Articles

Dialkylbiarylphosphine Complexes of Gold(I) Halides. Gold−Aryl π-Interactions in the Solid State

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Dialkylbiarylphosphines are an emerging ligand set that promote catalytic reactions of electrophilic late transition-element centers through dative interactions of the biaryl arm with the metal site. Presented here are syntheses and crystal structures of five new (dicyclohexylbiarylphosphine)gold(I) chlorides and bromides. X-ray diffraction crystallography reveals close approaches between gold(I) and the flanking *ipso* carbon (mean Au−C_{ipso} distance, compounds **2**−**6**: 3.156 Å). New compounds have been characterized by multinuclear NMR spectroscopy, X-ray diffraction crystallography, and combustion analysis.

Introduction

The dialkylbiarylphosphines of Buchwald and collaborators are certainly among the most spectacular organo-group 15 ligands to have emerged in the past decade.[1] They promote or enable a number of transformations, many palladium-catalyzed,[2–6] including the Suzuki−Miyaura coupling,[7–11] carbon−hydrogen bond functionalizations,[9] Sonogashira couplings of aryl chlorides,[12] Negishi coupling of hindered biaryls,[13] aromatic ether synthesis by coupling of aryl halides with alcohols,[14,15] and amidations and aminations of aryl sulfonates, aryl halides, and heteroaryl halides.[16,17] These phosphine ligands are believed to stabilize critical intermediates in metal-mediated catalytic cycles. Experimental evidence indicates that the non-phosphorus-bound aryl group binds the metal center in a side-on manner. Control experiments with a ligand bearing cyclohexyl in place of the pendant arene ring,[2] molecular modeling, and structural studies of chemically competent palladium complexes indicate Pd−π aryl bonding interactions.

Structurally characterized palladium complexes of dialkylbiarylphosphines have appeared occasionally. In 2002, Buchwald and co-workers[18] disclosed the crystal structure of a (dibenzylideneacetone)Pd(0) complex of (9-phenanthryl)dicyclohexylphosphine. Close approaches of palladium to two 9-phenanthryl carbon atoms (2.298(6) Å to the *ipso* carbon and 2.323(6) Å to the *ortho*-methine carbon) were noted. Fink and collaborators[19] published a crystal structure of the palladium(0) bis-phosphine adduct of (*o*-biphenyl)dicyclohexylphosphine. This structure features a single close contact between palladium and the *ipso* carbon of one phosphine ligand, at 2.676(5) Å. The coordinating aryl group is planar and without significant alteration of ring C−C bond lengths. Variable-temperature NMR experiments indicate that the complex is stereochemically nonrigid. Vilar and co-workers[20] reported three crystal structures of palladium complexes of (*o*-biphenyl)di(*tert*-butyl)phosphine: one a dibenzylideneacetone adduct of palladium(0), along with metal−metal bonded dibromo and dichloro palladium(I) complexes, each bearing a single phosphine ligand. In the Pd(0) complex, the metal atom approaches within 2.401(6) Å of the

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aryl carbon *ortho* to the *ipso* position. In the two palladium(I) structures, Pd−*ipso* carbon distances range from 2.113(8) to 2.140(6) Å; arene coordination is described as μ^2-η^3:η^3.

Crystal structures and electron topographical analyses have been reported for complexes of mononuclear Pd(0) and for a metal−metal bonded dimer of Pd(I) with (2,2′-dimethoxybiphenyl)dicyclohexylphosphine.[21] In the mononuclear Pd(0) complex, which carries an η^2-dibenzylideneacetone coligand, the Pd−C_{ipso} distance is 2.374(3) Å. Density-functional calculations combined with an atoms-in-molecules analysis[22,23] find a single (3, −1) bond critical point between palladium and the *ipso* carbon of the ligand. Di or higher hapticity is thereby excluded. In the dimeric Pd(I) complex, each metal center exhibits sidewise interactions with two aryl groups: one with the arene ring appended to its own phosphine ligand and the other with the aryl group bound to the remote phosphine that ligates the other metal atom. The maximal symmetry of the dimer is C_{2h}. In the crystal structure of the tetrafluoroborate salt, the dimer resides on an inversion center. The two Pd−C interactions are distinctly different, despite a similarity of Pd−C distances (2.1970(16) and 2.1901(17) Å). The interaction between Pd(I) and the *ipso* carbon of its own ligand is describable as a σ-complex or Wheland intermediate, where the pendant aryl group has characteristics of a benzene ring undergoing electrophilic attack. The side-on interaction with the aryl carbon of the remote phosphine is a typical π-interaction. The Pd(I) dimer is competent in Suzuki−Miyaura coupling reactions; low loadings of dimer support catalysis with coupling products recoverable in high yields.[21] Recent calculations of (phosphine)Pd(0) monomers find stabilizing η^1-Pd−biaryl interactions and emphasize the need for including the full ligand in computational analyses.[24]

