ORGANOMETALLICS

Gold(I) Chloride Complexes of Polyphosphine Ligands with Electron-Rich Arene Spacer: Gold—Arene Interactions

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Supporting Information

ABSTRACT: The reactions of Au(tht)Cl (tht = tetrahydrothiophene) with the electron-rich-arene-spacer-containing polyphosphine ligands N,N'-bis((diphenylphosphino)methyl)benzene-1,4-diamine (Dpba), N,N'-bis((diphenylphosphino)methyl)naphthalene-1,5-diamine (Dpna), N,N,N',N'- tetrakis((diphenylphosphino)methyl) benzene-1,4-diamine (Pbaa), N,N,N',N'-tetrakis-((diphenylphosphino)methyl)naphthalene-1,5-diamine (Phaa), and N,N,N',N'-tetrakis((diphenylphosphino)methyl)biphenyl-4,4'-diamine



Au $\cdots \pi$ interactions

(Pbbaa) lead to $[Dpba(AuCl)_2]^1(1)$, $[Dpna(AuCl)_2]^2(2)$, $[Pnaa(AuCl)_4](3)$, $[Pbbaa(AuCl)_4(4)$. and $[Pbaa(AuCl)_4](5)$, which are characterized by ¹H and ³¹P NMR, IR, elemental analysis, and X-ray crystal structure analysis. These complexes exhibit weak Au—arene interactions with the electron-rich arene spacer, while the Au—arene interactions are modified by a combination of electronic and steric effects from the ligands. Different from monomeric complexes 1, 2, 3, and 4, complex 5 in the solid state exhibits a centrosymmetric trimeric unit that is constructed by intermolecular Au…Au interactions between the central molecule and the two symmetry-related terminal molecules and in which the conformation of the central molecule is different from that of the two symmetric terminal molecules. On the basis of the Kochi's geometric criteria and the crystal structural parameters relating to Au—arene interactions, the Au…C_{arene} contacts in 3 and 4 feature nearly η^2 -arene interactions, while the Au…C_{arene} contacts in 5 can be described as η^1 -arene interactions, and the Au…C_{arene} contacts in 1 and 2 are very weak due to intermolecular N–H…Cl interactions.

■ INTRODUCTION

Gold catalysis is one of the most active areas of research in organic synthesis.^{1,2} Some gold complexes are proved to be effective in the activation of alkynes, alkenes, allenes, and even arenes,^{3,4} associated with π -coordination with low η^2 -hapticity (or, in special cases, η^1 and η^3). However, only a few π complexes could be isolated due to dissociation in air and moisture. In many catalytic processes, organo-gold halides are catalyst precursors and a silver salt as a cocatalyst, giving rise to cationic active gold species in the catalytic system.⁵ However, the Ag⁺ could lead to unwanted side reactions due to the practical deficiency regarding the light sensitivity, the easy reduction to metallic silver, and the coorperative effects of Au-Ag metallophilic interactions, leading to some limitations for effective catalysis.⁶ Therefore, the development of silver-free gold catalysts is advantageous. Sterically hindered ligands such as phosphines, bulky N-heterocyclic carbenes, and triazadienyl have been demonstrated to be particularly useful to develop highly active and selective gold catalysts, by strengthening the stability of gold cations.⁷ The excellent and extensively researched supporting ligand is bulky dialky(2-biphenylyl)phosphine,⁸ whose gold complexes exhibit effective catalysis for cross-coupling reaction, cycloaddition reaction, or goldcatalyzed transformation of unsaturated hydrocarbons. In neutral AuCl and gold cationic complexes with bulky biphenylphosphines, the gold atom weakly interacts with the terminal phenyl ring, which is placed above or aside the Au atom (Scheme 1). Such weak Au $\cdots\pi$ interactions might provide

