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Gold(I) Triphenylphosphine Complexes Incorporating Pentaarylfulleride Ligands

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Two gold(I) complexes, $(Ph_3P)Au[C_{60}(4\text{-}MeC_6H_4)_5]$ (**1**) and $(Ph_3P)Au[C_{60}(4\text{-}t\text{-}BuC_6H_4)_5]$ (**2**), were prepared in excellent yield and characterized by single-crystal X-ray diffraction. Complex **1**, grown from two solvent systems, has different coordination modes of the fullerene-embedded Cp ring to the $(PPh_3)Au$ fragment. For **1**·$(ODCB)_2$, the cyclopentadienyl ring coordinates to the $(Ph_3P)Au$ fragment in an η^1 fashion distorted toward η^3 geometry, while in **1**·$(CHCl_3)_2(CS_2)$, crystal packing forces produce enough distortion to give near η^2 coordination.

Over the past decade, the group of Nakamura has developed a clean and high-yielding route to pentafunctionalized fullerene derivatives with badminton shuttlecock-like shapes.[1] The 6,9,12,15,18-addition pattern in these compounds is such that a cyclopentadiene unit is isolated by a ring of five sp^3 carbon atoms (Figures 1). Deprotonation of the embedded cyclopentadiene ring produces a slightly convex cyclopentadienyl ligand, the potential of which was soon realized with the crystallographic characterization of the first pentahaptofullerene metal complex, $Tl(\eta^5\text{-}C_{60}Ph_5)$.[2a] An exploration of the organometallic chemistry of these novel ligands followed, utilizing metals from groups 6,[2b] 7,[2c] 8,[2c−i] 9,[2c,j,k] and 10.[2l] Recently, Bouwkamp and Meetsma attempted to extend the series to include early transition metals, resulting in isolation of a discrete cationic zirconium complex with a noncoordinating pentaarylfulleride anion.[2m] So far, there have been no reports of crystallographically characterized pentaarylfullerene complexes involving group 11 metals.[3]

Phosphinegold(I) cyclopentadienyl complexes are particularly interesting because they tend to exhibit unusual coordination lying between $\eta^1(\sigma)$ and η^3.[4] It has been suggested that there is an isolobal relationship[5a] between the proton and cationic $(PR_3)Au^+$ fragment.[5b,c] The empty hybrid $6s/6p_z$ orbital of $(PR_3)Au^+$ may behave in a manner similar to that of the s orbital of H^+, whereas the vacant degenerate $6p_x/6p_y$ orbital pair is too high in energy to interact with filled cyclopentadienyl orbitals. Deviation from η^5-type coordination reduces unfavorable filled−filled interactions between the lower-energy gold-based 5d orbitals and filled cyclopentadienyl orbitals, and an energetic compromise is reached at a point between η^1 and η^3.[5b−d] However, there have been relatively few examples of the isolation and structural characterization of these complexes.[4] Pentaarylfullerene derivatives are large, rigid, and often crystalline and offer a unique opportunity to explore the role of solvents on crystal packing and molecular conformation.[6] Here we describe the synthesis of stable $(Ph_3P)Au^I$ complexes incorporating fullerene-embedded cyclopentadienyl ligands and their characterization by single-crystal X-ray diffraction.

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Table 1. Interatomic Distances (Å) and Bond Angles for Complexes **1** and **2**

	1·$(\text{ODCB})_2$	**1**·$(\text{CHCl}_3)_2(\text{CS}_2)$	**2**·$(\text{CHCl}_3)_3$
Au(1)−P(1)	2.260(2)	2.2602(11)	2.254(2)
Au(1)−C(1)	2.1602(15)	2.176(4)	2.155(7)
Au(1)−C(2)	2.823(7)	2.590(4)	2.729(9)
Au(1)−C(5)	2.782(5)	3.050(4)	2.854(8)
Au(1)−C(9)	3.066(7)	3.038(4)	3.084(4)
C(1)−C(2)	1.469(7)	1.474(5)	1.494(10)
C(2)−C(3)	1.381(8)	1.380(5)	1.374(10)
C(3)−C(4)	1.441(8)	1.423(5)	1.425(11)
C(4)−C(5)	1.388(7)	1.383(5)	1.381(10)
C(5)−C(1)	1.467(8)	1.477(5)	1.477(10)
C(9)−C(1)−Au(1)	110.6(3)	108.4(2)	111.7(4)
C(2)−C(1)−Au(1)	100.4(4)	88.2(2)	95.1(5)
C(5)−C(1)−Au(1)	98.3(4)	111.8(2)	101.9(5)
P(1)−Au(1)−C(1)	176.97(16)	172.12(10)	177.3(2)