The combined evidence indicates, as originally suggested,[2] that dialkylbiarylphosphine ligands supply monophosphine−palladium complexes in significant quantities, and efficient catalyses of broad scope result.

Gold-mediated organometallic catalysis is in an ascendancy.[25–34] Much recent effort has focused on cyclizations and other transformations of functionalized olefins, allenes, and alkynes. In many such processes, (phosphine)- or (*N*-heterocyclic carbene)gold(I) halides are catalyst precursors. Here also, dialkylbiarylphosphines are emerging as supporting ligands.

Echavarren and co-workers have applied (biarylphosphine) gold(I) complexes in the intramolecular cyclopropanation of dienynes,[35] in cyclizations of 1,6-enynes,[36] in cyclization reactions of alkynes with indoles,[37] in rearrangements and [2 + 2] cycloadditions of enynes,[38] and in [4 + 2] intramolecular cycloadditions of 1,3-enynes with olefins.[39] Recently, Widenhoefer and co-workers[40] reported that the gold complex generated from [P(t-Bu)$_2$(o-biphenyl)]AuCl and AgOTf in dioxane catalyzes intramolecular hydrofunctionalizations of allenes with nitrogen, carbon, and oxygen nucleophiles. A related protocol permits the *exo*-hydroamination of *N*-alkenyl carbamates.[41] In many such reactions, the dialkylbiarylphosphine ligand is essential to catalyst reactivity and selectivity. The influence of flanking aryl groups in gold catalysis is a matter of continuing study.

Zhang and collaborators have reported crystal structures of (phosphine)gold(I) cations bearing pendant anthracene moieties. In one such structure,[42] the ligand is a 9,10-diphosphinoanthracene with η^6 coordination of gold to the central ring. More recently these authors[43] have published two crystal structures of gold(I) monophosphine complexes again bearing pendant anthracenes. Both cations possess η^2 interactions between Au and the anthracene substituent. A related, neutral compound of the same ligand exhibits no metal–ligand π-interaction.

Echavarren and co-workers[44] have disclosed crystal structures of three (dialkylbiarylphosphine)gold(I) chlorides and of several solvated (phosphine)gold(I) cations. The solvate complexes are stated to be active catalysts for cyclization, rearrangement, and intramolecular cyclopropanation reactions of enynes and for the cyclization of alkynes with indoles.

Reported here are synthetic and structural studies of gold(I) complexes of dicyclohexylbiarylphosphines. Compounds are designated as in Chart 1; structures of **2−6** have not been previously reported.

Experimental Section

All solvents and reagents were used as received. Procedures for gold(I) bromides were done in air; syntheses of chlorides were performed in a nitrogen-filled glovebox. Microanalyses (C, H, and N) were performed by Quantitative Technologies Inc. ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectra were recorded on a Varian AS-400 spectrometer operating at 400, 161.8, and 100 MHz, respectively; chemical shifts were determined relative to the solvent residual peaks (^{1}H, ^{13}C{^{1}H}) or to 85% aqueous phosphoric acid (^{31}P{^{1}H}). Tetrachloroauric acid and the phosphine ligands PCy$_2$(o-biphenyl),[45,46]

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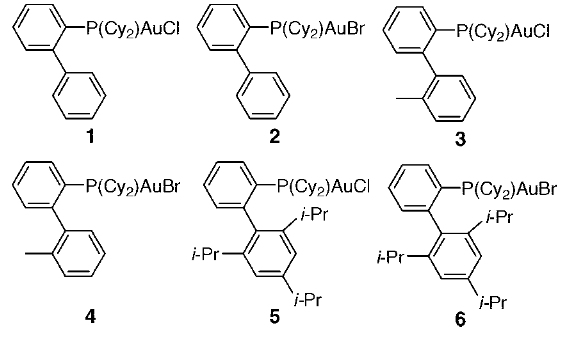
Chart 1. Designation of Compounds



PCy$_2$(2′-methylbiphenyl),[45,46] and PCy$_2$(2′,4′,6′-triisopropylbiphenyl)[47] were purchased from Strem Chemicals, Inc.

