Arene Complexes

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Cationic η^1/η^2-Gold(I) Complexes of Simple Arenes[**]

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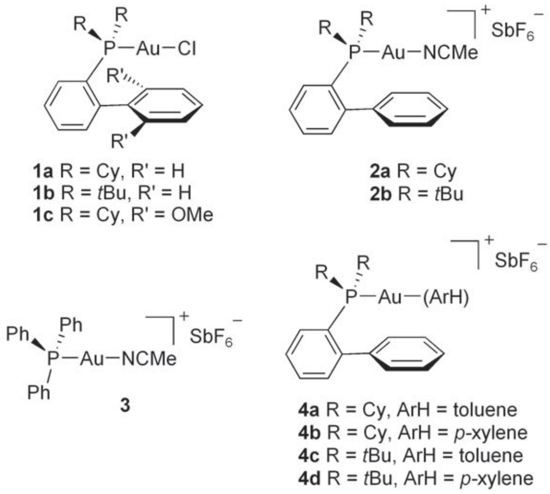
Bulky biphenylphosphane ligands have been particularly successful in Pd-catalyzed reactions.[1] These ligands have led to the isolation of new Pd^I complexes, which display unusual Pd–arene interactions and enhanced reactivity in cross-coupling processes.[2]

We have used bulky biphenylphosphanes for the preparation of Au^I complexes **1a–c** (Scheme 1), whose cationic derivatives are very active catalysts that allow for the cyclization of 1,6-enynes substituted at the alkyne function with aryl or alkenyl groups.[3] Instead of preparing the cationic complexes by chloride abstraction with Ag^I salts in situ, we have sought to use stable $[Au(PR_3)(L)]^+A^-$ (L = ligand) complexes with a weakly coordinating ligand that could be replaced by the alkyne functionality of the reacting enyne.



Scheme 1. Neutral and cationic Au^I complexes.

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Thus, complexes **2a,b** with an acetonitrile ligand have been prepared as stable white salts that are particularly active for the alkoxycyclization, skeletal rearrangement,[4–6] and intramolecular cyclopropanation[7] of a variety of enynes.[8] These complexes also catalyze the cyclization of indoles with alkynes.[9] Cationic complex **3** with triphenylphosphane is also an excellent catalyst for the intramolecular cyclopropanation of dienynes.[7,10] Importantly, the use of **2a,b** or **3** as catalysts allows reactions to be carried out in the absence of Ag^I, which can lead to unwanted side reactions.[11]

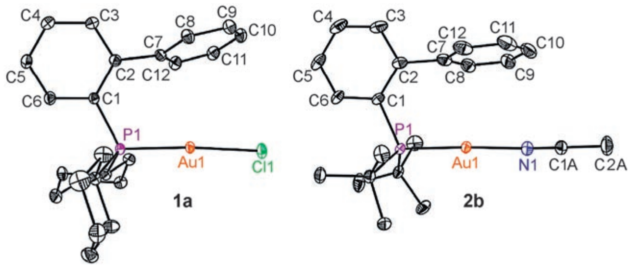


Figure 1. Ortep plots (50%) of complexes **1a** and **2b** (only the complex cation is shown for **2b**). The hydrogen atoms have been omitted for clarity.

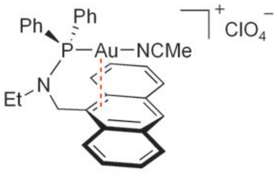
Table 1: Selected distances [Å] for **1a–c**, **2a,b**, **3**, and **4a–d**.[a]

	Au–P	Au···Cl,N,C2A/C3A/C4A[b]	Au···Ar[c]	Au···C7/C8/C12/O1[d]
1a	2.2364(6)	2.2912(6)		3.15/3.55/3.83
1b	2.254(3)	2.303(4)		3.16/3.40/3.40
1c	2.2378(5)	2.3089(5)		3.27/3.13/3.92/3.27
2a	2.2466(3)	2.0338(9)		3.02/3.25/3.24
2b	2.2539(7)	2.046(2)		3.04/3.28/3.38
3	2.2282(12)	2.038(5)		
4a	2.2459(13)	2.535(6)/2.263(5)/2.689(6)	2.244(5)	3.22/3.10/3.69
4b	2.2400(17)	2.338(7)/2.341(7)	2.229(7)	3.15/3.45/3.33
4c	2.2643(10)	2.299(5)/2.423(5)	2.233(5)	3.03/3.42/3.14
4d A	2.2657(11)	2.300(4)/2.354(4)	2.200(4)	3.04/3.00/3.64
4d B	2.2636(10)	2.308(4)/2.370(4)	2.221(4)	3.04/3.41/3.21

[a] Compound **4d** has two independent molecules (A and B). [b] Distances are from Au to Cl for **1a–c**, to N for **2a,b** and **3**, and to C2A/C3A/C4A for **4a–d**. [c] The shortest distance between the Au center and the plane of the complexed arene. [d] These distances are only approximations.