Scheme 1



additional stabilization to the transition states or intermediates in the reactions of biphenylphosphine gold complexes with alkynes, allenes, or alkenes, which were isolated as crystalline compounds and proved to be stable toward air and moisture. Moreover, their cationic complexes can make catalytic transformations possible under silver-free conditions. The introduction of an electron-donating group (e.g., alkoxy) into the terminal phen is well documented to increase the electron density in the biphenyl backbone and stabilize intermediate complexes due to the reinforcement of the weak interactions between the metal and the arene ring. Similar weak interactions between Au and an anthracene ring were also found by Zhang's

Received: December 23, 2011 Published: March 2, 2012 group in the ditertiary phosphine anthracene-based gold complex.⁹ These ligand-unsupported Au $\cdots \pi$ interactions (the Au····C_{arene} distance is in the range of 2.95-3.38 Å) are distinguished from the ligand-supported Au $\cdots \pi$ interactions (the distance is less than 2.50 Å), which were investigated by Schmidbaur.1e To understand the nature of these weak interactions better in the Au-catalytic system and to pursue new highly reactive and selective catalysts, we endeavored to develop some new functionally semirigid phosphine ligands, N,N'-bis((diphenylphosphino)methyl)benzene-1,4-diamine (Dpba), N,N'-bis((diphenylphosphino)methyl)naphthalene-1,5-diamine (Dpna) N,N,N',N'-tetrakis((diphenylphosphino)methyl)benzene-1,4-diamine (Pbaa), N,N,N',N'-tetrakis-((diphenylphosphino)methyl)naphthalene-1,5-diamine (Pnaa), and N,N,N',N'-tetrakis((diphenylphosphino)methyl)biphenyl-4,4'-diamine (Pbbaa), involving an arene diamine moiety of which the lone electron pairs on the nitrogen atoms donate to the arene ring featuring an electron-rich arene spacer¹⁰ that is presumably favorable for the donation of π -electrons to the Au center. These ligands were exploited to construct Cu-P complexes in which electron-rich arene rings are involved in $\pi \cdots \hat{\pi}$ and C-H $\cdots \pi$ interactions. Changing the size of the central arene to tune its electron density can modify the Au-arene interactions. By the reaction of Au(tht)Cl (tht = tetrahydrothiophene) with these polyphosphine ligands, complexes $[Dpba(AuCl)_2]$ (1), $[Dpna(AuCl)_2]$ (2), $[Pnaa(AuCl)_4]$ (3), $[Pbbaa(AuCl)_4]$ (4), and $[Pbaa(AuCl)_4]$ (5) are afforded. Ligands and their Au complexes are enumerated in Chart 1.

Chart 1

| Ph ₂ P-H N | Ph ₂ P- Ph ₂ P-N-□-N | PPh ₂ PPh ₂ |
|----------------------------|---|--------------------------------------|
| phenyi Dpba | phenyl | Pbaa |
| | $\Box = \begin{cases} naphthyl \end{cases}$ | Pnaa |
| naphthyi Dpna | biphenyl | Pbbaa |
| [Dpha(AuCl) ₂] | 1 | |
| [Dpna(AuCl) ₂] | 2 | |
| [Pnaa(AuCl) ₄] | 3 | |
| [Pbbaa(AuCl)4] | 4 | |
| [Pbaa(AuCl) ₄] | 5 | |

Complexes 1 and 2 are dinuclear complexes supported by diphosphines Dpba and Dpna, respectively, while 3, 4, and 5 are tetranuclear based on tetraphosphine Pnaa, Pbbaa, and Pbaa, respectively. In the solid state of 5, three molecules of $[Pbaa(AuCl)_4]$ are linked by significant aurophilic interactions into a trimeric unit in which two different conformations of $[Pbaa(AuCl)_4]$ are exhibited (Scheme 2). Here we detail the

Scheme 2



synthesis and structures of these AuCl complexes and try to understand the electronic and steric control of the semirigid ligands over the Au $\cdots \pi$ interactions.

