Syntheses and Structures of Cationic Bis(gold) Cyclopentadienyl Complexes

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ABSTRACT: Reaction of (**P**)AuOTf [**P** = P(*t*-Bu)$_2$*o*-biphenyl] with cyclopentadienyl lithium reagents C_5H_5Li, C_5H_4MeLi, and C_5HMe_4Li forms the corresponding gold η^1-cyclopentadienyl complexes (**P**)Au(η^1-C_5H_5) (**3a**), (**P**)Au(η^1-C_5H_4Me) (**3b**), and (**P**)Au(η^1-C_5HMe_4) (**3c**), respectively in >60% isolated yield. Treatment of complexes **3a** or **3b** with (**P**)AuNTf$_2$ forms the corresponding cationic bis(gold) cyclopentadienyl complexes *trans*-{[(**P**)Au]$_2$(η^1,η^1-cyclopentadien-1,3-yl)}$^+$ NTf$_2^-$ (**4a**), and *trans*-{[(**P**)Au]$_2$(η^1,η^1-methylcyclopentadien-1,3-yl)}$^+$ NTf$_2^-$ (**4b**), respectively, in near quantitative yield which were characterized in solution and by X-ray crystallography. Both **4a** and **4b** undergo migration of the gold atoms about the cyclopentadienyl ring, which is fast on the NMR time scale at –80 °C. In the solid-state, the gold atoms of **4a** and **4b** are positioned on opposite faces of the cyclopentadienyl ring above and below the C1 and C3 carbon atoms. Reaction of **3c** with (**P**)AuNTf$_2$ similarly forms the cationic bis(gold) tetramethylcyclopentadienyl complex {[(**P**)Au]$_2$(C_5HMe_4)}$^+$ NTf$_2^-$ (**4c**) although the structure of this complex remains obscure. The binding affinity of mono(gold) complexes **3a-3c** toward exogenous (**P**)Au$^+$ exceeds that of the corresponding unmetallated cyclopentadienes by more than three orders of magnitude. Protodeauration of bis(gold) complexes **4** with acetic acid at –80 °C is > 1500 times slower than is protodeauration of the corresponding monogold complexes **3** under identical conditions.

INTRODUCTION

A distinguishing feature of gold (I) complexes bearing unsaturated hydrocarbyl ligands, e.g., aryl, vinyl, and alkynyl, is their tendency to bind an exogenous twelve electron gold fragment (LAu$^+$) to form stable cationic bis(gold) complexes.[1-11] Bis(gold) aryl and alkenyl complexes typically comprise a *gem*-diaurated carbon atom stabilized by an aurophilic Au–Au bond.[2-7] Within this binding motif, the electronic structure varies between the limiting structures of a three-center, two-electron Au–C–Au bond or as a pair of two-electron Au–C bonds adjacent to a carbenium ion (Figure 1).[2,3,11] In comparison, cationic bis(gold) alkynyl and some bis(gold) alkenyl complexes adopt an η^1,η^2-structure possessing discrete and often rapidly interconverting σ- and π-bound gold atoms.[4,9] Regardless of structure, these cationic bis(gold) complexes are characterized by their markedly lower reactivity with respect to electrophilic deauration relative to the corresponding neutral mono(gold) hydrocarbyl complexes.[2-5,9] Owing to the diminished reactivity of cationic bis(gold) complexes toward electrophiles combined with the potentially high association constants for their formation,[11] cationic bis(gold) complexes are often formed under catalytic conditions, typically as off-cycle catalyst reservoirs.[5,10]

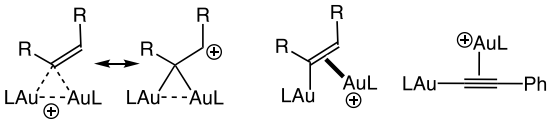
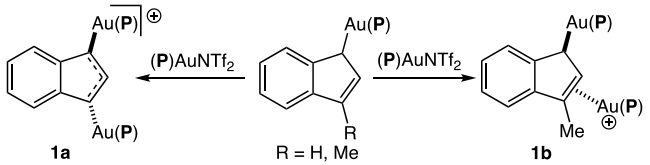


Figure 1. Binding modes of cationic bis(gold) complexes.

We have recently validated a new class of cationic bis(gold) complexes through the synthesis and characterization of cationic bis(gold) indenyl complexes **1a** and **1b** generated via the reaction of the corresponding mono(gold) η^1-indenyl complexes with (**P**)AuNTf$_2$ (Scheme 1).[12] The structures of bis(gold) indenyl complexes **1** are substitution dependent; the unsubstituted inden-1-yl complex **1a** adopts a ~C2 symmetric *trans*-1,3-η^1,η^1 orientation, whereas the 3-methyl-inden-1-yl complex **1b** adopts a *trans*-η^1,η^2 orientation comprising isolated Au–C σ- and π-bonds (Scheme 1). The latter η^1,η^2 orientation has been documented for a number of transition metal μ-allyl complexes.[13] Conversely, the *trans*-1,3-η^1,η^1 structure of **1a** has been previously observed only in the solid state for electrophilic In,[14] Sc,[15] Mn,[16] and Ga[17] cyclopentadienyl complexes with no evidence that these interactions persist in solution. Among the late transition metals, perhaps the closest analogs to complex **1a** are the dinuclear Ni and Pd μ-allyl, μ-indenyl, and μ-cyclopentadienyl complexes,[18,19] which are nevertheless distinct from **1a** owing to the cis arrangement of metals, the presence of a M–M bond, and a shorter M–C$_{int}$ bond owing to M → allyl π-back bonding contributions that are absent in **1a**.[19]



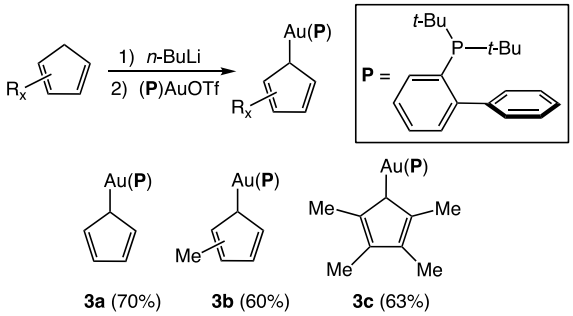
Scheme 1. Cationic bis(gold) indenyl complexes 1a and 1b.