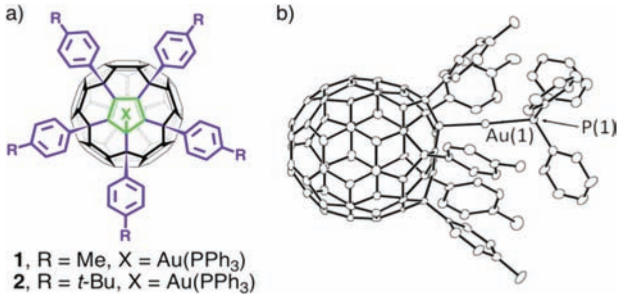

Figure 1. (a) Generalized structure for pentaarylfullerenes. (b) ORTEP representation of the crystallographically determined molecular structure of compound **1**·$(\text{ODCB})_2$. Hydrogen atoms are omitted for clarity.

Treatment of a solution of K[(4-Me-$C_6H_4)_5C_{60}$] in tetrahydrofuran with (PPh_3)AuCl, followed by isolation by chromatography on silica gel ($\text{CS}_2/\text{CH}_2\text{Cl}_2$ gradient), afforded $(\text{PPh}_3)\text{Au}[\text{C}_{60}(4\text{-MeC}_6\text{H}_4)_5]$ (**1**) in 70% yield.[7] Similarly, the 4-*tert*-butylphenyl derivative $(\text{PPh}_3)\text{Au}[\text{C}_{60}(4\text{-}t\text{-BuC}_6\text{H}_4)_5]$ (**2**) was prepared in 95% yield. In the presence of excess *tert*-butoxide, both complexes decompose to the parent pentaarylfullerenes and several oxygenated fullerene derivatives, significantly reducing yields of the reactions. Once isolated, **1** and **2** are relatively stable to air and water and can be handled without any special precautions.

X-ray diffraction analysis of single crystals of compound **1** grown from 1,2-dichlorobenzene (ODCB) indicates solvent inclusion with **1**·$(\text{ODCB})_2$ stoichiometry.[7] Salient crystallographic data can be found in Table 1 and representations of the structure in Figures 1 and 2a,b.

The cyclopentadienyl anion in **1**·$(\text{ODCB})_2$ coordinates in an η^1 fashion to the (PPh_3)Au fragment, with slight distortion toward η^3 geometry. The Au(1)−C(1) distance is 2.1602(15) Å. The Au(1)···C(2) and Au(1)···C(5) distances, at 2.823(7) and 2.782(5) Å, respectively, are relatively short, reflecting the slight preference for η^3 coordination. The Au(1)−C(1) bond is elongated in comparison to a typical Au−C(sp^3) σ bond (2.06−2.10 Å).[8] The corresponding angles, Au(1)−C(1)−C(2) and Au(1)−C(1)−C(5), are 98.3(4) and 100.4(4)°, indicating an approximately symmetrical disposition of the (PPh_3)Au fragment above the cyclopentadienyl ring. Atoms P(1), Au(1), and C(1) are nearly collinear, with a P(1)−Au(1)−C(1) angle of 176.97(16)°. The cyclopentadienyl ring has well-defined diene character with bond-length alternation (Table 1). Compared to other phosphinegold(I) cyclopentadienyl complexes, the cyclopentadienyl ring is markedly nonplanar, with a fold angle between the two mean planes comprising atoms C(1), C(2), C(5) and C(2), C(3), C(4), C(5) of 7.6(6)°. This may be ascribed to the curvature of the embedded cyclopentadienyl ring in **1**·$(\text{ODCB})_2$. Atoms C(2), C(3), C(4), and C(5) are sp^2-hybridized with little pyramidalization, whereas C(1) has appreciable sp^3 character and pyramidalization [the sum of angles C(9)−C(1)−C(2), C(9)−C(1)−C(5), and C(2)−C(1)−C(5) is 344(1)°]. These values suggest that the geometry of the cyclopentadienyl ring in **1**·$(\text{ODCB})_2$ is similar to that of the cyclopentadiene unit in the parent pentaarylhydro[60]fullerene with a σ-bonded hydrogen atom. In **1**·$(\text{ODCB})_2$, however, the Au(1)−C(1)−C(9) angle of 110.6(3)° is significantly greater than the Au(1)−C(1)−C(2) and Au(1)−C(1)−C(5) angles of 100.4(4) and 98.3(4)°, respectively, indicating a deviation from η^1 toward η^3 coordination.