[(PCy$_2$(*o*-biphenyl))AuBr] (2). In 30 mL of dichloromethane was dissolved [(PCy$_2$(*o*-biphenyl))AuCl][48] (419 mg, 0.719 mmol), and to this solution was added a 25 mL aqueous solution of KBr (475 mg, 3.99 mmol). The biphasic mixture was stirred 4 h, and the organic layer was collected. The aqueous layer was washed once with dichloromethane (10 mL), and the organic layers were combined, washed with water (2 × 10 mL), dried with MgSO$_4$, and filtered. The filtrate was stripped of solvent via rotary evaporation, and pentane was added to the resultant white residue. Repeated scraping of the residue with a spatula into the pentane liberated a free-flowing solid, which was collected and dried. Yield: 416 mg (92%). ^{1}H NMR (C$_6$D$_6$): δ 7.44 (t, *J* = 7.2 Hz, 1H, 2′-biphenyl), 7.29–7.37 (m, 3H, 2′-biphenyl), 7.09 (d, *J* = 6.8 Hz, 2H, 2′-biphenyl), 6.94–7.02 (m, 3H, 2′-biphenyl), 0.77–1.29 (m, 22H, C_6H_{11}). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 46.0 ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 149.45 (d, *J* = 11.4 Hz), 141.71 (d, *J* = 5.4 Hz), 134.31 (d, *J* = 7.7 Hz), 132.67 (d, *J* = 7.7 Hz), 130.60 (d, *J* = 2.2 Hz), 129.48 (s), 129.19 (s), 128.96 (s), 127.41 (d, *J* = 8.4 Hz), 126.20 (s), 125.71 (s), 36.89 (d, *J* = 32.1 Hz), 31.15 (d, *J* = 4.5 Hz), 29.54 (s), 26.74 (s), 26.61 (s), 26.46 (s), 25.67 (s) ppm. Anal. Calcd for $C_{24}H_{31}AuBrP$: C, 45.95; H, 4.98. Found: C, 45.66; H, 5.06.

(PCy$_2$(2′-methylbiphenyl))AuCl (3). In a glovebox, (PCy$_2$(2′-methylbiphenyl) (488 mg, 1.34 mmol) was dissolved in 15 mL of toluene, and to this solution was added [Au(tht)Cl] (tht = tetrahydrothiophene) (424 mg, 1.32 mmol). The resultant solution was stirred 24 h under argon, during which it became a white suspension. The suspension was stripped of solvent in vacuo to yield a white residue, to which pentane was added. Repeated scraping of the residue with a spatula into the pentane liberated a free-flowing solid, which was collected and dried. Yield: 765 mg (97%). ^{1}H NMR (C$_6$D$_6$): δ 7.53 (td, *J* = 7.6, 1.6 Hz, 1H, 2′-methylbiphenyl), 7.41 (d, *J* = 7.6 Hz, 1H, 2′-methylbiphenyl), 7.23 (t, *J* = 7.6 Hz, 1H, 2′-methylbiphenyl), 6.88–7.14 (m, 5H, 2′-methylbiphenyl), 1.99 (s, 3H, CH_3), 0.78–1.91 (m, 22H, C_6H_{11}). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 38.6 ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 149.61 (d, *J* = 13.0 Hz), 141.06 (d, *J* = 6.1 Hz), 135.64 (s), 132.87 (d, *J* = 4.5 Hz), 132.64 (d, *J* = 7.6 Hz), 132.00 (s), 130.83 (d, *J* = 2.3 Hz), 129.98 (s), 129.47 (s), 127.21 (d, *J* = 7.6 Hz), 126.08 (s), 125.90 (s), 125.58 (s), 37.41 (d, *J* = 32.1 Hz), 35.30 (d, *J* = 34.3 Hz), 30.84 (m), 29.71 (s) 29.00 (s), 26.95 (s), 26.82 (d, *J* = 4.6 Hz), 26.63 (d, *J* = 3.8 Hz), 26.48 (s), 26.34 (s), 25.77 (d, *J* = 10.6 Hz), 21.13 (s) ppm. Anal. Calcd for $C_{25}H_{33}AuClP$: C, 50.30; H, 5.57. Found: C, 50.09; H, 5.45.