In contrast to Ag^I, whose complexes with arenes have been thoroughly investigated,[12] only three examples in which the Au^I center interacts with an arene have been reported.[13] These have been described by Zhang and co-workers as η²-arene complexes with an intramolecular interaction with an anthracene unit that is covalently attached to the phosphane ligand. Thus, the Au complex **5** shows the strongest η²-anthracene–Au^I interaction, with Au···C distances of 2.958 and 3.097 Å,[13b] whereas other anthracene complexes show Au···C close contacts between 3.020 and 3.246 Å.[13]

We wanted to determine if the proximity of the arene ring parallel to the Au–P bonds of complexes **2a,b** played any role in stabilizing these complexes by arene–Au interactions. As part of this study, we found that crystallization of **2a,b** from toluene or *p*-xylene leads to the isolation of the first Au^I complexes **4a–d** of simple arenes that show η¹/η² coordination. Herein, we report the single-crystal structures of Au^I complexes **4a–d**, as well as those of **1a–c**, **2a,b**, and **3**.[14]



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X-ray structures **1a** and **2b**, representative of neutral (**1a–c**) and cationic (**2a,b**) complexes,[15–20] are shown in Figure 1. The relevant distances and angles are shown in Tables 1 and 2, respectively.

The Au–P and Au–Cl bond lengths of **1a–c** are around 2.24 and 2.30 Å, respectively, which are similar to those found in $[AuCl(PPh_3)]$[21,22] and related Au^I complexes.[23] The Au–N lengths (around 2.04 Å) in **2a,b** and **3** correspond to that found in cationic acetonitrile complex **5** (2.043 Å)[13b] and are slightly longer than that reported for $[Au(NCMe)_2]SbF_6$ (1.96 Å).[24] Cationic complexes **2a,b** show a greater bending of the P-Au-NCMe angle (174.43 and 173.06°) than complex **3** (177.10°) with a triphenylphosphane moiety as the ligand.

For neutral complexes **1a–c**, the average distance between the Au center and the covering arene ring is 3.15 Å. This distance is slightly shorter in cationic complexes **2a,b** (3.03 Å; Figure 2). These values are similar to those found by Zhang et al. for Au–anthracene complexes such as **5**.[13]

In contrast, the arene–Au^I interactions with toluene or *p*-xylene ligands in complexes **4a–d** are considerably stronger

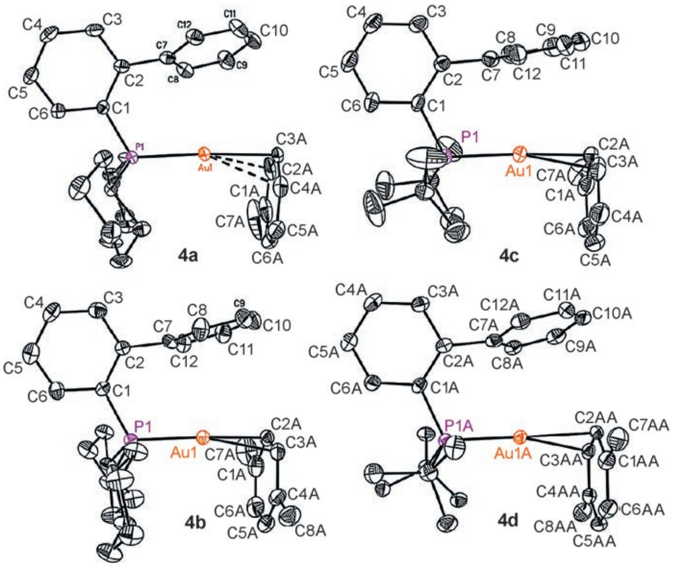

Figure 2. Ortep plots (50%) of the cationic part of the complexes **4a–d**. The hydrogen atoms have been omitted for clarity.