Owing both to the potential relevance of cationic bis(gold) allyl complexes under catalytic conditions[21] and the novel structure of **1a**, we sought to expand the scope of cationic bis(gold) allyl complexes beyond the indenyl framework. In doing so, we hoped to gain additional information regarding the factors that influence the structure and stability of these complexes.

Similarly, because assignment of the novel *trans*-1,3-η^1,η^1 structure of **1a** relied heavily on computation,[12] we sought to validate this unusual bonding arrangement experimentally via X-ray crystallography. Here we report that mononuclear gold η^1-cyclopentadienyl complexes react with exogenous LAu^+ to form the corresponding cationic bis(gold) cyclopentadienyl complexes. Single crystal X-ray analysis of bis(gold) cyclopentadienyl and methylcyclopentadienyl complexes established the *trans*-1,3-η^1,η^1 structure of these complexes.

RESULTS AND DISCUSSION

Synthesis of gold cyclopentadienyl complexes. Toward the objective of expanding the scope of cationic bis(gold) allyl complexes, gold cyclopentadienyl complexes emerged as attractive targets for investigation. In contrast to the dearth of simple aliphatic gold η^1-allyl complexes,[22,23] substituted and unsubstituted gold(I) cyclopentadienyl complexes containing a triphenylphosphine or trialkylphosphine ligand have been known for decades,[24,25] although the less substituted C_5H_5 and C_5H_4Me complexes display limited thermal stability.[25] Guided by our investigation of gold indenyl complexes,[12] we reasoned that employment of the more sterically hindered P(*t*-Bu)$_2$*o*-biphenyl (**P**) supporting ligand might enhance the thermal stability of mono(gold) cyclopentadienyl complexes allowing for isolation and investigation. To this end, transmetalation of cyclopentadienyl-, methylcyclopentadienyl- or 2,3,4,5-tetramethylcyclopentadienyllithium with (**P**)AuOTf in THF at 25 °C led to isolation of the gold cyclopentadienyl complexes (**P**)Au(η^1-C_5H_5) (**3a**), (**P**)Au(η^1-C_5H_4Me) (**3b**), and (**P**)Au(η^1-C_5HMe_4) (**3c**), respectively, in >60% yield as yellow-brown solids (Scheme 2). Complexes **3** were stable indefinitely under N_2 at 4° C in the solid state but decomposed within 12 h in solution at room temperature taking on a purple hue, suggesting the formation of colloidal gold(0),[26] with formation of free cyclopentadiene and cyclopentadienide.



Scheme 2. Synthesis of gold cyclopentadienyl complexes 3.

In accord with previous observations regarding gold cyclopentadienyl[24,25] and transition metal η^1-cyclopentadienyl complexes,[27] NMR spectroscopy of **3a** was consistent with rapid migration of gold about the cyclopentadienyl ring, presumably via successive [1,5] sigmatropic rearrangements.[28] For example, the ^{1}H NMR spectrum of **3a** at –80 °C displayed a five-proton singlet at δ 5.54 assigned to the cyclopentadienyl protons while the ^{13}C NMR spectrum of **3a** at –80 °C displayed a single resonance at δ 109.6 (d, J_{CP} = 7.0 Hz) assigned to the cyclopentadienyl carbon atoms. In the solid state, **3a** adopts a distorted η^1-cyclopentadien-1-yl structure with weak interactions between the gold atom and the C2 and C5 cyclopentadienyl carbon atoms (Figure 2), as has been documented for other gold cyclopentadienyl complexes.[24,25] For example, the Au–C1–C2 (101°) and Au–C1–C5 (95.9°) bond angles are compressed relative to an idealized Au–C(sp^3) bond. The Au–C1 (2.140 Å) bond distance is typical of a Au–C(sp^3) bond,[29] with longer Au–C2 (2.807 Å) and Au–C5 (2.714 Å) distances. The structure of **3a** displays an interesting distortion away from Cs symmetry with the cyclopentadienyl ligand rotated toward one of the phosphorus-bound *t*-Bu groups with concomitant displacement of the protruding ortho phenyl group away from the cyclopentadiene ligand (Figure 2).

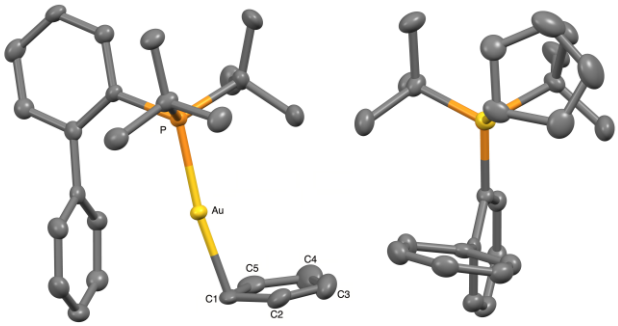
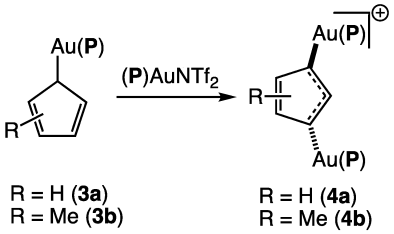


Figure 2. Ortep diagram of (**P**)Au(C_5H_5) (**3a**) with ellipsoids shown at 50% probability and with hydrogen atoms omitted for clarity (left). Identical structure viewed along the Au–P bond (right). Calculated bond lengths (Å) and bond angles (°): Au–P = 2.271(1), Au1–C1 = 2.140(5), Au–C2 = 2.807(4), Au–C5 = 2.714(6), C1–C2 = 1.442(5), C2–C3 = 1.353(7), C3–C4 = 1.433(7), C4–C5 = 1.366(6), C1–C5 = 1.463(6), P–Au–C1 = 171.9(1), Au–C1–C2 = 101.4(3), Au–C1–C5 = 95.9(3).