EXPERIMENTAL SECTION

General Procedures. All chemicals were of reagent grade and were used as received without further purification. IR spectra were recorded as KBr pellets on a Perkin-Elmer FT-IR spectrometer in the range 4000–450 cm⁻¹. Elemental analyses were performed with a Carlo ERBA 1106 analyzer. ¹H and ³¹P{¹H} spectra were recorded on a Bruker Avance DMX400 spectrometer at 400.13 MHz. Phosphine ligands were synthesized according to ref 11.

Synthesis. 1·0.5(*CH*₂*Cl*₂). A mixture of [AuCl(THT)] (0.0320 g, 0.1 mmol) and Dpba (0.0260 g, 0.05 mmol) in 5 mL of *CH*₂*Cl*₂ was stirred at room temperature for 2 h. The resulting yellow solution was diffused by diethyl ether in a 0 °C refrigerator. Four days later, yellow block crystals were afforded. Yield: 50%. Anal. Calcd for $C_{32,5}H_{31}N_2P_2Cl_3Au_2$: C, 38.54; H, 3.06; N, 2.77. Found: C, 38.26; H, 3.15; N, 3.04; IR (cm⁻¹): 3349 (s), 1619 (m), 1517 (vs), 1482 (s), 12435 (s), 1252 (s), 1105 (s), 743 (s), 619 (s), 518 (s). ¹H NMR (400 MHz, DMSO): δ 7.56–7.81 (m, 20H, P-C₆H₅), 6.61(s, 4H, N-C₆H₄-N), 5.46 (s, 2H, NH), 4.50 (s, 4H, P-CH₂-N). ³¹P{¹H} NMR (DMSO): 22.11.

2. A mixture of [AuCl(THT)] (0.0320 g, 0.1 mmol) and Dpna (0.0270 g, 0.05 mmol) in 7 mL of CH₂Cl₂/DMF mixed solvent (volume ratio of 2:5) was stirred at room temperature for 2 h. The resulting scarlet solution was diffused by diethyl ether in a 0 °C refrigerator. Four days later, pink crystals were afforded. Yield: 40%. Anal. Calcd for $C_{36}H_{32}N_2P_2Cl_2Au_2$: C, 42.39; H, 3.14; N, 2.75. Found: C, 42.53; H, 3.44; N, 2.58; IR (cm⁻¹): 3336 (vs), 1636 (m), 1536 (s), 1436 (s), 1107 (s), 747 (s), 691 (s). ¹H NMR (400 MHz, DMSO): δ 7.79–7.56 (m, 20H, P-C₆H₅), 7.23–6.95 (m, 6H, N-C₁₀H₆-N), 6.50 (s, 2H, NH), 4.79–4.78 (d, 4H, P-CH₂-N). ³¹P{¹H} NMR (DMSO): δ 21.01.

3·2(*CH*₂*Cl*₂). After the mixture of [AuCl(THT)] (0.0320 g, 0.1 mmol) and Pnaa (0.0240 g, 0.025 mmol) in 5 mL of CH₃CN was stirred at room temperature for 1 h, the resulting white deposit was filtered and dissolved in 6 mL of DMF/CH₂Cl₂ (volume ratio of 1:1). The white solution was diffused by diethyl ether in a 0 °C refrigerator. Seven days later, colorless prism crystals were afforded. Yield: 35%. Anal. Calcd for C₆₄H₅₈N₂P₄Cl₈Au₄: C, 37.46; H, 2.83; N, 1.37. Found: C, 37.71; H, 2.60; N, 1.52; IR (cm⁻¹): 1608 (m), 1498 (s), 1435 (s), 1198 (m), 1104 (s), 864(s), 747 (s), 691 (s), 519 (s). ¹H NMR (400 MHz, DMSO): δ 7.54–7.37 (m, 40H, P-C₆H₅), 7.13–6.64(m, 6H, N-C₁₀H₆-N), 5.09–4.85 (m, 8H, P-CH₂-N). ³¹P{¹H} NMR (CDCl₃): δ 18.35.