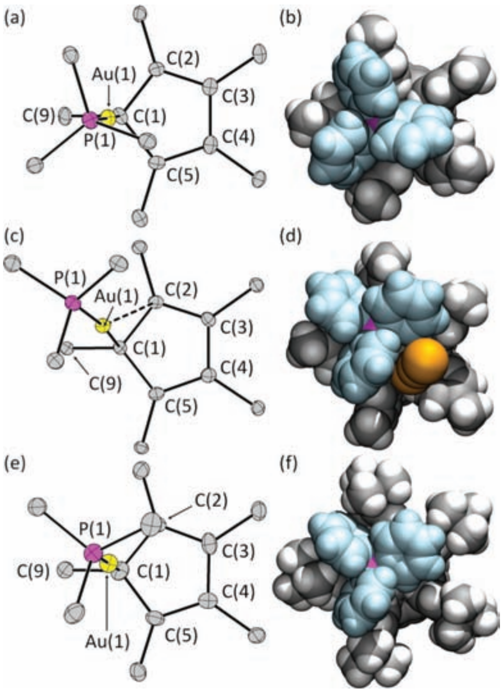

Figure 2. ORTEP plots of partial structures with atom numbering and space-filling representations of the crystal structures of **1**·$(\text{ODCB})_2$ (a and b), **1**·$(\text{CHCl}_3)_2(\text{CS}_2)$ (c and d), and **2**·$(\text{CHCl}_3)_3$ (e and f). Views of the structures are down the quasi-C_5 axes of the fullerene ligands. The phenyl groups of the (PPh_3)Au fragment are displayed in blue in the space-filling representations, with the occluded CS_2 molecule colored orange in part d.

X-ray diffraction was also performed on a single crystal of compound **1** grown from $\text{CS}_2/\text{CHCl}_3$ (Figure 2c,d).[7] Under these conditions, compound **1** crystallizes in the $C2/c$ space group with occluded CS_2 and CHCl_3 molecules with stoichiometry **1**·$(\text{CHCl}_3)_2(\text{CS}_2)$. Similarly to the ODCB solvate, the embedded cyclopentadienyl anion coordinates primarily in an η^1 fashion to the (PPh_3)Au fragment (Figure 2c). However, in this case, there is a significant deviation toward η^2 coordination. Although the principal Au(1)−C(1) interatomic distance of 2.2602(11) Å is identical with that of the ODCB solvate, the secondary interactions Au(1)···C(2) and Au(1)···C(5) have distances of 2.590(4) and 3.050(4) Å, respectively, and the corresponding angles Au(1)−C(1)−C(2) and Au(1)−C(1)−C(5) are 88.2(2) and 111.8(2)°, illustrating

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[7] See the Supporting Information.

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the asymmetry of the metal–ligand coordination. This deviation is much more pronounced than that reported for the $\eta^1 \rightarrow \eta^2$ distorted complexes $(Ph_3P)Au(Ph_2C_5H_3)$,[4a] and fluorenyl derivative $(PPh_3)Au[\sigma\text{-}CH(C_6H_4)_2]$.[4b] Despite the $\eta^1 \rightarrow \eta^2$ distortion in **1**$\cdot(CHCl_3)_2(CS_2)$, the cyclopentadienyl ring is essentially isostructural with that of **1**$\cdot(ODCB)_2$ in terms of bond-length alternation (Table 1), nonplanarity, and carbon atom pyramidalization. This suggests that the slight deviation from η^1 coordination does not involve a fundamental change in metal–ligand bonding and may be a consequence of crystal packing forces. These forces, which can be as large as a few kilocalories per mole, are particularly influential in instances of molecules with shallow potential energy surfaces associated with their deformation. In the case of phosphinegold(I) cyclopentadienyl complexes, these forces may be of comparable magnitude to the energetic barrier to "ring whizzing" via an $\eta^1 \rightarrow \eta^2 \rightarrow \eta^1$ mechanism, which has been calculated to be ca. 3.9 kcal/mol for the simplified system $(H_3P)AuC_5H_5$.[9] A similar phenomenon was observed in the nonfluxional phosphinegold(I) σ-fluorenyl complex, mentioned above. In that case, three symmetry-independent molecules are present in the unit cell, each with slightly different coordination modes describing a pendulum-like distortion toward η^2 from the η^1 minimum. With **1**$\cdot(CHCl_3)_2(CS_2)$, a linear CS_2 molecule resides in the small cavity between the $(PPh_3)Au$ fragment and adjacent tolyl group (Figure 2d), providing the impetus for deviation toward η^2 coordination. In the case of **1**$\cdot(ODCB)_2$, the solvent molecules are too large to enter this cavity, which is instead filled via a slight rotation of an adjacent tolyl group (Figure 2b), resulting in coordination lying between η^1 and η^3.