(Figure 2).[25–29] In all cases, the plane of the aromatic ring forms an angle to the vector of the Au–P bond close to 90° (Table 2). The shortest distances between the Au atom and the plane of the aromatic ring of the π-complexed arenes are 2.20–2.24 Å (Table 1). Importantly, these values are markedly shorter than those found for Ag^I–arene complexes (2.41 ± 0.05 Å),[12a] which is probably due to rather large relativistic effects at the Au center.[22] The distances between the Au atom and the covering arene ring for **4a**–**d** are 3.03–3.22 Å, similar to those found for **1a**–**c** and **2a**,**b**.

Table 2: Selected angles [°] for **1a**–**c**, **2a**, **b**, **3**, and **4a**–**d**.[a]

	P-Au-Cl,N,XA[b]	Au1-P1-C2-C7	C1-C2-C7-C8(C12)	Au ⊥ Ar[c]
1a	175.596(19)	14.2(1)	63.9(3)	
1b	172.56(14)	0.0	87.3	
1c	176.145(18)	18.9(1)	88.7(2) (−99.0(2))	
2a	174.43(3)	9.1(1)	81.90(16)	
2b	173.06(7)	0.0(1)	86.8(3)	
3	177.10(16)			
4a	174.64(16)	7.8(1)	63.5(9)	6.32
4b	171.4 (aprox.)	4.9(1)	77.6(9)	7.21
4c	171.2 (aprox.)	1.7(1)	78.8(6) (−85.9(7))	2.66
4d A	173.7 (aprox.)	0.9(1)	72.6(6)	0.62
4d B	171.9 (aprox.)	3.8(2)	79.8(5)	5.37

[a] Compound **4d** has two independent molecules (A and B). [b] XA is C3A in **4a** and the point centered between C2A and C3A in the rest of molecules. [c] The angle formed between the vector of the Au–P bond and the normal of the aromatic plane C1A–C6A (arene).

Compound **4a**, which is complexed to toluene, shows a η^1-arene interaction with the shortest atom–atom distance from the Au center to C3A (2.263 Å) and secondary interactions to C2A and C4A (2.535 and 2.689 Å). The Au atom in *p*-xylene complex **4b** shows almost a η^2-arene interaction (2.338 and 2.341 Å with C2A and C3A, respectively). Complex **4c** shows a distorted η^1-arene interaction with the shortest atom–atom distance from the Au center to C2A (2.299 Å) and a secondary interaction to C3A (2.423 Å). Curiously, the Au atom in **4a** is more strongly bonded to the *meta* position of the toluene ring, whereas the strongest interaction in **4c** occurs with the *ortho* position. Complex **4d**, which contains two independent molecules in the crystal packing, shows a distorted η^2-arene interaction with a stronger bond to C2 than to C3. According to the geometrical criteria introduced by Kochi and co-workers,[29] the hapticity of complexes would be $\eta = 1.42$ (**4a**), 1.69 (**4b**), 1.41 (**4c**), and 1.52/1.56 (two independent molecules of **4d**).

The shortest intermolecular Au···Au distance was found for **1a** (5.4 Å), whereas this distance ranges from 7.6 to 9.7 Å for **1b**,**c**, **2a**,**b**, **3**, and **4a**–**d**, all of which are beyond the accepted contact limit of 3.6 Å for significant aurophilic interactions.[30]

Broad signals were observed in the ^{31}P{^{1}H} NMR (202.5 MHz) spectra of the arene–Au^I complexes in CD_2Cl_2 at room temperature, thus indicating a fluxional character of these complexes. The broad resonance around $\delta = 68$ ppm for **4c** leads to a sharp signal at $\delta = 65.70$ ppm upon cooling to 200 K. Addition of water to the solution of **4c** in CD_2Cl_2 leads to a new signal at $\delta = 60.40$ ppm (300 K), which corresponds to the aquo complex. By comparison, the ^{31}P NMR resonance of acetonitrile complex **2b** was observed at $\delta = 60.53$ ppm (300 K).

In summary, we have characterized the first Au^I complexes of simple arenes, which show separation between the Au center and the mean aromatic plane of 2.20–2.24 Å. These Au^I–arene bonds are much shorter than the related Ag^I–arene bonds. Weaker interactions have been found between the Au center and the arene parallel to the P–Au bond.

Experimental Section

X-ray structure determinations: Crystals of **1a** were obtained by slow evaporation of CH_2Cl_2 at room temperature using a synthetic fiber as crystallizing base; crystals of **1b**,**c** and **2a**,**b** were obtained by slow evaporation of CH_2Cl_2 at room temperature; crystals of **3** were obtained by slow evaporation of $CHCl_3$; crystals **4a**–**d** were obtained by evaporation at room temperature, after heating a solution in an aromatic solvent (toluene or *p*-xylene) of **2a** or **2b**. Although the analyzed crystals are stable under atmospheric conditions, they were prepared under inert conditions and immersed in perfluoropolyether as a protecting oil for manipulation.