4. After the mixture of [AuCl(THT)] (0.0320 g, 0.1 mmol) and Pbbaa (0.0240 g, 0.025 mmol) in 5 mL of CH₃CN was stirred at room temperature for 1 h, the resulting white deposit was filtered and dissolved in 8 mL of CH₂Cl₂/toluene (volume ratio of 1:1). This solution was diffused by diethyl ether in a 0 °C refrigerator. Half a month later, colorless plate crystals were afforded. Yield: 21%. Anal. Calcd for C₆₄H₅₆N₂P₄Cl₄Au₄: C, 40.29; H, 2.94; N, 1.47. Found: C, 40.45; H, 3.24; N, 1.62; IR (cm⁻¹): 1589 (m), 1482 (s), 1435 (s), 1102 (s), 863 (s), 742 (s), 690 (s), 522 (s). ¹H NMR (400 MHz, CDCl₃): δ 7.49–7.39 (m, 40H, P-C₆H₅), 7.16–6.71(m, 8H, N-C₆H₄-N), 4.77 (s, 8H, P-CH₂-N). ³¹P{¹H} NMR (CDCl₃): δ 17.06.

5·(*CH*₂*Cl*₂)·0.5(*Et*₂*O*). A mixture of [AuCl(THT)] (0.0320 g, 0.1 mmol) and Pbaa (0.0230 g, 0.025 mmol) in 7 mL of CH₂Cl₂ was stirred at room temperature for 2 h. The resulting colorless solution was diffused by diethyl ether in a 0 °C refrigerator. Four days later, colorless needle crystals were afforded. Yield: 50%. Anal. Calcd for C₆₀H_{56.5}N₂OP₄Cl₆Au₄: C, 37.00; H, 2.90; N, 1.44. Found: C, 37.35; H, 2.89; N, 1.25; IR (cm⁻¹): 1635 (m), 1512 (s), 1435 (s), 1102 (vs), 868 (m), 745 (s), 691 (s), 513 (s). ¹H NMR (400 MHz, DMSO): δ 7.75–7.49 (m, 40H, P-C₆H₅), 6.56(s, 4H, N-C₆H₄-N), 4.78 (s, 8H, P-CH₂-N). ³¹P{¹H} NMR (DMSO): δ 18.96.