X-ray diffraction analysis was also performed on a single crystal of **2**$\cdot(CHCl_3)_3$ obtained from $CHCl_3/CS_2$ (Figure 2e, f). The cyclopentadienyl ring of **2**$\cdot(CHCl_3)_3$ coordinates to the $(PPh_3)Au$ fragment essentially isostructurally with that of **1**$\cdot(ODCB)_2$, both having η^1 geometries leaning slightly toward η^3. Additional weak interactions between Au(1)$\cdots$C(2) and Au(1)$\cdots$C(5) are reflected by short distances of 2.729(9) and 2.854(8) Å, respectively, indicating a very slight distortion toward η^2 coordination.

The ^1H and ^{13}C NMR spectra of compound **2** indicate time-averaged C_5 symmetry. There is no significant broadening or coalescence of the signals down to −80 °C ($CS_2/CHCl_3$), indicating that metallotropic isomerization is very fast despite the hindered environment of the cyclopentadienyl ring. Fluxional behavior has been observed in ^1H and ^{13}C NMR experiments with other phosphinegold(I) cyclopentadienyl complexes[4c–f,9] and is probably due to fast $\eta^1 \rightarrow \eta^2 \rightarrow \eta^1$ metallotropic isomerization with concomitant $sp^2 \rightarrow sp^3$ rehybridization of the cyclopentadienyl carbon atoms. In previous studies, splitting of the cyclopentadienyl proton signal(s) due to $^3J[^{31}P-^1H]$ coupling was observable at low temperatures,[4d,9] whereas no splitting arises from a reduction in the molecular symmetry. In the present case, no proton is present on the cyclopentadienyl ring. There have been only two reports of analogous ^{13}C NMR experiments involving the C_5 ring, in which $^2J[^{31}P-^{13}C]$ coupling values between 5.6 and 11.0 Hz were observed.[4c,d] In compounds **1** and **2**, the signals corresponding to the cyclopentadienyl carbon atoms appear as doublets ($^2J[^{31}P-^{13}C]$ = 5.2 and 6.0 Hz, respectively) at 25 °C. These results show that metallotropic isomerization is still fast in compounds **1** and **2** despite the hindered environment of the cyclopentadienyl-like ring. Nonfluxional behavior has been found in the sterically hindered and stereochemically rigid tetraphenylcyclopentadienyl derivative $(PPh_3)Au(\eta^1\text{-}C_5Ph_4H)$.[4g,h] In light of the current results, this is most likely due to stabilization of the isomer containing the least sterically hindered Au–C–H unit relative to isomers containing the Au–C–Ph unit rather than destabilization of the η^2 transition state due to hindrance from the neighboring aryl groups. In the cases of compounds **1** and **2**, each carbon atom of the embedded cyclopentadienyl ligand is equivalent. Thus, there is no preference for coordination to a particular atom, favoring the fluxional behavior. The fluorenyl derivative, mentioned above, is also nonfluxional at room temperature because an $sp^2 \rightarrow sp^3$ change in the hybridization of the carbon atoms within the planar phenylene rings would be energetically unfavorable.[4b] With compounds **1** and **2**, the activation energy associated with an analogous change in the hybridization of the carbon atoms within the embedded cyclopentadienyl ring is presumably not great enough to appreciably slow the rate of isomerization.

In conclusion, the crowded environment around the cyclopentadienyl ring in the pentaarylfullerene ligand does not prevent η^1 coordination to the bulky $(PPh_3)Au$ fragment. Significant deviation toward η^2 coordination, induced by crystal packing forces, is observed in the solvate **1**$\cdot(CHCl_3)_2(CS_2)$. In addition, the crowded pentaarylfullerene environment does not reduce the rate of metallotropic isomerization appreciably; time-averaged C_5 symmetry is observed in the ^1H and ^{13}C NMR spectra down to −80 °C. It is possible that the five aryl groups flanking the fullerene-embedded cyclopentadienyl ring stabilize the complex by impeding associative ligand-exchange reactions at the metal center. Investigation of analogous copper(I) and silver(I) complexes is currently underway.

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Supporting Information Available: Experimental procedures, spectroscopic data, and CIF files for compounds **1**$\cdot(CHCl_3)_2(CS_2)$, **1**$\cdot(ODCB)_2$, and **2**$\cdot(CHCl_3)_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

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