3(7)	C(5)–C(3)–C(4)	111.4(8)
C(7)–C(6)–P	110.0(6)	C(8)–C(6)–P	110.0(6)
C(8)–C(6)–C(7)	111.2(7)	C(12)–C(11)–P	122.7(1)
C(16)–C(11)–P	117.0(1)	C(22)–C(21)–C(2)	121.3(4)
C(26)–C(21)–C(2)	118.7(4)		

group is expected since there is no plane of symmetry containing the P–C bond.[25]

Preparation of Binuclear Gold(I) Complexes. The simplest routes to monomeric gold alkynyl phosphine complexes of the type [RC≡CAu(PR$_3$)] include the reaction of [(AuC≡CR)$_x$] with PR$_3$ (eq 2)[26] and the reaction of RC≡CH with [ClAu(PR$_3$)] in the presence of a strong base (eq 3).[27] Thus, it is expected that polymer compounds might be prepared from the similar reaction of a linear gold(I) diacetylide complex [(AuC≡C—Ar—C≡CAu)$_x$] with a bridging diphosphine or the reaction of a dinuclear gold(I) diphosphine complex [ClAuPR$_2$—Ar—PR$_2$AuCl] with a potentially bridging diethynylarene, HC≡C—Ar—C≡CH in the presence of a base. Thus the complexes [(AuC≡C—Ar—C≡CAu)$_x$] and [ClAuPR$_2$—Ar—PR$_2$AuCl] were prepared as potential polymer precursors.

$$(\mathrm{AuC{\equiv}CR})_x + \mathrm{PR_3} \rightarrow \mathrm{RC{\equiv}C{-}Au{-}PR_3} \quad (2)$$

$$\mathrm{ClAu(PR_3)} + \mathrm{RC{\equiv}CH} + \mathrm{B} \rightarrow \mathrm{RC{\equiv}C{-}Au(PR_3)} + \mathrm{BH^+X^-} \quad (3)$$

The complexes [(Au—C≡C—Ar—C≡C—Au)$_x$] (**1a**, Ar = 4,4′-C_6H_4-C_6H_4; **1b**, Ar = 1,4-C_6H_4; **1c**, Ar = 1,4-C_6H_2-2,5-Me_2) were prepared from the essentially quantitative reactions of 2 equiv of [AuCl(SMe$_2$)] with the appropriate diethynylarene in the presence of sodium acetate as a base (eq 4). All the complexes are air stable, yellow powders

$$2[\mathrm{AuCl(SMe_2)}] + \mathrm{HC{\equiv}C{-}Ar{-}C{\equiv}CH} + 2\mathrm{NaO_2CMe} \rightarrow (\mathrm{Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}Au})_x + 2\mathrm{NaCl} + 2\mathrm{HO_2CMe} \quad (4)$$

which are insoluble in common organic solvents. They were characterized by elemental analysis, IR spectroscopy, and their subsequent reactions (see below). The ν(C≡C) bands in the infrared spectra were observed as weak bands around 2000 cm^{-1}. These digold complexes resemble in appearance (phenylethynyl)gold(I) which is proposed to be a coordination polymer in which the acetylide is σ-bonded to one gold atom and π-bonded to another.[26] The digold diacetylides are probably also polymeric in nature. To our knowledge, similar dinuclear gold(I) acetylide complexes are rare, the only characterized example being the explosive gold(I) acetylide Au_2C_2 which was reported as early as 1900.[28] Complexes **1a**–**1c** do not appear to be explosive but should be handled with caution.

The complexes [ClAuPR$_2$-Ar-PR$_2$AuCl] (**2a**, R = Ph, Ar = 1,4-C_6H_4; **2b**, R = i-Pr, Ar = 4,4′-C_6H_4–C_6H_4) were readily prepared from the reactions of 2 equiv of [AuCl(SMe$_2$)] with PR$_2$–Ar–PR$_2$ (eq 5). The compounds were

$$2\mathrm{AuCl(SMe_2)} + \mathrm{Pr_2{-}Ar{-}PR_2} \rightarrow \mathrm{ClAuPR_2{-}Ar{-}PR_2AuCl} + 2\mathrm{SMe_2} \quad (5)$$

characterized by elemental analysis and NMR (^{1}H and ^{31}P) spectroscopy. The ^{31}P resonances for the Au complexes shifted (40 ppm for **2a** and 49 ppm for **2b**) downfield compared to the free ligands. The downfield shift is in the range reported for the phosphine coordination chemical shifts of [AuCl(PR$_3$)] complexes, for example, 38.7 ppm for [AuCl(PPh$_3$)] and 55.0 ppm for [AuCl(PPhEt$_2$)].[29] Like the free ligand, the ^{1}H NMR spectrum of [ClAuP(i-Pr)$_2$C$_6$H$_4$–C$_6$H$_4$P(i-Pr)$_2$AuCl], **2b**, displays two sets of