Table 1. Crystallographic Data for Complexes 1-5

| | 1 | 2 | 3 | 4 | 5 |
|--------------------------------------|--|--|--|---|--|
| formula | $C_{32.5}H_{31}N_2P_2Cl_3Au_2\\$ | $C_{36}H_{32}N_2P_2Cl_2Au_2\\$ | $C_{64}H_{58}N_2P_4Cl_8Au_4\\$ | $C_{64}H_{56}N_2P_4Cl_4Au_4$ | $C_{58}H_{52}N_2P_4Cl_4Au_4\\$ |
| fw | 1011.82 | 1019.41 | 2050.47 | 1906.65 | 1830.56 |
| cryst syst | monoclinic | monoclinic | triclinic | monoclinic | triclinic |
| space group | C2/c | $P2_1/n$ | $P\overline{1}$ | P2 ₁ /c | $P\overline{1}$ |
| a (Å) | 28.201(6) | 9.6892(4) | 9.8229(18) | 17.476(3) | 15.4246(6) |
| b (Å) | 11.827(3) | 14.2541(5) | 11.518(2) | 11.628(2) | 16.2064(5) |
| c (Å) | 10.764(2) | 12.3140(5) | 15.667(3) | 17.143(3) | 20.1659(7) |
| α (deg) | 90 | 90 | 69.607(3) | 90 | 83.8890(10) |
| β (deg) | 106.932(5) | 105.922(4) | 82.607(3) | 117.887(3) | 85.1360(10) |
| γ (deg) | 90 | 90 | 72.291(3) | 90 | 74.7730(10) |
| V (Å ³) | 3434.5(13) | 1635.45(11) | 1582.2(5) | 3079.1(10) | 4827.9(3) |
| Ζ | 4 | 2 | 1 | 2 | 3 |
| $\mu(Mo K\alpha) \ (cm^{-1})$ | 0.8885 | 0.9251 | 0.9726 | 0.9818 | 0.9389 |
| T (K) | 153 | 293 | 110 | 110 | 153 |
| $ ho_{ m calc}~({ m g~cm}^{-3})$ | 1.957 | 2.070 | 2.152 | 2.056 | 1.889 |
| λ (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| index ranges | $-33 \le h \le 33, -13 \le k \le 14, -12 \le l \le 12$ | $-11 \le h \le 11, -16 \le k \le 16, -14 \le l \le 11$ | $-11 \le h \le 11, -13 \le k \le 13, -18 \le l \le 18$ | $-21 \le h \le 21, -8 \le k \le 14, -20 \le l \le 21$ | $-18 \le h \le 18, -19 \le k \le 18, -23 \le l \le 23$ |
| indep reflectns (R_{int}) | 3015 (0.1422) | 2836 (0.0383) | 5493 (0.0263) | 6635 (0.0545) | 16671 (0.0692) |
| obsd reflectns $[I > 2\sigma(I)]$ | 1969 | 2064 | 4548 | 4913 | 11 281 |
| params | 195 | 199 | 370 | 316 | 973 |
| goodness-of-fit | 1.075 | 0.932 | 1.095 | 1.021 | 1.139 |
| $R \left[I > 2\sigma(I) \right]$ | 0.0773 | 0.0315 | 0.0295 | 0.0433 | 0.0591 |
| $R_{\rm w}\left[I>2\sigma(I)\right]$ | 0.1904 | 0.0744 | 0.0878 | 0.1051 | 0.1512 |
| R (all data) | 0.1151 | 0.0467 | 0.0407 | 0.0712 | 0.0895 |
| $R_{\rm w}$ (all data) | 0.2274 | 0.0785 | 0.0940 | 0.1244 | 0.1874 |

X-ray Crystallography. Reflection intensity data for these five complexes were collected on a Oxford "Xcalibur, Sapphire3, Gemini Ultra" diffractometer with graphite-monochromated Mo K α radiation (l = 0.71073 Å) using the ω technique. All the structures were solved by direct methods and refined with the full-matrix least-squares on F^2 using SHELXTL. Anisotropic thermal parameters were used in the last cycles of refinement for the non-hydrogen atoms. All hydrogen atoms were introduced into the last cycle of the refinement from geometrical calculations and refined by using a riding model. During the structure refinement of **5**, the unidentified and badly disordered solvent molecules (probably CH₂Cl₂ and diethyl ether) were removed with the Squeeze option in PLATON. Crystal and structure refinement data are summarized in Table 1. The selected geometric parameters are shown in Table 2.

Table 2. Selected Geometric Parameters Related to Au-Arene Interactions (Å and deg)

| complex | Au-P | Au-Cl | Au–Ar ^a | P-Au-Cl | dihedral angle ¹ |
|----------------|---------|---------|--------------------|----------|-----------------------------|
| 1 (Au1) | 2.22(4) | 2.28(5) | 3.56 | 178.2(2) | |
| 2 (Au1) | 2.22(2) | 2.29(2) | 3.55 | 177.2(1) | |
| 3 (Au2) | 2.23(1) | 2.30(2) | 3.20 | 177.2(1) | 75.1 |
| 4 (Au1) | 2.23(2) | 2.30(2) | 3.35 | 178.3(1) | 66.0 |
| 5 | | | | | |
| Au2 | 2.23(4) | 2.29(4) | 3.42 | 175.0(1) | 73.7 |
| Au5 | 2.24(4) | 2.29(3) | 3.17 | 176.6(2) | 72.1 |
| Au6 | 2.23(4) | 2.30(4) | 3.07 | 175.4(1) | 77.9 |

^aShortest distance between Au and the plane of the central arene. ^bDihedral angle between the plane of the central arene and the P– Au–Cl over or below the central arene.

