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Gold(I) η^2 -Arene Complexes

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The reaction of 9-{[*N*-*n*-propyl-*N*-(diphenylphosphino)amino]methyl}anthracene (1) with Au(SMe₂)Cl yields complex 2 with an armopening configuration. The latter is treated with AgClO₄ to form complex 4 and then respectively reacted with acetonitrile, pyridine, and triphenylphosphine sulfide to afford novel gold(I) η^2 -arene complexes 3a–c, which have arm-closing configurations and feeble or weak fluorescence emissions. The observation can be attributed to charge transfer from the anthracene unit to the Au⁺ ion. When the solution of 3a or 4 in CH₂Cl₂ was added with 1 equiv of Ph₃P, complex 5 with the arm-opening configuration was formed and strong emission was restored.

As far as the group 11 metal-arene π complex is concerned, there are numerous η^2 -bonding complexes between Ag⁺ and the aromatic compound¹ and a few of the Cu⁺ analogues;² surprisingly, no gold(1+) η^2 -arene complex is reported. In 2003, we presented a new molecular design and gave the first gold(I) arene complex,³ which is formed by the reaction of chelated diphosphine ligand 9,10-bis{[*Nn*-propyl-*N*-(diphenyphosphino)amino]methyl}anthracene with the Au⁺ ion and adopts a η^6 -coordination mode.

Herein we report some novel gold(I) η^2 -arene complexes, their substitution reaction, and molecular responsive fluorescence spectral variation. In the first place, as shown in Scheme 1, 9-{[*N*-*n*-propyl-*N*-(diphenylphosphino)amino]methyl}anthracene (1) was prepared by the reaction of 9-[(*N*propylamino)methyl)]anthracene with Ph₂PCl. Then, the reaction of 1 with a stoichiometric amount of Au(SMe₂)Cl gave complex 2, which converted to complexes 3**a**-**c** by treatment with AgClO₄ and reaction with acetonitrile, pyridine, and triphenylphosphine sulfide, respectively. Scheme 1



The molecular structures of complexes **2** and **3a**–**c** have been determined by X-ray diffraction analysis.^{4,5} As shown in Figure 1, the linear two-coordinated Au unit Cl(1)– Au(1)–P(1) (178.37°) is perpendicular to the anthracene ring in **2** (an arm-opening configuration). When the Cl atom is substituted by a CH₃CN, pyridine, or Ph₃P=S molecule in elimination and coordination reactions, similar linear twocoordinated Au units P(1)–Au(1)–N(2) (179.59°; **3a**), P(1)– Au(1)–N(2) (177.07°; **3b**), and P(1)–Au(1)–S(1) (172.0°; **3c**) fold toward the anthracene planes (arm-closing configurations) (Figures 2 and 3 and the Supporting Information). The angles Au(1)–P(1)–N(1) are 111.06° (**3a**), 112.54° (**3b**),

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⁽⁴⁾ Crystal data for **2**: $C_{30}H_{28}$ AuClNP, M = 665.92, monoclinic, space group P2(1)/c, a = 9.595(3) Å, b = 16.081(5) Å, c = 17.189(5) Å, $\alpha = 90^{\circ}$, $\beta = 92.575(5)^{\circ}$, $\gamma = 90^{\circ}$, V = 2649.4(14) Å³, Z = 4, $D_c = 1.669$ g cm⁻³, F(000) = 1304, μ (Mo K α) = 5.733 cm⁻¹, T = 293(2) K, 5415 variables refined with 15 061 reflections with $I > 2\sigma(I)$ to R = 0.0511.