Data Collection: Measurements were made on a Bruker-Nonius diffractometer equipped with a APPEX 2 4 K CCD area detector, a FR591 rotating anode with $Mo_{K\alpha}$ radiation, Montel mirrors as a monochromator, and a Kryoflex low-temperature device ($T = -173\,^{\circ}C$). Full-sphere data collection was used with ω and ϕ scans.

Programs used: Data collection Apex2V. 1.0–22 (Bruker-Nonius 2004), data reduction Saint + Version 6.22 (Bruker-Nonius 2001), and absorption correction SADABS V. 2.10 (2003).

Structure solution and refinement: SHELXTL Version 6.10 (Sheldrick, 2000) was used.[31,32]

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[15] Crystal data for **1a** at 100 K: $C_{24}H_{31}Au_1Cl_1P_1$, 582.87 g mol^{-1}, triclinic, $P\bar{1}$, $a = 9.7118(9)$, $b = 9.9657(9)$, $c = 12.1248(12)$ Å, $\alpha = 110.860(2)$, $\beta = 96.215(2)$, $\gamma = 93.468(3)$°, $V = 1083.92(18)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.786$ Mg m^{-3}, $R_1 = 0.0293$ (0.0375), $wR2 = 0.0754$ (0.0786), for 10 704 reflections with $I > 2\sigma(I)$ (for 12 288 reflections ($R_{int} = 0.0251$) with a total measured of 22 170 reflections), goodness-of-fit on $F^2 = 1.027$, largest diff. peak (hole) = 3.426- (−2.170) e Å$^-$.

[16] Crystal data for **1b** at 100 K: $C_{20}H_{27}Au_1Cl_1P_1$, 530.80 g mol^{-1}, orthorhombic, *Pnma*, $a = 18.127(3)$, $b = 10.7748(18)$, $c = 10.6483(16)$ Å, $V = 2079.8(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.695$ Mg m^{-3}, $R_1 = 0.1249$ (0.1821), $wR2 = 0.2369$ (0.2628), for 4123 reflections with $I > 2\sigma(I)$ (for 6173 reflections ($R_{int} = 0.0732$) with a total measured of 36 777 reflections), goodness-of-fit on $F^2 = 1.205$, largest diff. peak (hole) = 6.868 (−3.855) e Å^{-3}; this structure shows pseudosymmetry; refinement in $Pna2_1$ led to $R_1 = 0.1013$ with negative atomic displacement parameters as a result of correlation effects.

[17] Crystal data for **1c** at 100 K: $C_{27}H_{36}Au_1Cl_4P_1O_2$, 762.29 g mol^{-1}, monoclinic, *C2/c*, $a = 29.968(2)$, $b = 10.3999(7)$, $c = 20.0425(14)$ Å, $\beta = 109.644(2)$°, $V = 5883.0(7)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.721$ Mg m^{-3}, $R_1 = 0.0331$ (0.0415), $wR2 = 0.0817$ (0.0868), for 14 474 reflections with $I > 2\sigma(I)$ (for 17 005 reflections ($R_{int} = 0.0646$) with a total measured of 56 899 reflections), goodness-of-fit on $F^2 = 1.024$, largest diff. peak (hole) = 3.020 (−2.245) e Å^{-3}.

[18] Crystal data for **2a** at 100 K: $C_{22}H_{30}Au_1F_6N_1P_1Sb_1$, 772.16 g mol^{-1}, monoclinic, $P2_1/c$, $a = 8.1165(2)$, $b = 22.5583(4)$, $c = 14.3141(3)$ Å, $\beta = 102.0380(10)$°, $V = 2563.20(9)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.001$ Mg m^{-3}, $R_1 = 0.0166$ (0.0378), $wR2 = 0.0197$ (0.0387), for 13 337 reflections with $I > 2\sigma(I)$ (for 14 489 reflections ($R_{int} = 0.0187$) with a total measured of 50 577 reflections), goodness-of-fit on $F^2 = 1.027$, largest diff. peak (hole) = 2.069 (−0.990) e Å^{-3}.