RESULTS AND DISCUSSION

The structures of these five complexes were determined by Xray single-crystal diffraction analysis. In these five complexes, each phosphine group is coordinated with one AuCl. As expected, the overall geometry about each gold(I) center is essentially linear, exhibiting the two-coordinated Au unit P– Au–Cl. The Au–P and Au–Cl bond lengths are unremarkable, falling within the range of bond lengths for crystallographically characterized phosphine-ligated gold(I) chlorides.¹² The P– Au–Cl bond angles range from 169° to 179°. The geometry about each P is tetrahedral, as expected. Dpba in I takes as a *cis*coordination mode, while Dpna in 2 performs as a *trans*coordination mode, to bridge two AuCl units (Figures 1 and 2). The P–Au–Cl units in 1 and 2 lie on each side of the central arene spacers with the shortest Au…C_{arene} distances of 3.46 Å (Au1–C1) in 1 and 3.55 Å (Au1–C1) in 2. These Au…C



Figure 1. Molecular structure of 1, showing the very weak $\mathrm{Au}{\cdots}\mathrm{C}_{\mathrm{arene}}$ contact.



Figure 2. Molecular structure of 2, showing the Au \cdots C_{arene} contact.

distances are well above the sum of the van der Waals radii (3.36 Å) of carbon and gold,¹³ showing atypical, weak Au $\cdots \pi_{arene}$ interactions. In 1, neighboring molecules are bridged to each other via two intermolecular N-H--Cl interactions into a one-dimensional chain (Figure S1). But in 2, each molecule performs as a four-linker to bridge four neighboring molecules via N-H…Cl contacts, resulting in a two-dimensional structure along the *ab* plane (Figure S2). Due to the N-H…Cl contacts, the P-Au-Cl units deviate significantly from the central arene plane, resulting in very weak Au…Carene contacts. In order to eliminate the influence of N-H…Cl on the Au-arene interaction and increase the electronic and steric control over the Aumarene interactions, ligands Pnaa, Pbbaa, and Pbaa, in which the hydrogens on the N atoms are substituted completely by Ph₂PCH₂ units, are applied to build complexes 3, 4, and 5, respectively. Both 3 and 4 are centrosymmetric with the inversion center located at the center of the arene spacer (Figures 3 and 4), while the coordination modes of Pnaa and



Figure 3. Molecular structure of 3, showing the $\text{Au}{\cdots}\text{C}_{\text{arene}}$ interactions.



Figure 4. Molecular structure of 4, showing the $Au{\cdots}C_{arene}$ interactions.

Pbaa are the same as *syn-anti:syn-anti* (Scheme 2a). The two Ph₂PCH₂ units tethered to the same N atom take a syn-anti conformation to coordinate to AuCl, producing one P-Au-Cl unit located above or below the arene spacer and another P-Au-Cl unit stretched away from the arene spacer. The overall structure can be described as being that of two symmetryrelated P-Au-Cl units located above and below the plane of arene spacer, respectively, while the other two symmetryrelated P-Au-Cl units are stretched out from the two termini of the arene spacer, respectively. This geometric conformation is attributed to a combination of electronic and steric properties of the ligand. The P-Au-Cl units above or below the central arene plane in 3 and 4 are tilted to the corresponding central arene planes by approximately 75.1° and 66.0°, respectively, possibly due to the π ---chloride repulsion. The most significant feature of these structures is the interactions between Au and the C atoms of the central arene ring. The distances of Au2-C2 (3.20 Å/C_{ipso}) and Au2-C3 (3.30 Å/C_{ortho}) in 3, and Au1- $C1(3.35 \text{ Å}/C_{ipso})$ and $Au1-C2 (3.37 \text{ Å}/C_{ortho})$ in 4, are comparable with those of $Au-C_{arene}$ in biphenylphosphine AuCl complexes (the average distance of Au $-C_{arene} = 3.15$ Å). Moreover, the Au– C_{arene} distances in 3 are slightly shorter than those in 4, which may correspond to the higher electron density of the anthrance ring that enhances the $\mathrm{Au-C}_{\mathrm{arene}}$ interactions in 3. The asymmetric unit of 5 contains one and a half crystallographically independent molecules of [Pbaa(AuCl)₄]; these are generated symmetrically into a centrosymmetric trimeric unit in which molecules are aggregated through strong intermolecular aurophilic interactions (Figure 5). The inversion