As was the case with **3a**, the spectroscopy of methylcyclopentadienyl complex **3b** was consistent with facile migration of gold about the methylcyclopentadienyl ligand. The ^{1}H NMR spectrum of **3b** at –80 °C displayed a three-proton singlet at δ 1.99 assigned to the cyclopentadienyl methyl group and a pair of two proton singlets at δ 5.22 and 5.04 assigned to the cyclopentadienyl CH protons. Similarly, the ^{13}C NMR spectrum of **3b** at –80 °C displayed a singlet at δ 16.2 assigned to the cyclopentadienyl methyl group and two broad phosphorus-coupled doublets at δ 107.0 (J_{HP} = 10.6 Hz) and 109.0 (J_{HP} = 9.1 Hz) assigned to the two cyclopentadienyl CH carbon atoms. In contrast, the spectroscopy of tetramethylcyclopentadienyl complex **3c** was consistent with a static structure with gold bound to the cyclopentadienyl CH carbon atom. In particular, the ^{1}H NMR spectrum of **3c** at –80 °C displayed a phosphorus-coupled doublet at δ 2.12 (J_{HP} = 14.8 Hz) assigned to cyclopentadienyl CH proton. The ^{13}C NMR spectrum of **3c** at –80 °C displayed a phosphorus-coupled doublet at δ 71.2 (J_{CP} = 61.3 Hz) assigned to the cyclopentadienyl CH carbon atom. Worth noting, this phosphorous-carbon coupling constant is much larger than is J_{CP} observed for the cyclopentadienyl CH carbon resonances of complexes **3a** and **3b**, even when considering the fluxionality of the latter structures. For example, the 7.0 Hz doublet observed for **3a** presumably reflects the time-averaged composite of one 35 Hz doublet and four singlets (i.e. J_{CP} = 0 Hz). The significantly larger phosphorous-carbon coupling constant observed for **3c** (J_{CP} = 61.3 Hz) presumably reflects the greater s-orbital character of the Au–C bond of **3c** relative to the Au–C bonds of **3a** and **3b**.

Synthesis of cationic bis(gold) cyclopentadienyl complexes. Reaction of an equimolar mixture of **3a** or **3b** with (**P**)AuNTf$_2$ in CH_2Cl_2 at 25 °C rapidly (≤ 1 min) and

quantitatively formed the corresponding cationic bis(gold) cyclopentadienyl complexes *trans*-{[(**P**)Au]$_2$(η^1,η^1-cyclopentadien-1,3-yl)}$^+$ NTf$_2^-$ [**4a**; NTf$_2$ = (CF$_3$SO$_2$)$_2$N], and *trans*-{[(**P**)Au]$_2$(η^1,η^1-methylcyclopentadien-1,3-yl)}$^+$ NTf$_2^-$ (**4b**), respectively (Scheme 3). Both **4a** and **4b** were isolated as yellow-brown crystals via slow diffusion of hexanes into concentrated CH_2Cl_2 solutions and were characterized by spectroscopy and by X-ray crystallography.



Scheme 3. Synthesis of cationic bis(gold) cyclopentadienyl complexes 4a and 4b.

In the solid state, **4a** adopts approximate C_2 symmetry about the cyclopentadiene ring with the gold atoms positioned on opposite faces of the cyclopentadienyl ring above and below the C1 and C3 carbon atoms (Figure 3). The Au1–C1 and Au2–C3 bond lengths of 2.180 Å are nominally longer the Au–C1 bond in monogold complex **3a** (2.140 Å). Both gold atoms of **4a** are displaced slightly toward the central C2 carbon atom with Au1–C1–C2 and Au2–C3–C2 angles of 90.9 and 89.3°, respectively, compared to Au1–C1–C5 and Au2–C3–C4 angles of 95.7 and 97.7°, respectively, and with Au1–C2 and Au2–C2 distances of 2.611 and 2.604 Å, respectively, compared to Au1–C5 and Au2–C4 distances of 2.73 and 2.754(6) Å, respectively. The ortho phenyl rings of the P(*t*-Bu)$_2$*o*-biphenyl ligands are directed toward the cyclopentadienyl ring with closest Au–C$_{arene}$ contacts of 3.02 Å. Bonding within the cyclopentadienyl ligand, notably the shorter the C4–C5 bond (1.344 Å) and longer C3–C4 (1.451) and C1–C5 (1.442) bonds. points to distortion toward isolated allyl and alkenyl groups.

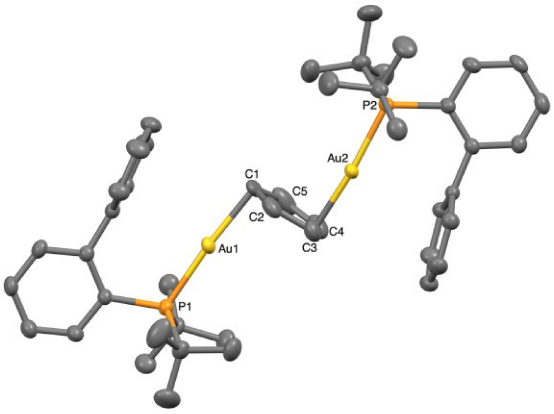


Figure 3. Ortep diagram of *trans*-{[(**P**)Au]$_2$(η^1,η^1-cyclopentadien-1,3-yl)}$^+$ NTf$_2^-$ (**4a**) with ellipsoids shown at 50% probability and with counterion and hydrogen atoms omitted for clarity. Calculated bond lengths (Å) and bond angles (°): Au1–C1 = 2.180(7), Au1–C2 = 2.611(7), Au1–C5 = 2.73(1), Au2–C3 = 2.180(7), Au2–C2 = 2.604(7), Au2–C4 = 2.754(6), C1–C2 = 1.405(8), C2–C3 = 1.416(8), C3–C4 = 1.451(7), C4–C5 = 1.344(9), C1–C5 = 1.442(9), P1–Au1–C1 = 174.2(2), P1–Au1–C2 = 147.8(1), P2–Au2–C3 = 173.6(2), P2–Au2–C2 = 141.9(1), Au1–C1–C2 = 90.9(4), Au1–C1–C5 = 95.7(4), Au2–C3–C2 = 89.3(4), Au2–C3–C4 = 97.7(4).