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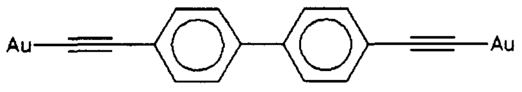
[27] (a) Bruce, M. I.; Horn, E.; Matisons, J. G.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1163. (b) Cross, R.; Davidson, R. J.; McLennan, M. F. *J. Chem. Soc., Dalton Trans.* **1986**, 411. (c) Cross, R.; Davidson, R. J.; McLennan, M. F. *J. Organomet. Chem.* **1984**, *265*, C37.

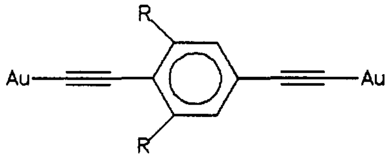
[28] Matthews, J. A.; Watters, L. L. *J. Am. Chem. Soc.* **1900**, *22*, 108.

[29] See, for example: (a) Attar, S.; Bearden, W. H.; Alcock, N. W.; Alyea, E. C.; Nelson, J. H. *Inorg. Chem.* **1990**, *29*, 425. (b) Al-Sa'ady, A. H.; McAuliffe, C. A.; Moss, K.; ("Dick") Parish, R. V.; Field, R. *J. Chem. Soc., Dalton Trans.* **1984**, 491.

Chart I

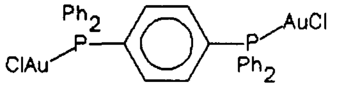


1a

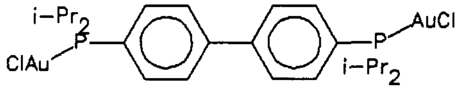


1b, R = H

1c, R = Me

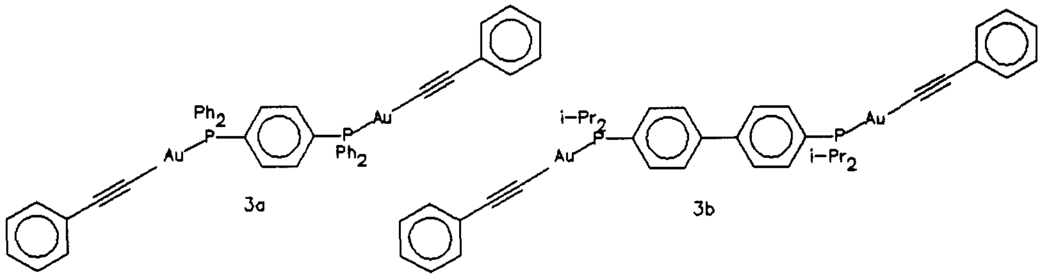


2a



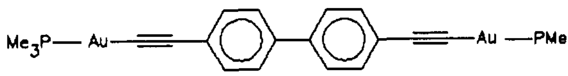
2b

Chart II

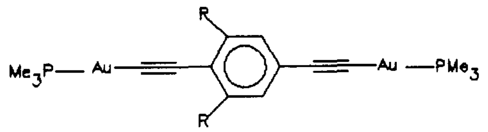


3a

3b



4a



4b, R = H

4c, R = Me

methyl signals and one signal for the aromatic and the P–CH protons (see data in Experimental Section).

Reactivity of the Precursor Dinuclear Gold(I) Complexes: The Modeling Reactions. As expected, dinuclear gold(I) phosphine acetylide complexes were readily prepared from either [$ClAuPR_2$—Ar—PR_2AuCl], **2**, or [($AuC{\equiv}C$—Ar—$C{\equiv}CAu)_x$], 1. Treatment of **2a** or **2b** with $PhC{\equiv}CH$ in the presence of KOH or MeONa produced the corresponding diacetylide complexes [$PhC{\equiv}CAuPR_2$—Ar—$PR_2AuC{\equiv}CPh$], **3a** or **3b**, respectively (eq 6). In the IR spectrum, a weak band at 2112 cm^{-1},

$$ClAuPR_2{-}Ar{-}PR_2AuCl + 2PhC{\equiv}CH + 2KOH \rightarrow PhC{\equiv}CAuPR_2{-}Ar{-}PR_2AuC{\equiv}CPh + 2H_2O + 2KCl \quad (6)$$