[(PCy$_2$(2′-methylbiphenyl))AuBr] (4). In 40 mL of dichloromethane was dissolved [(PCy$_2$(2′-methylbiphenyl))AuCl] (749 mg, 1.25 mmol), and to this solution was added a 30 mL aqueous solution of KBr (840 mg, 7.06 mmol). The biphasic mixture was stirred 4 h, and the organic layer was collected. The aqueous layer was washed once with dichloromethane (10 mL), and the organic layers were combined, washed with water (2 × 10 mL), dried with MgSO$_4$, and filtered. The filtrate was stripped of solvent via rotary evaporation, and pentane was added to the resultant white residue. Repeated scraping of the residue with a spatula into the pentane liberated a free-flowing solid, which was collected and dried. Yield: 749 mg (93%). ^{1}H NMR (C$_6$D$_6$): δ 7.53 (td, *J* = 7.6, 1.2 Hz, 1H, 2′-methylbiphenyl), 7.39 (d, *J* = 7.6 Hz, 1H, 2′-methylbiphenyl), 7.22 (t, *J* = 7.6 Hz, 1H, 2′-methylbiphenyl), 7.09–7.14 (m, 1H, 2′-methylbiphenyl), 6.98–7.04 (m, 3H, 2′-methylbiphenyl), 6.89–6.93 (m, 1H, 2′-methylbiphenyl), 1.98 (s, 3H, CH_3), 0.69–1.98 (m, 22H, C_6H_{11}). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 40.6 ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 149.56 (d, *J* = 13.7 Hz), 141.17 (d, *J* = 6.1 Hz), 135.59 (s), 132.93 (d, *J* = 3.8 Hz), 132.64 (d, *J* = 7.7 Hz), 132.20 (s), 130.87 (d, *J* = 2.3 Hz), 130.00 (s), 129.43 (s), 127.29 (d, *J* = 7.7 Hz), 126.21 (s), 125.96 (s), 125.71 (s), 37.52 (d, *J* = 31.3 Hz), 35.42 (d, *J* = 33.5 Hz) 30.78 (m), 29.69 (s), 29.00 (s), 26.97 (s), 26.83 (d, *J* = 4.6 Hz), 26.65 (d, *J* = 3.8 Hz), 26.51 (s), 26.37 (s), 25.79 (d, *J* = 7.6 Hz), 21.12 (s) ppm. Anal. Calcd for $C_{25}H_{33}AuBrP$: C, 46.82; H, 5.19. Found: C, 46.82; H, 5.04.

[(PCy$_2$(2′,4′,6′-triisopropylbiphenyl))AuCl] (5). In a glovebox, PCy$_2$(2′,4′,6′-triisopropylbiphenyl) (560 mg, 1.17 mmol) was dissolved in 20 mL of toluene, and to this solution was added [(tht)AuCl] (364 mg, 1.14 mol). The [(tht)AuCl] remained suspended initially, but the suspension shortly became a solution. After stirring 20 h, the solvent was stripped via rotary evaporation, and pentane was added to the remaining white residue. The residue was scraped repeatedly into the pentane, and the white powder that separated was collected and dried. Yield: 755 mg (91%). ^{1}H NMR (C$_6$D$_6$): δ 7.40 (s, 2H, 2′,4′,6′-triisopropylbiphenyl), 7.16–7.19 (m, 1H, 2′,4′,6′-triisopropylbiphenyl), 6.93–7.06 (m, 3H, 2′,4′,6′-triisopropylbiphenyl), 3.17 (sep, *J* = 6.8 Hz, 1H, $CH(CH_3)_2$), 2.43 (sep, *J* = 6.8 Hz, 2H, $CH(CH_3)_2$), 1.59 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.51 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$) 1.05 (d, *J* = 6.4 Hz, 6H, $CH(CH_3)_2$), 0.78–1.81 (m, 22H, C_6H_{11}) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 36.0 ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 150.96 (s), 148.12 (d, *J* = 14.5 Hz), 145.83 (s), 135.91 (d, *J* = 6.1 Hz), 134.04 (d, *J* = 8.4 Hz), 132.22 (d, *J* = 3.1 Hz), 130.37 (d, *J* = 2.3 Hz), 127.16 (d, *J* = 6.9 Hz), 122.36 (s), 37.37 (d, *J* = 33.6 Hz), 35.17 (s), 31.46 (d, *J* = 2.3 Hz), 31.18 (s), 30.23 (s), 27.16 (d, *J* = 13.8 Hz), 26.79 (d, *J* = 13.0 Hz), 26.08 (s), 25.83 (s), 24.92 (s), 23.41 (s) ppm. Anal. Calcd for $C_{33}H_{49}AuClP$: C, 55.89; H, 6.96. Found: C, 55.81; H, 6.80.