Figure 5. Structure of a trimer in **5**, showing Au…Au interactions. Phenyl groups are deleted for clarity.

center is located at the centroid of the arene spacer in the central molecule. In this trimeric unit, Pbaa adopts two different geometric conformations, *syn-anti:syn-anti* and *syn-syn:anti-anti* (Scheme 2), to link AuCl units. In the central molecule, Pbaa performs as a *syn-anti:syn-anti* mode, like that in 3 and 4 to bridge four AuCl molecules (Figure 6a). The P2–Au2–Cl2 and its symmetry-related units are located above and below the central arene plane, respectively, with the tilt angle between P2–Au2–Cl2 and the arene plane of 73.8°. The shortest and second shortest atom-atom distances from the Au2 center to C_{arene} are 3.43 (C_{ipso}) and 3.52 Å (C_{ortho}), respectively. These values are a little longer than those in 3 and 4, but comparable with those in 1 and 2. However, in the two symmetry-related terminal molecules, Pbaa performs as a *syn-syn:anti-anti*



Figure 6. Geometries of the central (a) and terminal (b) molecules in the trimer, showing Au $\cdots \pi$ interactions. Phenyl groups are deleted for clarity.

conformation in which two PPh2CH2 units bound to one N atom link two AuCl molecules by the syn-syn coordination mode, which supports the intramolecular Au-Au interaction between Au3 and Au4 (3.10 Å) (Figure 6b),¹⁴ while the other two Ph2PCH2 moieties appended to another N atom take an anti-anti mode to link two AuCl, leading to these two P-Au-Cl units locating above and below the central arene plane (P5– Au5–Cl5, P6–Au6–Cl6), which are involved in intramolecular Au…C interactions. The shortest and second shortest distances from Au to C atoms are 3.18 (Au5-C34) and 3.52 Å (Au5-C33) relative to Au5, and 3.07 (Au6–C32) and 3.59 Å (Au6– C31) relative to Au6, featuring a highly asymmetric coordination mode of Au…C, which could be described as either a η^1 or a distorted η^2 bond. The intermolecular Au…Au interactions between Au5 and Au1 (3.36 Å) and their symmetry-related atoms lead to the aggregation between the central and terminal molecules into a trimeric unit. Furthermore, these trimeric units are extended into a onedimensinal chain by interunit, weak Au-Au interactions between Au6 and its symmetric atoms (3.51 Å) from neighboring trimeric units (Figure 7). The Au-Au distances



Figure 7. One-dimensional chain constructed by trimers through Au…Au interactions. Phenyl groups are deleted for clarity.

(3.18 and 3.36 Å) within the trimeric unit are longer than those between the units (3.51 Å), while they are all below the sum of

two van der Waals radii (3.80 Å).¹⁴ All five complexes exhibit only one ³¹P singlet. The chemical shifts of ³¹P in 1 and 2 are approximate, while those in 3, 4, and 5 are also similar. The feature of one ³¹P singlet shows that these polyphosphine Au complexes are flexible in solution, and the behavior of 5 in DMSO solution is similar to 3 and 4, presenting only one flexible monomer.