assignable to $\nu(C{\equiv}C)$, was observed for [$PhC{\equiv}CAuP(i\text{-}Pr)_2C_6H_4$—$C_6H_4P(i\text{-}Pr)_2AuC{\equiv}CPh$], **3b**, whereas $\nu(C{\equiv}C)$ must be too weak to be observed for the analogous compound [$PhC{\equiv}CAuPPh_2C_6H_4PPh_2AuC{\equiv}CPh$], **3a**. The ^{31}P NMR spectra display resonances at 39.8 ppm for **3a** and 60.5 ppm for **3b**; both are shifted downfield compared to the parent chloride gold(I) complexes. This is in agreement with the reported observation that the ^{31}P chemical shifts for alkynylgold monophosphine complexes are slightly downfield from those of the analogous chlorogold complexes.[27b] Like the free ligand and the corresponding chloride complex, the ^1H NMR spectrum of [$PhC{\equiv}CAuP(i\text{-}Pr)_2C_6H_4$—$C_6H_4P(i\text{-}Pr)_2AuC{\equiv}CPh$], **3b**, displays two sets of methyl signals (see data in Experimental Section).

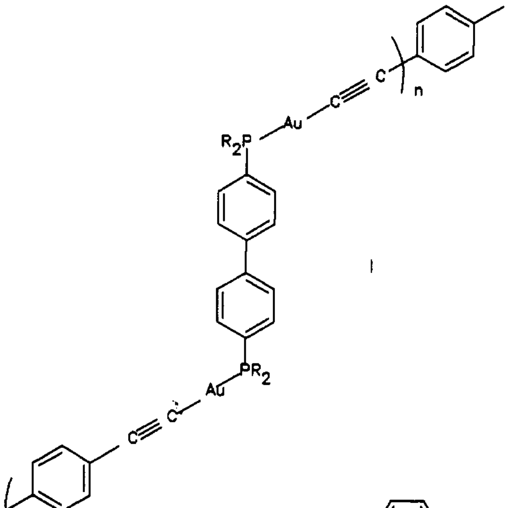
Reactions of the diacetylide complexes [(Au—$C{\equiv}C$—Ar—$C{\equiv}C$—$Au)_x$], **1**, with 2 equiv of PMe_3 produced the corresponding phosphine complexes [Me_3PAu—$C{\equiv}C$—Ar—$C{\equiv}C$—$AuPMe_3$] (**4a**, Ar = 4,4′-C_6H_4—C_6H_4; **4b**, 1,4-C_6H_4; **4c**, 1,4-C_6H_2-2,5-Me_2) (eq 7). The same compounds were also readily obtained from the reaction of [$ClAu(PMe_3)$] with $HC{\equiv}C$—Ar—$C{\equiv}CH$ in the presence of MeONa or KOH (eq 8). The PMe_3 complexes were characterized by elemental analysis and NMR (^1H and ^{31}P) and IR spectroscopy. In particular, the ^{31}P NMR spectra of the complexes in chloroform show a singlet

$$\mathrm{Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}Au + 2PMe_3 \rightarrow Me_3PAu{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}AuPMe_3} \tag{7}$$

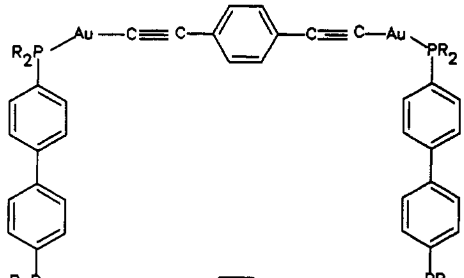
$$\mathrm{2ClAuPMe_3 + HC{\equiv}C{-}Ar{-}C{\equiv}CH + 2KOH \rightarrow Me_3PAu{-}C{\equiv}C{-}Ar{-}C{\equiv}CPMe_3 + 2H_2O + 2KCl} \tag{8}$$

around −1 ppm; the ^{1}H NMR spectra in chloroform display resonances for PMe_3 groups at ca. 1.5 ppm and the expected peaks of the arylacetylides; the IR spectra exhibit bands around 2110 cm^{-1}, assignable to C≡C stretching.