[(PCy$_2$(2′,4′,6′-triisopropylbiphenyl))AuBr] (6). In 20 mL of dichloromethane was dissolved [(PCy$_2$(2′,4′,6′-triisopropylbiphenyl))AuCl] (214 mg, 0.30 mmol), and to this solution was added a 15 mL aqueous solution of KBr (210 mg, 1.76 mmol). The biphasic mixture was stirred 4 h, and the organic layer was collected. The aqueous layer was washed twice with dichloromethane (5 mL), and the organic layers were combined, washed with water (2 × 10 mL), dried with MgSO$_4$, and filtered. The filtrate was stripped of solvent via rotary evaporation, and pentane was added to the resultant white residue. Repeated scraping of the residue with a spatula into the pentane liberated a free-flowing solid, which was collected and dried. Yield: 173 mg (76%). ^{1}H NMR (C$_6$D$_6$): δ 7.38 (s, 2H, 2′,4′,6′-triisopropylbiphenyl), 7.12–7.17 (m, 1H, 2′,4′,6′-triisopropylbiphenyl), 6.94–7.07 (m, 3H, 2′,4′,6′-triisopropylbiphenyl), 3.20 (sep, *J* = 6.8 Hz, 1H, $CH(CH_3)_2$), 2.43 (sep, *J* = 6.8 Hz, 2H, $CH(CH_3)_2$), 1.58 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$), 1.51 (d, *J* = 6.8 Hz, 6H, $CH(CH_3)_2$) 1.05 (d, *J* = 6.4 Hz, 6H, $CH(CH_3)_2$), 0.79–1.83 (m, 22H, C_6H_{11}) ppm. ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ 37.9 ppm. ^{13}C{^{1}H} NMR (C$_6$D$_6$): δ 150.82 (s), 148.00 (d, *J* = 14.5 Hz), 145.79 (s), 136.02 (d, *J* = 6.2 Hz), 134.03 (d, *J* = 7.6 Hz), 132.37 (d, *J* = 3.0 Hz), 130.44 (d, *J* = 2.3 Hz), 127.28 (d, *J* = 6.8 Hz), 122.45 (s),

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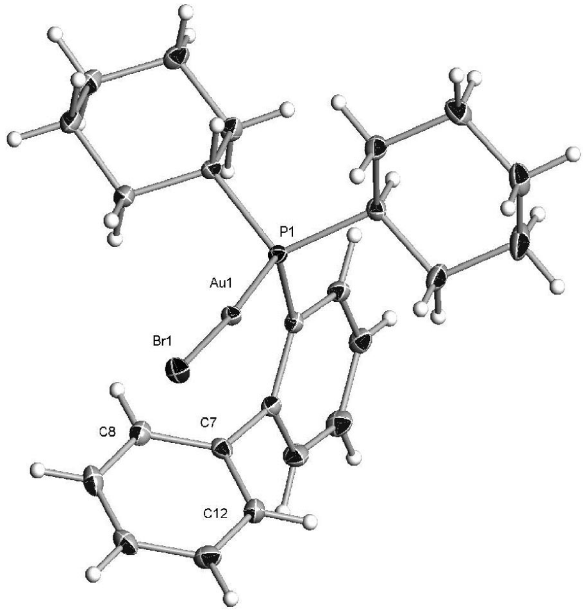

Figure 1. Crystal structure of **2** (50% probability). Data were collected at 100 K. A partial numbering scheme is shown.