⁽⁵⁾ Crystal data for **3a**: C₃₂H₃₁AuClN₂O₄P, *M* = 770.97, triclinic, space group *P*1, *a* = 9.419(3) Å, *b* = 12.900(4) Å, *c* = 13.893(4) Å, *α* = 110.198(4)°, *β* = 104.902(5)°, *γ* = 95.536(4)°, *V* = 1498.8(7) Å³, *Z* = 2, *D_c* = 1.708 g cm⁻³, *F*(000) = 760, μ(Mo Kα) = 5.090 cm⁻¹, *T* = 293(2) K, 6964 variables refined with 9710 reflections with *I* > 2*σ*(*I*) to *R* = 0.0415. Crystal data for **3b**: C₃₅H₃₃AuClN₂O₄P, *M* = 809.02, orthorhombic, space group *Pna2*(1), *a* = 10.2098(10) Å, *b* = 23.903(2) Å, *c* = 13.1372(13) Å, *α* = 90°, *β* = 90°, *γ* = 90°, *V* = 3206.1(5) Å³, *Z* = 4, *D_c* = 1.676 g cm⁻³, *F*(000) = 1600, μ(Mo Kα) = 4.763 cm⁻¹, *T* = 293(2) K, 7598 variables refined with 20 644 reflections with *I* > 2*σ*(*I*) to *R* = 0.0317. Crystal data for **3c**: C₄₈H₄₃AuClNO₄P₂S, *M* = 1024.25, monoclinic, space group *P*(21)/*c*, *a* = 13.248(3) Å, *b* = 16.329(3) Å, *c* = 20.240(4) Å, *α* = 90°, *β* = 90.25(3)°, *γ* = 90°, *V* = 4378.7(15) Å³, *Z* = 4, *D_c* = 1.554 g cm⁻³, *F*(000) = 2048, μ(Mo Kα) = 3.586 cm⁻¹, *T* = 293(2) K, 7652 variables refined with 20 309 reflections with *I* > 2*σ*(*I*) to *R* = 0.1154. Diffractometer: Bruker Smart 1000 CCD diffractometer employing graphite-monochromatized Mo Kα radiation (*λ* = 0.710 73 Å).



Figure 1. ORTEP drawing for **2** with 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): Au(1)-P(1) 2.234, Au(1)-Cl(1) 2.286; Cl(1)-Au(1)-P(1) 178.37, Au(1)-P(1)-N(1) 112.96.



Figure 2. ORTEP drawing for **3a** with 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): Au(1)-C(17) 2.958, Au(1)-C(30) 3.097; P(1)-Au(1)-N(2) 179.59, Au(1)-P(1)-N(1) 111.06, Au(1)-N(2)-C(31) 169.5.



Figure 3. ORTEP drawing for **3b** with 30% probability ellipsoids. Selected bond distances (Å) and angles (deg): Au(1)-C(2) 3.02, Au(1)-C(3) 3.163; P(1)-Au(1)-N(2) 177.07, Au(1)-P(1)-N(1) 112.54.

and 114.4° (**3c**), which are comparable to that of our gold-(I) η^6 -arene complex (117.43°). In the latter, the existence of the three-center bond has been supported by density functional theory calculation.³

The distances of Au(1)–C(17) and Au(1)–C(30) (2.958 and 3.097 Å) in **3a**, Au(1)–C(2) and Au(1)–C(3) (3.020 and 3.163 Å) in **3b**, and Au(1)–C(2) and Au(1)–C(15) (3.077 and 3.119 Å) in **3c** are comparable with those of C arene–Au⁺ (3.118–3.246 Å) in our gold(I) η^6 -arene complex and exhibit a η^2 -binding mode between the Au⁺ and



Figure 4. Fluorescence emission spectra ($\lambda_{ex} = 370$ nm) of ligand 1 and complexes 2, 3a-c, and 4 in CH₂Cl₂.

anthracene units. Another feature of complex 3a is the $\pi - \pi$ interaction between the coordinated acetonitrile and the anthracene unit. The Au(1)-N(2)-C(31) angle (169.5°) has a deviation from linearity and indicates the presence of a secondary interaction with the anthracene unit. The $N(2) \equiv$ C(31) bond in CH_3CN and the C(24)-C(25) bond in the anthracene ring adopt a cross-configuration, and the distance between the middle points of the two bonds (3.29 Å) is relatively short and comparable with the $\pi - \pi$ stacking distance in graphite. The distances of N(2)-C(24), N(2)-C(25), C(31)-C(24), and C(31)-C(25) fall in the range of 3.349-3.499 Å. The Au(1)-N(2) distance (2.043 Å) is longer than that of the only reported Au⁺–NCCH₃ complex $[Au(NCCH_3)_2][SbF_6]$ (1.97 Å).⁶ Whereas there is no the overlapping part between the coordinated pyridine and the anthracene unit in space in **3b** and the dihedral angle is 4.56°, the $\pi - \pi$ interaction does not exist.