Molecular Structures of [PhC≡CAuP(*i*-Pr)$_2$C$_6$H$_4$—C$_6$H$_4$P(*i*-Pr)$_2$AuC≡CPh]. The molecular structure of [PhC≡CAuP(*i*-Pr)$_2$C$_6$H$_4$—C$_6$H$_4$P(*i*-Pr)$_2$-AuC≡CPh] is shown in Figure 1 and selected bond lengths and angles are presented in Table III. The molecule possesses a center of symmetry at the center of the C(14)—C(14′) bond, and hence the gold acetylide units are arranged strictly in the *anti* conformation. If this conformation is retained in the analogous diethynylbenzene derivative (see below), then a polymer, I, rather than a cyclic dimer, II, or oligomer will be expected. The biphenyl aromatic rings are essentially coplanar, thus allowing delocalization of π-electrons through the biphenyl unit. However, the distance C(14)—C(14′) of 1.528(9) Å suggests little multiple bond character. Because of the planarity of the biphenyl group, the ortho hydrogen atoms give a relatively short nonbonded distance H(15)···H(13′) = 1.84 Å. The torsion angle Au—P—C(11)—C(16), which defines the conformation of the ethynylgold group with respect to the biphenyl unit is 38.5(4)°, and the angle between the phenyl planes of the phenylethynyl and biphenyl groups is 63.1(1)°. The conformation of the isopropyl substituents in the solid state is such that all the methyl groups on each *i*-Pr$_2$P group are inequivalent. The bulkier methyl substituents are staggered with respect to the other substituents on phosphorus. The Au—P bond distance (2.282(2) Å) is at the upper end of the Au—P bonds observed in several other gold phosphine complexes, for example, Au$_2$Cl$_2$(μ-dpma) (2.239(4), 2.233(4) Å) (dpma = (bis(diphenylphosphino)methyl)phenylarsine),[30a] Au$_3$Cl$_3$-(μ-dpma) (2.227(4), 2.234(4) Å),[30a] Au$_2$Cl$_2$(μ-*trans*-Ph$_2$-PCH=CHPPh$_2$), (2.235(2) Å),[30b] Au$_2$Cl$_2$(μ-*cis*-Ph$_2$-PCH=CHPPh$_2$) (2.226(4), 2.239(5) Å),[30c] Au$_2$Cl$_2$(μ-Ph$_2$PCH$_2$CH$_2$PPh$_2$) (2.242(6), 2.237(6) Å),[30d] Au$_3$Cl$_3$(μ-Ph$_2$PCH$_2$)$_3$CMe (mean 2.239 Å),[30e] Au$_2$Cl$_2$(μ-Ph$_2$-PCH$_2$PPh$_2$) (2.238(5), 2.288(7) Å),[30f] Au(C≡CC$_6$F$_5$)(PPh$_3$) (2.274(1) Å),[31a] Au(C≡CCH$_2$OMe)(P(C$_6$H$_4$Me-4)$_3$) (2.274(3) Å),[31b] and C$_2$[Au(P(C$_6$H$_4$Me-3)$_3$)]$_2$ (2.270(4), 2.284(3) Å),[31c] consistent with a high *trans* influence of the alkynyl group. All other bond distances are unexceptional. There are no short intermolecular Au···Au contacts of the type commonly found in gold(I) complexes, presumably because the bulky isopropyl substituents prevent a close approach. The angles C(1)—Au—P (172.9(3)°) and Au—C(1)—C(2) (172.7(9)°) are roughly linear and are in the range reported for other gold acetylide complexes.[31] The angle Au—P—C(11) is 109.8°, as expected for tetrahedral phosphorus. Because this angle is not linear, the polymer formed from diethynylbenzene cannot be strictly linear but would have a kinked structure I.



I



II

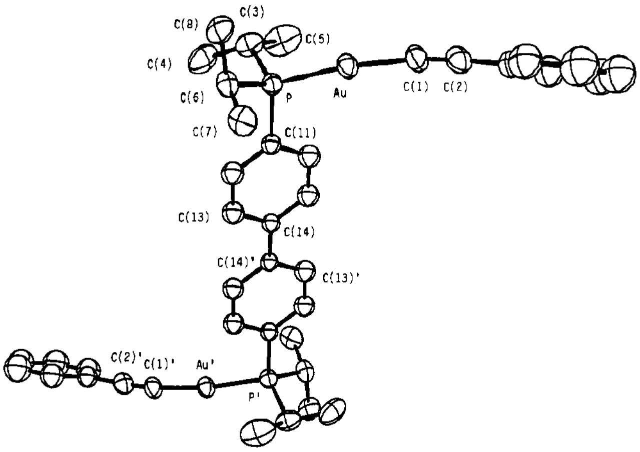


Figure 1. The molecular structure of [PhC≡CAuP(*i*-Pr)$_2$C$_6$H$_4$-C$_6$H$_4$P(*i*-Pr)$_2$AuC≡CPh]. Hydrogen atoms are omitted for clarity.

Synthesis of Polymers. Yellow polymeric complexes were prepared either from the reaction of a linear gold(I) diacetylide complex [{AuC≡C—Ar—C≡CAu}$_x$], **1**, with a diphosphine or from the reaction of a dinuclear gold(I) diphosphine complex [ClAuPr$_2$—Ar—Pr$_2$AuCl], **2**, with a diethynylarene in the presence of a base.