The Au–C bond lengths and bond angles of bis(gold) cyclopentadienyl complex **4a** are similar to the values determined computationally for bis(gold) indenyl complex **1a** (Au1–C1 distance of 2.204, Au1–C2 = 2.697, Au–C1–C2 = 93.3, Au–C1–C9 = 103.8), which suggests that similar Au–C bonding interactions are involved in both complexes. The Au-indenyl bonding of **1a** was interpreted as arising from overlap between the filled antisymmetric $2\pi_a$ and $1\pi_a$ indenyl molecular orbitals with the symmetric combination of the P–Au anti-bonding orbitals [$\phi_a(\sigma^*)$] (Figure 4). The cyclopentadienyl $2\pi_b$ molecular orbital is related to the indenyl $2\pi_a$ and $1\pi_a$ molecular orbitals, which contain in phase ($1\pi_a$) and out of phase ($2\pi_a$) contributions of the phenyl π system. Therefore, the primary gold-cyclopentadienyl bonding interaction of **4a** presumably involves overlap between the filled antisymmetric cyclopentadienyl $2\pi_b$ molecular orbital with P–Au anti-bonding orbitals $\phi_a(\sigma^*)$ (Figure 4). The similarity of the metal-ligand bonding interactions for bridging indenyl and cyclopentadienyl ligands was likewise noted for dipalladium μ-cyclopentadienyl and μ-indenyl complexes.[19]

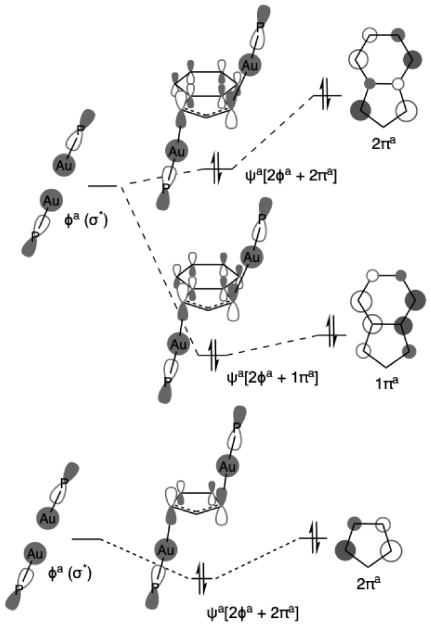
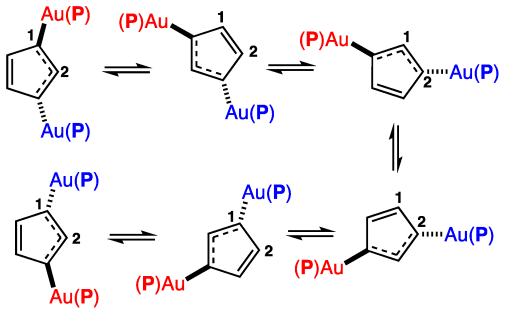


Figure 4. Orbital mixing diagrams describing the gold-indenyl bonding of **1a** (top) and (b) the gold cyclopentadienyl bonding of **4a** (bottom).

As was the case with the parent mono(gold) complex **3a**, the spectroscopy of **4a** is consistent with facile migration of the two gold atoms about the cyclopentadienyl ring. For example, the ^{1}H NMR spectrum of **4a** at –80 °C displayed a five-proton singlet at δ 5.43 assigned to the cyclopentadienyl protons and the ^{13}C NMR spectrum of **4a** at –80 °C displayed a single resonance at δ 108.0 assigned to the cyclopentadienyl carbon atoms. Sequential [1,5] migration of the two (**P**)Au groups of **4a** is sufficient to interconvert all positions of the cyclopentadienyl ligand and the absence of broadening of the cyclopentadienyl resonances in the ^{1}H and ^{13}C NMR spectra at –80 °C points to an extremely facile fluxional process (Scheme 4).



Scheme 4. Interconversion of the five cyclopentadienyl positions of 4a via sequential [1,5]-sigmatropic rearrangements.

The X-ray crystal structure of **4b** was complicated by the positional disorder of the cyclopentadienyl methyl group and the associated rotational disorder of one methyl group on each of the phosphorus atoms, corresponding to two regioisomeric forms of **4b** in the solid state (Figure 5). In the minor isomer the cyclopentadienyl methyl group (C6') is bonded to the cyclopentadienyl C2 carbon atom (**4ba**; 37% occupancy), and in the major isomer the cyclopentadienyl methyl group (C6) is bonded to the cyclopentadienyl C5 carbon atom (**4bb**; 63% occupancy). Although this positional disorder precluded detailed analysis of the bond distances and angles within the cyclopentadienyl ring, the crystal structure of **4b** established a distorted *trans*-1,3-η^1,η^1 structure analogous to that of **4a** with the gold atoms positioned on opposite faces of the cyclopentadienyl ring above and below the C1 and C3 carbon atoms (Figure 5).