By treatment with AgClO₄ in CH₂Cl₂, **2** can convert to **4**, which has much less fluorescence emission (vide infra) and probably has a stronger $\eta^2 - \pi$ -coordination action between the Au⁺ ion and the anthracene unit in comparison with **3a**-**c**. Complex **4** is very sensitive to light and air, cannot be separated out, and has been confirmed by ¹H and ³¹P NMR spectra. **3a**-**c** have unequivocally been proven to be gold-(I) η^2 -arene complexes.

Now, the question is, why are there different configurations among 2 and $3\mathbf{a}-\mathbf{c}$, all of which include a linear twocoordinated Au⁺ unit? Compared with the neutral complex 2, the electron densities on the gold atoms are less than those in complexes $3\mathbf{a}-\mathbf{c}$, which are unfavorable for the donation of a π electron toward the arene units. This point of view conflicts with the widely accepted Dewer-Chatt-Duncanson model,⁷ which predicts η^2 -bonding of silver(I) to a pair of aromatic carbon atoms by its π back-donation in the silver-(1+) arene complexes. According to the Mulliken assumption,⁸ the π interaction of arene with gold(I) should be dominated by charge transfer from arene to the Au⁺ ion.

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Figure 5. Fluorescence emission spectra ($\lambda_{ex} = 370 \text{ nm}$) of **4** (was prepared in situ by reacting **2** with AgClO₄ in CH₂Cl₂) and **5** (**4** + L₂) in CH₂Cl₂: (a) **4** (1 × 10⁻⁵ M) (17); (b) **4** (1 × 10⁻⁵ M) + PPh₃ (1 equiv) (243). The digit in parentheses represents the fluorescence relative intensity.

Fluorescence spectra of the free ligand 1 and complexes 2, 3a-c, and 4 are given in Figure 4. While the free ligand 1 in CH₂Cl₂ exhibits a strong emission centered at 415 nm, complex 2 gives an increased emission, which may be attributed to inhibition of the photoinduced electron transfer effect owing to the P atom donation to the Au atom. The emissions of 3a-c and 4 are weak and feeble owing to the formation of a charge-transfer complex between the anthracene unit and the Au⁺ ion. When a solution of 4 or 3a $(1 \times 10^{-5} \text{ M})$ in CH₂Cl₂ is added with an equivalent amount of L₂(Ph₃P), the fluorescence intensity significantly increases (Figure 5 and the Supporting Information). The above-

mentioned processes indicate that **5** with the arm-opening configuration can be formed from **3a** or **4** through the ligand substitution or binding reaction. The complex **5** has been confirmed by ¹H, ¹³C, and ³¹P NMR spectra and elemental analysis. In the ¹³C NMR spectrum, the C(9) resonance of the anthracence unit is at 134 ppm in **5**, whereas it is at 133 ppm in **3a**, and the upfield shift indicates that there is a secondary interaction between the anthracene unit and the coordinated acetonitrile owing to the arm-closing configuration.

In summary, $3\mathbf{a}-\mathbf{c}$ are the first reported gold(I) η^2 -arene complexes. We consider that the formation of these complexes is decided by the following factors: (1) the cationic state of the Au complex is the prerequisite; (2) because of the weak bonding of gold(I) η^2 -arene, preserving or breaking the bond to a great extent depends on the steric factor of the incoming ligand in the substitution or binding reaction.

We predict that new gold(I) η^2 -arene complexes can be prepared by the reaction of **3a** or **4** with P, N, or S compounds with end-group linear (like NCCH₃ and SPPh₃) or aromatic planar (like pyridine) structures on the coordinated atoms.

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Supporting Information Available: Synthetic procedures for 1-5, crystallographic data for 2 and 3a-c in CIF format, and fluorescence spectra for 3a and 5. This material is available free of charge via the Internet at http://pubs.acs.org.

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