Reactions of the linear digold complexes [(Au—C≡C—Ar—C≡C—Au)$_x$], **1a–1c**, with P(*i*-Pr)$_2$C$_6$H$_4$—C$_6$H$_4$P(*i*-Pr)$_2$ in CH$_2$Cl$_2$ produced light yellow powders [(Au—C≡

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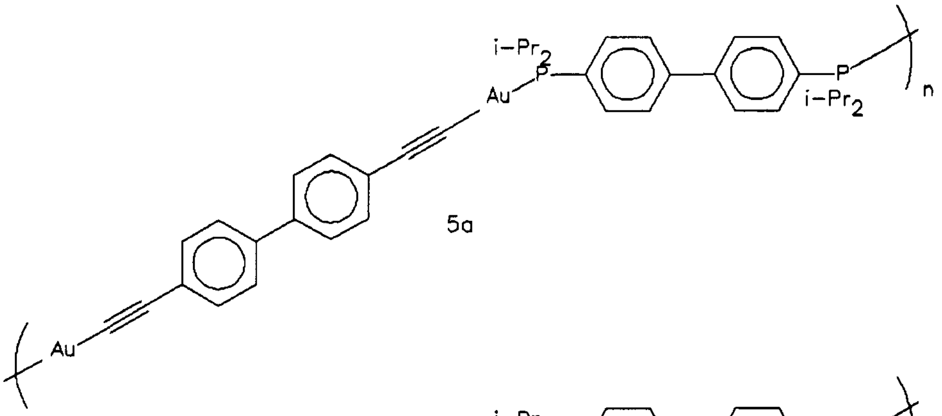
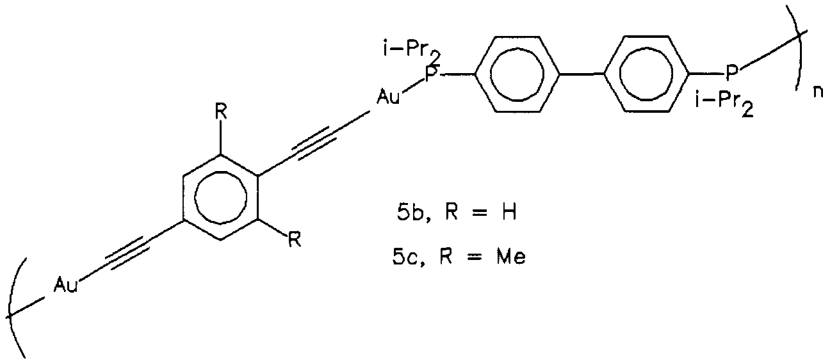
(31) (a) Carriedo, G. A.; Riera, V.; Solans, X.; Solans, J. *Acta Crystallogr.* **1988**, *C44*, 978. (b) Bruce, M. I.; Horn, E.; Matisons, J. G.; Snow, M. R. *Aust. J. Chem.* **1984**, *37*, 1163. (c) Bruce, M. I.; Grundy, K. R.; Liddell, M. J.; Snow, M. R.; Tiekink, E. R. T. *J. Organomet. Chem.* **1988**, *344*, C49. (d) Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1967**, *23*, 156.

Chart III



5a



5b, R = H

5c, R = Me

C—Ar—C≡C—AuP(i-Pr)$_2$C$_6$H$_4$—C$_6$H$_4$P(i-Pr)$_2$)$_x$] (**5a**, Ar = 4,4′-C$_6$H$_4$-C$_6$H$_4$; **5b**, Ar = 1,4-C$_6$H$_4$; **5c**, Ar = 1,4-C$_6$H$_2$-2,4-Me$_2$) (eq 9).

$$(\mathrm{Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}Au})_x + \mathrm{P}(i\text{-}\mathrm{Pr})_2\mathrm{C_6H_4{-}C_6H_4P}(i\text{-}\mathrm{Pr})_2 \rightarrow (\mathrm{Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}AuP}(i\text{-}\mathrm{Pr})_2\mathrm{C_6H_4{-}C_6H_4P}(i\text{-}\mathrm{Pr})_2)_x \quad (9)$$