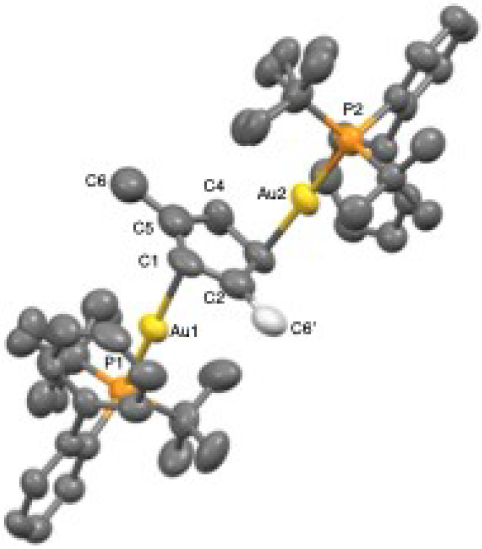


Figure 5. Ortep diagram of *trans*-{[(**P**)Au]$_2$(1,3-η^1,η^1-C_5H_4Me)}$^+$ NTf_2^- (**4b**) with ellipsoids shown at 50% probability and with counterion, hydrogen atoms, and minor occupancy P–Me groups omitted for clarity. Cyclopentadienyl methyl group C6 (dark gray, 63% occupancy) corresponds to major isomer **4bb**, while cyclopentadienyl methyl group C6' (light gray, 37% occupancy) corresponds to minor isomer **4ba**: Calculated bond lengths (Å) and bond angles (°): Au1–C1 = 2.19(2), Au1–C2 = 2.54(2), Au1–C5 = 2.74(3), Au2–C3 = 2.17(2), Au2–C2 = 2.71(2), Au2–C4 = 2.73(2), P1–Au1–C1 = 173.2(4), P2–Au2–C3 = 177.3(4), Au1–C1–C2 = 87(1), Au1–C1–C5 = 95(1), Au2–C3–C2 = 95(1), Au2–C3–C4 = 95(1).

Interestingly, the two gold atoms of **4b** are positioned unsymmetrically about the C1–C2–C3 unit with Au1 displaced toward C2 (Au1–C2 = 2.54 Å) and Au2 displaced away from C2 (Au1–C2 = 2.71 Å) relative to the more symmetric arrangement of the two gold atoms observed in **4a** (Au1/Au2–C2 = 2.611/2.604 Å), suggesting a slight distortion of Au1 toward an η^2 bonding mode. We considered and ultimately rejected the possibility that minor isomer **4ba** adopts an η^1,η^2 bonding mode in the solid state owing to the stabilizing effect of the C2 methyl group on the C1=C2 bond with this contribution superimposed on the dominant η^1,η^1-bonding of major isomer **4bb** in the disordered crystal (Figure 6). However, this possibility was rejected based on two observations. Firstly, we performed DFT analysis of *trans*-{1,3-η^1,η^1-[$(PMe_3)Au]_2$(2-C_5H_4Me)}$^+$ (η^1,η^1-**4ba***) and *trans*-{η^1,η^2-[$(PMe_3)Au]_2(C_5H_4Me)$}$^+$ (η^1,η^2-**4ba***) at the SMD(DCE)/TPSSh/aug-cc-pVTZ//B3LYP/6-31G(d) level of theory employing trimethylphosphine in place of P(*t*-Bu)$_2$*o*-biphenyl (**P**) for computational simplicity (Figure 6). These calculations identified η^1,η^1-**4ba*** as the lower energy structure and indeed, η^1,η^2-**4ba*** did not represent a local minimum and collapsed to η^1,η^1-**4ba*** upon attempted minimization. Secondly, there is no evidence for disorder of the Au1 atom in the crystal structure of **4b**; the Au1 ellipsoids is of normal shape and the electron density maps reveal no additional positions in which a disordered Au atom could reside.

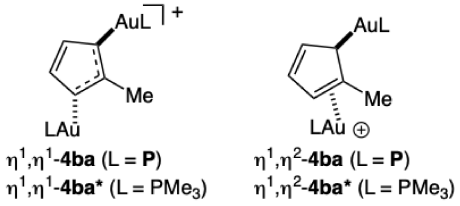
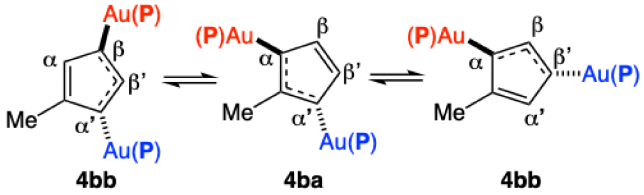


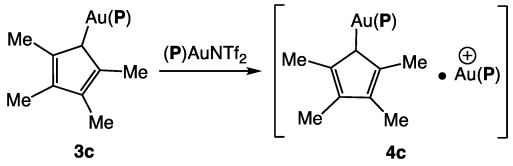
Figure 6. Structures of *trans*-1,3-η^1,η^1- and *trans*-η^1,η^2-$(LAu)_2(C_5H_4Me)$}$^+$ (L = **P**, PMe_3) bearing a C2 cyclopentadienyl methyl group.

NMR spectroscopy established the static or time-averaged two-fold symmetry of **4b** in solution. For example, the ^{1}H NMR spectrum of **4b** at –80 °C displayed a pair of two proton singlets at δ 5.13 and 4.80 assigned to the cyclopentadienyl protons, while the ^{13}C NMR spectrum a pair of closely spaced resonances at δ 103.5 and 103.7 assigned to the cyclopentadienyl CH carbon atoms and 11 additional C(sp^2) carbon resonances (δ 125-149). These data are consistent either with the presence of a static **4ba** regioisomer or with a rapidly interconverting mixture of **4bb** isomers. Given the fluxional nature of cyclopentadienyl complex **4a**, this latter scenario appears more likely. Two sequential [1,5]-migrations are sufficient to interconvert the cyclopentadienyl methine groups and (**P**)Au groups of **4bb** via **4ba** (Scheme 5). The absence of broadening in the ^{1}H and ^{13}C NMR spectra of **4b** at –80 °C points to a facile fluxional process.



Scheme 5. Interconversion of the potential isomers of 4b via sequential [1,5]-sigmatropic rearrangements.