37.60 (d, $J = 32.1$ Hz), 35.01 (s), 31.42 (d, $J = 2.3$ Hz), 31.12 (s), 30.27 (s), 27.18 (d, $J = 13.7$ Hz), 26.81 (d, $J = 13.0$ Hz), 26.05 (s), 25.83 (s), 24.96 (s), 23.48 (s) ppm. Anal. Calcd for $C_{33}H_{49}AuBrP$: C, 52.60; H, 6.55. Found: C, 52.66; H, 6.68.

Results

Syntheses. Compounds **2–6** were synthesized by modification of standard procedures. Chloro complexes were prepared from (tetrahydrothiophene)gold(I) chloride and 1 equiv of the corresponding phosphine. Bromo complexes were prepared from the chloride analogues in biphasic reaction mixtures consisting of methylene chloride solutions of gold complexes and aqueous brines of potassium bromide. Syntheses of chlorides were performed under nitrogen; bromides were prepared in air. Isolated yields range from 76 to 97%. Compounds were characterized by multinuclear NMR spectroscopy, elemental analysis, and X-ray diffraction crystallography.

Crystal Structures. X-ray quality crystals were grown for products **2–6**. Table S1 (Supporting Information) summarizes crystallographic data. Figure 1 depicts a thermal ellipsoid projection of the representative structure **2**; structures of **3–6** appear as Supporting Information. Table 1 summarizes significant interatomic distances and angles. The Au−P and Au−X (X = Br, Cl) bond lengths are unremarkable, falling within the range of bond lengths for crystallographically characterized phosphine-ligated gold(I) halides.[49–51] Au−P bond lengths range from ~2.23 to 2.25 Å, while Au−Cl and Au−Br distances average approximately 2.29 and 2.41 Å, respectively. Furthermore, P−Au−X bond angles (~174–177° for all products) approach linearity. In contrast with other gold(I) halides ligated by smaller phosphines (e.g., PMe_3),[52–55] there is no evidence for aurophilic contacts[56,57] in products **2–6**.

In all crystallographically characterized products there is an apparent interaction between gold and the π-face of the flanking phosphine biaryl group. Qualitatively similar interactions occur in the structure of **1**, in cationic gold(I) arene complexes,[44] and in complexes of anthracenyl-derived phosphine ligands.[42,43] Except for one independent molecule of **6**, all Au−C_{ipso} distances are conspicuously shorter than either Au−C_{ortho} length. For example, the Au−C_{ipso} distance in **5** is 3.125(4) Å; the Au−C_{ortho} distance is 3.200(5) Å. In the structure of **6**, one crystallographically independent molecule has an Au−C_{ipso} distance of 3.202(5) Å and an Au−C_{ortho} distance of 3.218(4) Å. For the isostructural complexes **3** and **4**, in which the phosphine does not possess C_s symmetry, both diastereomers (i.e., biaryl η^2 binding to the C_{ipso}/C_H carbon atom pair and the C_{ipso}/C_{Me} carbon atom pair) are found in the unit cell, but the interaction still shows the same asymmetric binding for both rotamers.

Steric encumbrance between gold and the pendant biaryls is evident crystallographically. In all complexes the Au−P and central (inter-ring) C−C bond vectors are nonparallel and the pendant aryl ring bends away from the Au−X bond, even though the *ipso* carbon (and in some cases an *ortho* carbon) of the flanking aryl group approaches within bonding distance of gold. Bending angles φ for each product appear in Table 2. A search of the crystal structures of **2–6** finds no close approaches (i.e., less than the sum of the van der Waals radii) of chlorine or bromine to any atom of the phosphine ligands.

NMR Spectroscopy. ^{1}H and ^{13}C{^{1}H} NMR measurements made on C_6D_6 solutions of **2–6** indicate that nuclides related by a pseudomirror plane are magnetically equivalent; the apparent symmetry is C_s, even for **3** and **4**. ^{31}P NMR resonances fall within the range δ 36.0–46.0 ppm.

Discussion

Gold(I) halide complexes of dialkylbiaryphosphines exhibit an interaction in the crystalline state with the flanking (non-phosphorus-bearing) aryl group of the ligand. In the five new structures disclosed here and in that of **1** reported previously,[44] the gold(I)−*ipso* carbon distance averages 3.16 Å, with the largest being 3.2018(4) Å observed on one independent molecule of **6**. These values are less than the sum of the van der Waals radii (3.36 Å) of carbon and gold.[58] The average distance between gold and the mean plane of the flanking aryl groups in **2–6** is 3.111 Å. There is no apparent correlation between the Au−C_{ipso} approach and halide identity, nor with substituents on the flanking phenyl ring.