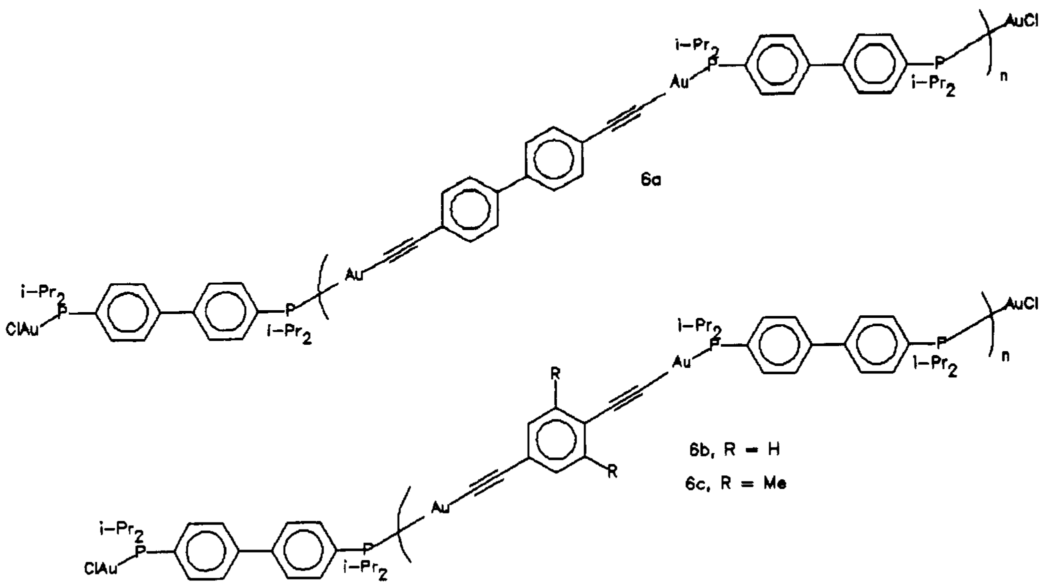
All the products are air-stable, pale-yellow solids which are insoluble in most organic solvents but slightly soluble in halogenated solvents such as dichloromethane and chloroform. They were characterized primarily by elemental analysis and NMR and IR spectroscopy. The ^{31}P NMR spectra display a singlet around 60.5 ppm, and the IR spectra show a weak IR band at 2110 cm^{-1}, assignable to ν(C≡C). The ^{31}P and IR spectral properties are very similar to those of the model dinuclear acetylide complex [PhC≡CAuP(i-Pr)$_2$C$_6$H$_4$—C$_6$H$_4$P(i-Pr)$_2$AuC≡CPh]. The ^{1}H NMR spectra show slightly broad resonances for the diphosphine and the aryldiacetylide ligands. The spectroscopic and solubility properties of the products suggest that they are polymeric in nature. In view of the *trans* disposition of the two phenylacetylide groups and the roughly linear geometry around the gold center in the X-ray structure of [PhC≡CAuP(i-Pr)$_2$C$_6$H$_4$—C$_6$H$_4$P(i-Pr)$_2$-AuC≡CPh], the products **5** are suggested to have a linear polymeric structure (the line drawing shows the more symmetrical head-to-tail structure, but the selectivity is not known). However, a cyclic polynuclear structure, and even a dinuclear cyclic structure, cannot be completely excluded. One sample gave a molecular weight by GPC of 15 000 (polystyrene standard) in tetrahydrofuran, with no evidence of low molecular weight impurities.

Similar yellow solids, **6**, which analyzed as [(Au—C≡C—Ar—C≡C—AuP(i-Pr)$_2$C$_6$H$_4$—C$_6$H$_4$P(i-Pr)$_2$)$_x$] (**6a**, Ar = 4,4′-C$_6$H$_4$-C$_6$H$_4$; **6b**, Ar = 1,4-C$_6$H$_4$; **6c**, Ar = 2,5-C$_6$H$_2$Me$_2$) were prepared from the reactions of [ClAuP(i-Pr)$_2$-C$_6$H$_4$—C$_6$H$_4$P(i-Pr)$_2$AuCl] with H—C≡C—Ar—C≡C—H (Ar = C$_6$H$_4$—C$_6$H$_4$, C$_6$H$_4$, 2,5-C$_6$H$_2$Me$_2$) in the presence of KOH or NaOMe (eq 10).

$$\mathrm{H{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}H} + \mathrm{ClAuP}(i\text{-}\mathrm{Pr})_2\mathrm{C_6H_4{-}C_6H_4P}(i\text{-}\mathrm{Pr})_2\mathrm{AuCl} + 2\mathrm{KOH} \rightarrow (\mathrm{Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}AuP}(i\text{-}\mathrm{Pr})_2\mathrm{C_6H_4{-}C_6H_4P}(i\text{-}\mathrm{Pr})_2)_x + 2\mathrm{H_2O} + 2\mathrm{KCl} \quad (10)$$