When an equimolar (~30 mM) mixture of the tetramethylcyclopentadienyl complex **3c** and (**P**)AuNTf$_2$ was dissolved in CD_2Cl_2 at room temperature, ^{31}P NMR analysis of the resulting solution at –80 °C revealed formation of the corresponding cationic bis(gold) complex {[(**P**)Au]$_2$(C_5HMe_4)}$^+$ NTf_2^- (**4c**) in >90% yield (Scheme 6). In contrast to bis(gold) complexes **4a** and **4b**, complex **4c** could not be isolated and was therefore characterized in solution without isolation. However, despite combined spectroscopic and computational analysis (see below), the structure of **4c** remains unclear. For example, the ^{13}C NMR spectrum of **4c** displays a pair of cyclopentadienyl methyl groups at δ 15.3 and 12.00 and 12 unique C(sp^2) carbon resonances (δ 116-150). Particularly notable is a phosphorus-coupled triplet at δ 85.1 (J_{CP} = 17 Hz) in the ^{13}C NMR spectrum of **4c** assigned to the cyclopentadienyl CH carbon atom. Both this resonance and the cyclopentadienyl CH resonance at δ 3.18 in the ^{1}H NMR spectrum of **4c** are shifted to higher frequency and display diminished J_{CP} and J_{HP} values relative to the mono(gold) complex **3c** [^{13}C{^{1}H} NMR: δ 71.19 (d, J = 61.3 Hz); ^{1}H NMR: δ 2.12 (d, J = 14.8 Hz)]. The ^{31}P NMR spectrum of **4c** displayed a single resonance at δ 60.4.



Scheme 6. Synthesis of cationic bis(gold) tetramethylcyclopentadienyl complex 4c.

The NMR spectra of **4c** established the static or time-averaged two-fold symmetry of **4c** in solution, while the phosphorus-coupled triplet at δ 85.1 (J_{CP} = 17 Hz) in the ^{13}C NMR spectrum pointed to a structure with two (**P**)Au groups bound to the CH cyclopentadienyl carbon atom. We initially considered two *gem*-diaurated structures consistent with this connectivity containing either a triangular (*cis,gem*-**4c**) or linear (*trans,gem*-**4c**) arrangement of the Au–C–Au atoms (Figure 7). Both structures are unusual; we are aware of no analog of *trans,gem*-**4c** and although *gem*-diaurated complexes are well known, the vast majority of these complexes contain a gold-bound C(sp^2) atom as opposed to the *gem*-diaurated C(sp^3) atom of complex *cis,gem*-**4c**.[1-11] Rather, the closest analogs to structure *cis,gem*-**4c** are the cationic bis(gold) methyl complexes first reported by Campos.[31,32]

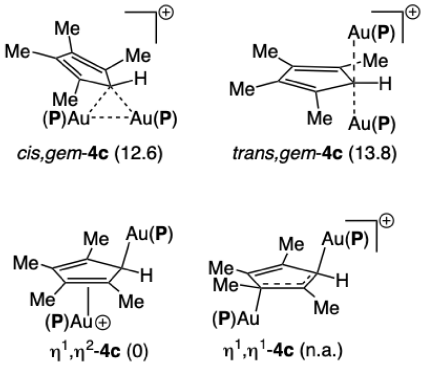


Figure 7. Optimized structures of potential isomers of {[(**P**)Au]$_2$(C_5HMe_4)}$^+$ (**4c**) with relative free energies in kcal/mol. The structure indicated as N/A was not located as a local minimum on the potential energy surface.

To distinguish between *cis,gem*-**4c** and *trans,gem*-**4c** and to gauge the viability of these structures, we investigated the relative stabilities of *cis,gem*-**4c** and *trans,gem*-**4c** and also the *trans*-η^1,η^1 isomer η^1,η^1-**4** and the *trans*-η^1,η^2 isomer η^1,η^2-**4c** computationally at the SMD(DCE)/TPSSh/aug-cc-pVTZ//B3LYP/6-31G(d) level of theory (Figure 7). Of the *gem*-diaurated structures, *cis,gem*-**4c** was nominally (1.2 kcal/mol) more stable than was *trans,gem*-**4c**. However, and in contrast to our expectations, these *gem*-diaurated structures were ≥12.6 kcal/mol less stable than was η^1,η^2-**4c**, whereas η^1,η^1-**4c** did not represent a local minimum and instead collapsed to η^1,η^2-**4c** upon minimization. Rapid exchange of the π-bound gold atom between the two cyclopentadienyl C=C bonds of η^1,η^2-**4c** would be anticipated by analogy to mononuclear cationic gold η^2-diene complexes.[33,34] Conversely, it is difficult to envision a fluxional process that would account for both the time-averaged, two-fold symmetry of **4c** and the coupling of both (**P**)Au groups to the cyclopentadienyl CH carbon atom as was established by NMR spectroscopy. Owing to the lack of congruency between the spectroscopy and computational modeling of **4c**, we refrain from assigning a defined structure to **4c**.

Relative binding affinities of mono(gold) cyclopentadienyl complexes. We sought to quantify the relative binding affinities of the mononuclear gold (η^1-cyclopentadienyl) complexes **3a-3c** and the corresponding unmetallated cyclopentadienes toward exogenous (**P**)Au$^+$. Our objectives here were to (1) evaluate the effect of ring substitution on the binding affinity of gold η^1-allyl complexes and (2) to gauge the effect of the σ-bound (**P**)Au group on the binding affinity relative to the unmetallated cyclic hydrocarbon. To this end, we determined equilibrium constants for the displacement of the benzonitrile from [(**P**)Au(NCPh)]$^+$ SbF_6^- (**5**) with **3a**, **3b**, **3c**, C_5H_6, C_5H_5Me, $C_5H_2Me_4$ in CD_2Cl_2 at –80 °C employing ^{31}P NMR analysis (eq 1).[30]

$$\underset{\textbf{5}}{\text{L} + [(\textbf{P})\text{Au(NCPh)}]^+} \underset{-80\ ^\circ\text{C}}{\overset{CD_2Cl_2}{\rightleftharpoons}} [(\textbf{P})\text{Au(L)}]^+ + \text{NCPh} \qquad \text{(eq 1)}$$