[19] Crystal data for **2b** at 100 K: $C_{31}H_{48}Au_1F_6N_1P_1Sb_1$, 898.39 g mol^{-1}, monoclinic, $P2_1/c$, $a = 14.5077(6)$, $b = 13.8576(7)$, $c = 17.2481(7)$ Å, $\beta = 97.5130(10)$°, $V = 3437.8(3)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.736$ Mg m^{-3}, $R_1 = 0.0430$ (0.1140), $wR2 = 0.0540$ (0.1206), for 16 335 reflections with $I > 2\sigma(I)$ (for 19 701 reflections ($R_{int} = 0.0515$) with a total measured of 68 445 reflections), goodness-of-fit on $F^2 = 1.046$, largest diff. peak (hole) = 7.561 (−4.242) e Å^{-3}.

[20] Crystal data for **3** at 100 K: $C_{20}H_{18}Au_1F_6N_1P_1Sb_1$, 737.04 g mol^{-1}, monoclinic, $P2_1/c$, $a = 11.2737(17)$, $b = 12.1210(19)$, $c = 16.933(3)$ Å, $\beta = 105.290(3)$°, $V = 2232.0(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 2.190$ Mg m^{-3}, $R_1 = 0.0648$ (0.1413), $wR2 = 0.1429$ (0.1815), for 6521 reflections with $I > 2\sigma(I)$ (for 12 943 reflections ($R_{int} = 0.1035$) with a total measured of 42 796 reflections), goodness-of-fit on $F^2 = 0.998$, largest diff. peak (hole) = 4.169- (−4.437) e Å^{-3}.

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[25] Crystal data for **4a** at 100 K: $C_{31}H_{39}Au_1F_6P_1Sb_1$, 875.31 g mol^{-1}, monoclinic, *Cc*, $a = 10.5275(7)$, $b = 16.2109(11)$, $c = 18.4159(11)$ Å, $\beta = 96.3960(10)$°, $V = 3123.3(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.861$ Mg m^{-3}, $R_1 = 0.0364$ (0.0481), $wR2 = 0.0795$ (0.0823), for 9026 reflections with $I > 2\sigma(I)$ (for 9026 reflections ($R_{int} = 0.0656$) with a total measured of 23 427 reflections), goodness-of-fit on $F^2 = 0.958$, largest diff. peak (hole) = 2.312- (−1.480) e Å^{-3}.

[26] Crystal data for **4b** at 100 K: $C_{32}H_{41}Au_1F_6P_1Sb_1$, 889.33 g mol^{-1}, orthorhombic, *Pbca*, $a = 17.7639(19)$, $b = 14.9629(15)$, $c = 24.063(3)$ Å, $V = 6396.0(11)$ Å^3, $Z = 8$, $\rho_{calcd} = 1.847$ Mg m^{-3}, $R_1 = 0.0713$ (0.1354), $wR2 = 0.1692$ (0.2045), for 8971 reflections with $I > 2\sigma(I)$ (for 15 680 reflections ($R_{int} = 0.1180$) with a total measured of 110 187 reflections), goodness-of-fit on $F^2 = 1.027$, largest diff. peak (hole) = 7.329 (−2.613) e Å^{-3}.

[27] Crystal data for **4c** at 273 K: $C_{27}H_{35}Au_1F_6P_1Sb_1$, 823.24 g mol^{-1}, monoclinic, $P2_1/n$, $a = 10.0342(7)$, $b = 25.189(3)$, $c = 11.8275(14)$ Å, $\beta = 95.413(4)$°, $V = 2976.1(6)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.837$ Mg m^{-3}, $R_1 = 0.0546$ (0.1040), $wR2 = 0.1752$ (0.2146), for 7585 reflections with $I > 2\sigma(I)$ (for 14 113 reflections ($R_{int} = 0.0509$) with a total measured of 55 182 reflections), goodness-of-fit on $F^2 = 1.022$, largest diff. peak (hole) = 3.350- (−1.696) e Å^{-3}; crystals of this compound break down by cooling to lower temperatures probably as a result of a phase transition.

[28] Crystal data for **4d** at 100 K: $C_{60}H_{79}Au_2F_{12}P_2Sb_2$, 1727.60 g mol^{-1}, monoclinic, $P2_1/c$, $a = 25.471(7)$, $b = 13.423(2)$, $c = 18.588(3)$ Å, $\beta = 92.598(9)$°, $V = 6349(2)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.808$ Mg m^{-3}, $R_1 =$

0.0468 (0.1072), $wR2 = 0.0878$ (0.1040), for 17284 reflections with $I > 2\sigma(I)$ (for 29337 reflections ($R_{\text{int}} = 0.0969$) with a total measured of 108860 reflections), goodness-of-fit on $F^2 = 0.930$, largest diff. peak (hole) = 2.749(−2.349) e Å^{-3}.

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[32] CCDC 605715–605724 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.