Again the solids are insoluble in most organic solvents but partially soluble in halogenated solvents such as dichloromethane and chloroform. They were characterized by elemental analysis and NMR and IR spectroscopy. The IR spectra of **6** (4000–650 cm^{-1}) were indistinguishable from those of the corresponding polymers **5**. The ^{31}P NMR spectra of **6** display a singlet around 60.5 ppm (major) and a singlet at 56.7 ppm (minor). The former signal is assigned to C≡CAuP whereas the latter is assigned to ClAuP by comparing the ^{31}P NMR properties of [PhC≡CAuP(i-Pr)$_2$C$_6$H$_4$—C$_6$H$_4$P(i-Pr)$_2$AuC≡CPh] and [ClAuP(i-Pr)$_2$-C$_6$H$_4$—C$_6$H$_4$P(i-Pr)$_2$AuCl]. The presence of signals assignable to ClAuP in the ^{31}P NMR of the products indicates that these polymers **6** have AuCl end groups, and this was confirmed by elemental analysis. From the relative intensity of C≡CAuP and ClAuP signals in the ^{31}P NMR spectra, the number of repeating units and hence the molecular weights for the soluble fraction of the polymer can be estimated. There are two possible structures with AuCl end groups, namely (i) one end of the polymer chain is AuCl (structure A) and (ii) both ends are AuCl (structure B). The intensity ratio of C≡CAuP to ClAuP is $(2x - 1)/1 = 2x - 1$ for structure A and is $2x/2 = x$ for structure B where x is the number of repeating units. For example, the intensity ratio was determined to be 27 for [(AuP(i-Pr)$_2$C$_6$H$_4$—C$_6$H$_4$P(i-Pr)$_2$Au—C≡C—C$_6$H$_4$—C≡C)$_x$], the x value can therefore be calculated to be 14 for

Chart IV



6a

6b, R = H

6c, R = Me

$$[\mathrm{Cl{-}(AuP(\mathit{i}\text{-}Pr)_2C_6H_4{-}C_6H_4P(\mathit{i}\text{-}Pr)_2Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C)_\mathit{x}{-}H}]$$

A

$$[\mathrm{Cl{-}(AuP(\mathit{i}\text{-}Pr)_2C_6H_4{-}C_6H_4P(\mathit{i}\text{-}Pr)_2Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C)_\mathit{x}{-}P(\mathit{i}\text{-}Pr)_2C_6H_4{-}C_6H_4P(\mathit{i}\text{-}Pr)_2AuCl}]$$

B

structure A or 27 for structure B. The molecular weight was thus estimated to be 13 700 for structure A or 27 000 for structure B. The insoluble fractions of the polymers almost certainly have higher molecular weights. Structure B is considered more probably than structure A for the polymers since no acetylenic C—H stretch could be detected in the FTIR spectra. The molecular weight of one sample was determined by GPC in tetrahydrofuran to be 18 000 compared to a polystyrene reference.

The thermal properties of the polymeric compounds $[(\mathrm{Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}AuP(\mathit{i}\text{-}Pr)_2C_6H_4{-}C_6H_4P(\mathit{i}\text{-}Pr)_2})_x]$ (Ar = C_6H_4—C_6H_4, 2,5-$C_6H_2Me_2$) have been studied using differential scanning calorimetry, DSC. Each sample displays a significant endothermic transition over a wide temperature range, 50–150 °C, and decomposes to metallic gold at temperatures above 250 °C.

Reactions of linear digold complexes $[(\mathrm{Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}Au})_x]$, **1**, with $PPh_2C_6H_4PPh_2$ in CH_2Cl_2 produced white powders which analyzed as $[(\mathrm{Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}AuPPh_2C_6H_4PPh_2})_x]$ (**7a**, Ar = C_6H_4-C_6H_4; **7b**, Ar = 1,4-C_6H_4; **7c**, Ar = 1,4-C_6H_2-2,5-Me_2) (eq 11).

$$(\mathrm{Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}Au})_x + \mathrm{PPh_2C_6H_4{-}C_6H_4PPh_2} \rightarrow (\mathrm{Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}AuPPh_2C_6H_4{-}C_6H_4PPh_2})_x \quad (11)$$

All the products are air stable solids which are insoluble in common organic solvents. They were characterized primarily by elemental analysis and IR spectroscopy. In particular, all the products have similar IR spectral properties and a weak IR band around 2110 cm^{-1}, assignable to $\nu(C{\equiv}C)$, was observed in each case. In view of their low solubility, the products **7** are presumed to have a polymeric structure like their analogs **5**. The insolubility makes it impossible to determine the molecular weight of the polymers or to characterize them in solution by NMR spectroscopy.