Binding of exogenous (**P**)Au$^+$ to gold cyclopentadienyl complexes **3a** and **3b** was highly favorable such that addition of **3a** or **3b** to a solution of **5** containing excess benzonitrile (55 mM) led to quantitative formation of bis(gold) complexes **4a** and **4b**, respectively. Assuming ≥ 5% of **5** would have been detected by ^{31}P NMR analysis, we set lower limits for the equilibrium constants for displacement of benzonitrile from **5** by **3a** and **3b** of $K_{eq} \geq 400$ and $K_{eq} \geq 400$, respectively (Table 1, entries 1 and 2). In comparison, the binding affinity of tetramethylcyclopentadienyl complex **3c** toward (**P**)Au$^+$ (K_{eq} = 8.6) was ≥35 times less favorable than for complexes **3a** and **3b** (Table 1, entry 3). Nevertheless, the binding affinities of gold cyclopentadienyl complexes **3a**, **3b**, and **3c** toward (**P**)Au$^+$ exceeds the binding affinities of the corresponding unmetallated cyclopentadienes C_5H_6 ($K_{eq} = 4.3 \pm 0.8 \times 10^{-2}$), C_5H_5Me ($K_{eq} = 0.22 \pm 0.02$), and $C_5H_2Me_4$ ($K_{eq} \leq 2.4 \times 10^{-3}$), respectively, by more than three orders of magnitude in each case (Table 1, entries 4-6).

Table 1. Equilibrium constants for the displacement of benzonitrile from [(P)Au(NCPh)]$^+$ SbF_6^- (5).

entry	L	(**P**)Au(L)$^+$	K_{eq}
1	**3a**	**4a**	≥400 [a]
2	**3b**	**4b**	≥400 [a]

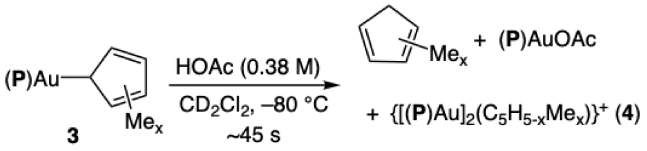
3	**3c**	**4c**	8.6 ± 0.6
4	C_5H_6	(**P**)Au(π-C_5H_6)	$(4.3 \pm 0.8) \times 10^{-2}$
5	C_5H_5Me	(**P**)Au(π-C_5H_5Me)	0.22 ± 0.02
6	$C_5H_2Me_4$	(**P**)Au(π-$C_5H_2Me_4$)	$\leq 2.4 \times 10^{-3}$ [b]

[a]Complex **5** not detected at equilibrium. [b]π-Complex not detected at equilibrium.

The much higher binding affinity of the gold cyclopentadienyl complexes **3** relative to the corresponding unmetallated cyclopentadienes was expected given our previous studies on mono and bis(gold) indenyl complexes[12] and mono and bis(gold) gold alkynyl complexes,[9] which also revealed higher LAu^+ binding affinity of the gold σ-complex relative to the free hydrocarbon. In all these cases, the greater binding affinity of the gold σ-complexes compared to the unmetallated hydrocarbons is likely due to the greater σ-donor ability of the LAu group relative to hydrogen, resulting in the greater electron donating ability of the gold σ-complex as compared to the unmetallated hydrocarbon. Although the structure of the bis(gold) tetramethylcyclopentadienyl complex **4c** remains unclear, the greater affinity of **3a** and **3b** toward exogenous (**P**)Au^+ relative to **3c** established the deleterious effect of the four cyclopentadienyl methyl groups on the stability of bis(gold) complex **4c**.

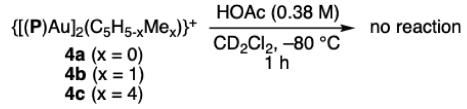
Protodeauration of gold cyclopentadienyl complexes. We also sought to evaluate the reactivity of bis(gold) cyclopentadienyl complexes **4** toward protodeauration relative to the corresponding mono(gold) complexes **3**. Treatment of monogold complexes **3a**, **3b**, or **3c** (~33 mM) with excess acetic acid (380 mM) in CD_2Cl_2 at –80 °C led, in each case, to complete consumption of **3** within ~45 s as judged by ^{31}P NMR analysis. ^1H and ^{31}P NMR analysis of the resulting solutions revealed formation of the corresponding cyclopentadiene as the exclusive organic product along with mixtures of (**P**)AuOAc and the corresponding bis(gold) complex **4** as the exclusive organometallic products. The ratio of (**P**)AuOAc:**4** was substrate dependent, ranging from (**P**)AuOAc:**4a** = 13:1 for the protodeauration of **3a,** (**P**)AuOAc:**4b** = 36:1 for the protodeauration of **3b**, and (**P**)AuOAc:**4c** = 3.3:1 for the protodeauration of **3c** (Table 2). Because the (**P**)AuOAc:**4** ratio does not track with the relative equilibrium binding affinities of **3** toward exogenous (**P**)Au^+ (**3a**/**3b** > **3c**), the (**P**)AuOAc:**4** ratio formed in the protodeauration of complexes **3** presumably reflects the kinetic selectivity. Assuming that (1) ≥10% of unreacted **3** would have been observed in the initial ^{31}P NMR spectrum of the solution of **3** and HOAc and (2) protodeauration obeys pseudo first-order kinetics, we can set a lower limit for the observed rate constant for the protodeauration of complexes **3** of $k_{obs} \geq 5 \times 10^{-2}$ s^{-1}.

Table 2. Reaction of gold cyclopentadienyl complexes 3 (33 mM) with acetic acid (0.38 M) in CD_2Cl_2 at –80 °C.



cmpd	x	(**P**)AuOAc:**4**
3a	0	13.3
3b	1	35.8
3c	4	3.3

In comparison to the rapid protodeauration of mono(gold) cyclopentadienyl complexes **3**, protodeauration of bis(gold) cyclopentadienyl complexes **4** was sluggish. Treatment of the bis(gold) complexes **4a**, **4b**, or **4c** (33 mM) with HOAc (0.38 M) in CD_2Cl_2 at –80 °C revealed no detectable consumption of **4** after 1 h (Scheme 7). Conservatively assuming that ≥10% consumption of **4** would have been observed in the ^1H and ^{31}P NMR spectra of solutions of **4** and HOAc and that protodeauration obeys pseudo first-order kinetics, we can set an upper limit for the observed rate constant for the protodeauration of complexes **4** of $k_{obs} \leq 3 \times 10^{-5}$ s^{-1}. Therefore, protodeauration of bis(gold) cyclopentadienyl complexes **4** is >1500 times slower than is protodeauration of the corresponding monogold cyclopentadienyl complexes **3** under identical conditions.