In these complexes, gold(I) can interact weakly with the electron-rich central arene ring. Concerning the structural feature of Au-Carene interactions, the P-Au-Cl units in 1 and 2 are located on each side of the central arene spacers due to N-H…Cl interactions, but the P-Au-Cl units related to the $Au{\cdots}C_{\text{arene}}$ interactions in 3, 4, and 5 are above and below the central arene planes. The shortest Au…C distances in 1, 2, and the central molecules of 5 (3.43–3.55 Å) are well above the sum of the van der Waals radii (3.36 Å) of carbon and gold, significantly deviated from the typical Au…C interaction. Nevertheless, the corresponding values in 3, 4, and the terminal molecules of 5 are in the range 3.07-3.35 Å, exhibiting common Au…C interactions, but distinguished from the ligand-supported Au-C interactions (below 2.5 Å).^{1e,3b} It is noteworthy that the distance of Au– C_{ipso} is shorter than that of $Au-C_{ortho}$ in 3 and 4 due to the *ipso* position corresponding to the highest electron density. Of course, the steric effect is also ignored for the Au-C_{arene} interactions. Due to the steric congestion, both the shortest and the second shortest Au- C_{arene} distances in the central molecule of 5 are beyond the sum of the van der Waals radii (3.36 Å) of carbon and gold, while the $Au-C_{ortho}$ contacts in the terminal molecules are remarkably shorter than the Au-Cipso values. For a further evaluation of these Au-arene interactions, Kochi's geometric criteria¹⁵ for the gold–arene plane in 3–5 are shown in Table 3. The β and D values are within $30 \pm 3^{\circ}$ and 3.1 ± 0.2 Å, respectively. The hapticity values of 3 and 4 are 1.79 and 1.94, respectively, while the d_1 and d_2 are approximate and within the sum of the van der Waals radii, featuring nearly η^2 arene interactions. However in 5, the hapticity parameters related to Au5 and Au6 are 1.56 and 1.59, respectively, showing that the coordination of Au to arene could be intermediate between η^1 and η^2 , but the strikingly inequivalent d_1 and d_2 values show that these Au-C arene interactions are highly asymmetric and should be described as η^1 -arene interactions. The structural features related to Au2 show a very weak η^2 -

Table 3. Structural Parameters of 3-5 Relating to Au-Arene Interactions^a

| , ⊸Au | Au |
|-------|---------------------|
| β | $d_1 \bigwedge d_2$ |
| | |
| | |

| complex | D [Å] | β [deg] | Δ [Å] | d_1 | d_2 | η^x |
|---------|-------|---------------|--------------|-------|-------|----------|
| 3 | 3.128 | 27.6 | 1.635 | 3.201 | 3.295 | 1.79 |
| 4 | 3.256 | 28.4 | 1.761 | 3.347 | 3.372 | 1.94 |
| 5 | | | | | | |
| Au2 | 3.376 | 16.8 | 1.019 | 3.416 | 3.509 | 1.71 |
| Au5 | 3.100 | 33.8 | 2.076 | 3.169 | 3.524 | 1.56 |
| Au6 | 2.946 | 37.4 | 2.253 | 3.069 | 3.591 | 1.59 |
| | | | | | | |

^{*a*}Kochi criteria for hapticity η^x , $x = 1 + 2(d_1^2 - D^2)^{1/2} / [(d_1^2 - D^2)^{1/2} + (d_2^2 - D^2)^{1/2}]$; d_1 and d_2 are the nearest and second-nearest Au–C distances; *D* is the distance between Au and the mean plane of the central arene. β is the angle between the normal vector of the arene ring and the vector passing through the centroid to the gold atom. Δ is the distance from Au to the ring normal vector passing through the centroid of the arene ring.

Organometallics

arene interactions between Au and arene. All Δ values are more than 1.33 Å, showing that the projection sites of Au are located outside the central arene planes. So these Au–C interactions are side-on, which is also observed in Au–biphenylphosphines complexes.

ASSOCIATED CONTENT

Supporting Information

This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work is financially sponsored by the National Natural Foundation of China (No. 20863001), the Natural Foundation of Guangxi Province (2011GXNSFA018041, 2010GXNSFF013001), and the Programme for Excellent Talents in Guangxi Higher Education Institution.

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