Reaction of $[\mathrm{ClAuPPh_2C_6H_4PPh_2AuCl}]$ with H—C≡C—Ar—C≡C—H (Ar = C_6H_4—C_6H_4, C_6H_4, $C_6H_2Me_2$) in the presence of KOH or NaOMe were carried out with the intention of preparing similar polymers. However, yellow solids which analyzed as $(\mathrm{Cl_2Au_2PPh_2C_6H_4PPh_2})(\mathrm{Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}AuPPh_2C_6H_4PPh_2})$ were formed, for which a probable structure is $[\mathrm{ClAuPPh_2C_6H_4PPh_2Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}AuPPh_2C_6H_4PPh_2AuCl}]$ (**8a**, Ar = 4,4′-C_6H_4-C_6H_4; **8b**, Ar = 1,4-C_6H_4; **8c**, Ar = 2,5-$C_6H_2Me_2$) (eq 12). The solids are insoluble in acetone or benzene

$$\mathrm{H{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}H} + 2\mathrm{ClAuPPh_2C_6H_4PPh_2AuCl} + 2\mathrm{KOH} \rightarrow [\mathrm{ClAuPPh_2C_6H_4PPh_2Au{-}C{\equiv}C{-}Ar{-}C{\equiv}C{-}AuPPh_2C_6H_4PPh_2AuCl}] + 2\mathrm{H_2O} + 2\mathrm{KCl} \quad (12)$$

but sparingly soluble in halogenated solvents such as dichloromethane and chloroform. In the IR spectra, a weak IR band at 2110 cm^{-1}, assignable to $\nu(C{\equiv}C)$, was observed, but there was no detectable peak due to ν(CC—H). The ^1H NMR spectra show the expected resonances for the diphosphine and the acetylide ligands. The ^{31}P NMR spectra display a singlet around 40 ppm and a singlet at 30 ppm. The former signal is assigned to C≡CAuP whereas the latter is assigned to ClAuP by comparing the ^{31}P NMR properties of $[\mathrm{PhC{\equiv}CAuPPh_2C_6H_4PPh_2AuC{\equiv}CPh}]$ and $[\mathrm{ClAuPPh_2C_6H_4PPh_2AuCl}]$. The intensity ratios of C≡CAuP to ClAuP of the products are approximately 1:1, and much smaller than those of $\mathrm{P(\mathit{i}\text{-}Pr)_2C_6H_4{-}C_6H_4P(\mathit{i}\text{-}Pr)_2}$ analogs. Presumably, complexes **8** are insoluble in the solvent used in the synthesis and so precipitate before further reaction to give oligomers or polymers can occur.

Conclusions

In most conjugated, linear, rigid-rod polymers the metal centers have been connected by neutral diisocyanide or dianionic diacetylide bridges with arene spacer groups. Conjugation then involves the p_π–p_π multiple bonds of the ligand with d_π orbitals of the transition metal. In this work, the use of neutral diphosphine bridges has been investigated. Two changes are introduced, which might have a significant bearing on polymer formation. Firstly, the polymers cannot be strictly linear because of the natural tetrahedral angle at phosphorus (structure **I**) and, potentially, this could allow the formation of cyclic dimers (structure **II**, for example) or trimers instead of the desired polymers. In practice, there was no evidence for the formation of such cyclic compounds and it is therefore established that the diphosphines with arene spacer groups will be useful for the synthesis of polymers. Secondly, the conjugation will involve p_π–p_π(CC), p_π–d_π (CP), and d_π–d_π(PAu) bonding effects and so is more complex and probably weaker than with, e.g., diisocyanide bridges. The yellow color of the polymers, compared to colorless monomeric analogs, suggests that there is some electron delocalization in the diphosphine bridged polymers, but a comparison with the extent of delocalization in diisocyanide bridged analogs is not yet possible.

Bulky substituents, such as the isopropyl groups used in this work, are easily incorporated into the diphosphine ligands and are obviously important for enhancing the solubility of the polymers and oligomers. This is a considerable advantage in preparing soluble polymers with metal centers such as gold(I) in the backbone, since it is clearly not possible to use ancillary ligands as solubilizing substituents on the metal. This is the technique commonly used with metal centers having higher coordination numbers. Hence the diphosphines should be very useful for the synthesis of polymers with metal centers in the backbone.

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Supplementary Material Available: Tables of anisotropic thermal parameters, calculated positional and thermal parameters for hydrogen atoms, weighted least-squares planes, and torsion angles for $PhC{\equiv}CAuP(i\text{-}Pr)_2C_6H_4{-}C_6H_4P(i\text{-}Pr)_2AuC{\equiv}CPh$ (2 pages). Ordering information is given on any current masthead page.

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