Recently Kochi and co-workers[59] have proposed a geometric estimation of hapticity, η^x:

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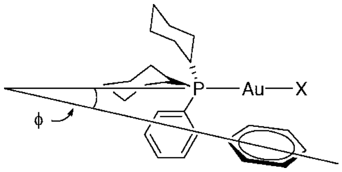
Table 1. Selected Interatomic Distances (Å) and Angles (deg) for 2–6, X = Cl, Br

compound	Au−P	Au−X	Au−C_{ipso}	Au−C_{ortho}	∠P−Au−X
2	2.2419(6)	2.4066(3)	3.1359(23)	3.2759(24), 3.5240(26)	175.527(16)
3	2.2360(12)	2.2874(11)	3.1929(53),[a] 3.129(23)	3.2606(51), 3.491(22) (C-Me); 3.7042(56), 3.331(23) (C-H)	175.53(4)
4	2.2497(15)	2.4042(7)	3.1707(67),[a] 3.126(23)	3.2391(63), 3.495(26) (CMe); 3.6771(75), 3.305(28) (CH)	175.39(4)
5	2.2349(11)	2.2900(11)	3.1252(44)	3.1998(51), 3.4497(45)	176.68(4)
6[b]	2.2466(11), 2.2471(11)	2.4116(5), 2.4089(5)	3.1690(39), 3.2018(40)	3.4723(40), 3.5853(40); 3.2478(39), 3.2183(40)	174.41(3), 174.51(3)

[a] The *o*-tolyl group is flip-disordered over two positions with an occupancy ratio of 0.844(5) to 0.156(5) (**3**) and 0.837(7) to 0.163(7) (**4**). [b] Two crystallographically independent molecules in the unit cell.

Table 2. Bending Angles (φ) for 2–6



compound	φ (deg)
2	14.1
3[a]	17.3, 15.1
4[a]	17.9, 15.1
5	15.6
6[b]	16.8, 20.3

[a] Two flip-disordered *o*-tolyl substituents per molecule. [b] Two crystallographically independent molecules in the unit cell.

$$x = 1 + 2\frac{\sqrt{d_1^2 - D^2}}{\sqrt{d_1^2 - D^2} + \sqrt{d_2^2 - D^2}} \qquad (1)$$

Here, d_1 and d_2 are the nearest and second-nearest Au−C distances; D is the length of the normal vector extending from gold to the mean plane of the six pendant aryl-ring carbons. Estimated hapticities range from $x = 1.32$ for one flip-disordered *o*-tolyl substituent of **3** to $x = 1.95$ for one independent molecule of **6**; Table 3 collects hapticity figures. For comparison, that of **1** from the published structure[44] is $x = 1.55$. This π-bonding to the pendant biaryl moieties ranges from something exceeding η^1 to nearly η^2. These structural observations, combined with the apparent C_s-symmetry in solution, suggest a comparatively flat potential energy landscape for side-on gold−carbon bonding, at least in neutral complexes.

Table 3. Hapticities η^x Calculated for the Crystal Structures of 1–6

compound	x
1	1.55[a]
2	1.55
3	1.83, 1.32[b]
4	1.82, 1.35[b]
5	1.78
6	1.79, 1.95[c]

[a] From ref 44. [b] Two flip-disordered *o*-tolyl substituents per molecule. [c] Two crystallographically independent molecules in the unit cell.

Conclusions

Air- and water-stable gold(I) halide complexes of dialkylbiarylphosphine ligands have been synthesized and structurally characterized. Crystal structures reveal at least an η^1 interaction between gold and the *ipso* carbon of the adjacent biaryl; one independent molecule of **6** undergoes an η^2 interaction between Au and the ligand *ipso* and *ortho* carbons. Such sidewise interactions have precedent in palladium chemistry,[9,21] where they are held to stabilize catalytic intermediates.[2]

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Supporting Information Available: Crystallographic (CIF) data. This material is available free of charge via the Internet at http://pubs.acs.org.

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