Scheme 7. Reaction of bis(gold) cyclopentadienyl complexes **4** (33 mM) with acetic acid (0.38 M) in CD_2Cl_2 at –80 °C.

CONCLUSIONS

The neutral gold cyclopentadienyl complexes (**P**)Au(η[1]-C_5H_5) (**3a**) and (**P**)Au(η[1]-C_5H_4Me) (**3b**) react with (**P**)$AuNTf_2$ to form the cationic bis(gold) complexes *trans*-{[(**P**)Au]$_2$(η[1],η[1]-cyclopentadien-1,3-yl)}$^+$ NTf_2^- (**4a**) and *trans*-{[(**P**)Au]$_2$(η[1],η[1]-methylcyclopentadien-1,3-yl)}$^+$ NTf_2^- (**4b**), respectively, which were characterized in solution and the solid state. Complexes **4a** and **4b** are highly fluxional in solution at –80 °C with the gold atoms migrating about the cyclopentadienyl ring, presumably via sequential [1,5] sigmatropic rearrangement. In the solid-state, the gold atoms of **4a** and **4b** are positioned on opposite faces of the cyclopentadienyl ring above and below the C1 and C3 carbon atoms. The gold tetramethylcyclopentadienyl complex (**P**)Au(η[1]-C_5HMe_4) (**3b**) also reacts with (**P**)$AuNTf_2$ to form the cationic bis(gold) complex {[(**P**)Au]$_2$(C_5HMe_4)}$^+$ NTf_2^- (**4c**), although the structure of this complex was not firmly established.

The Au–C bond lengths and angles of **4a** (and also **4b**) are similar to those previously calculated for the *trans*-η[1],η[1]-inden-1,3-yl complex **1a**, pointing to analogous orbital interactions in both complexes that, in the case of **4a**, presumably involves overlap of the symmetric combination of the P–Au anti-bonding orbitals [$\phi_a(\sigma^*)$] with the filled antisymmetric cyclopentadienyl $2\pi_b$ molecular orbital. This bonding model is similar to that proposed to describe the M–C bonding interactions in dinuclear palladium and nickel μ-allyl, μ-cyclopentadienyl and μ-indenyl complexes, but lacks the M→C backbonding interactions present in these latter complexes.[18,19] Also worth noting is that computational analyses of these dinuclear Pd and Ni complexes support a common bonding model for μ-cyclopentadienyl, indenyl, and simple allyl ligands.[19] In a similar way, the common bonding interaction of *trans*-η[1],η[1]-cyclopentadienyl and indenyl gold complexes suggests that the *trans*-η[1],η[1] bonding motif might also extend to simple gold allyl complexes, although this contention remains untested.

The mono(gold) cyclopentadienyl complexes **3a** and **3b** display higher (≥ 35-fold) binding affinity toward exogenous (**P**)Au^+ than does the mono(gold) tetramethylcyclopentadienyl

complex **3c**, pointing to destabilization of bis(gold) complex **4c** by the four cyclopentadienyl methyl groups. Nevertheless, the binding affinities of the mono(gold) cyclopentadienyl complexes **3** toward exogenous (**P**)Au$^+$ exceed those of the corresponding unmetallated cyclopentadienes by more than three orders of magnitude, presumably due to the greater σ-donor ability of the (**P**)Au fragment relative to a hydrogen atom. The reactivity of the bis(gold) cyclopentadienyl complexes **4** toward protodeauration was more than three orders of magnitude lower than for the corresponding mono(gold) cyclopentadienyl complexes **3**. Both the aggregation behavior of mono(gold) cyclopentadienyl complexes **3** and the protodeauration behavior of cationic bis(gold) cyclopentadienyl complexes **4** mirror the reactivity of the corresponding indenyl complexes.[12] Although the extent to which this reactivity is similarly mirrored by simple gold allyl complexes has not been established, the high association constants of the mono(gold) cyclopentadienyl and indenyl complexes toward exogenous LAu$^+$ and sluggish protodeauration of the resulting cationic bis(gold) complexes points to the potential relevance of cationic bis(gold)allyl complexes in gold(I)-catalyzed processes that involve gold η^1-allyl intermediates.

EXPERIMENTAL SECTION

[P(*t*-Bu)$_2$*o*-biphenyl]Au(η^1-C$_5$H$_5$) (3a). Cyclopentadiene (22 μL, 0.27 mmol) was added via syringe to a solution of *n*-butyllithium (0.12 mL, 0.30 mmol, 2.5 M in hexanes) in THF (3 mL) at 0 °C and the solution was stirred for 1 h. A solution of (**P**)AuOTf (0.18 g, 0.27 mmol) in THF (3 mL) was added via syringe to the solution of cyclopentadienyl lithium at 0 °C and the resulting solution was stirred overnight at room temperature. The solvent was evaporated under vacuum and the residue was washed with hexane (3 × 8 mL) to give a brown solid that was dissolved in CH_2Cl_2, filtered (0.22 mM mesh), and evaporated under vacuum to give **3a** (0.11 g, 70%) as a pale brown solid. Crystals suitable for X-ray diffraction were grown by slow diffusion of hexanes into a concentrated CH_2Cl_2 solution of **3a** at –20 °C. ^{1}H NMR (700 MHz, CD_2Cl_2, –80 °C): δ 7.75 (t, *J* = 7.31 Hz, 1H), 7.52 – 7.40 (m, 5H), 7.19 (d, *J* = 7.2 Hz, 3H), 5.54 (s, 5H), 1.08 (d, *J* = 15.2 Hz, 18H). ^{13}C{^{1}H} NMR (176 MHz, CD_2Cl_2, –80 °C): δ 148.63 (d, *J* = 15.5 Hz), 142.60 (d, *J* = 6.1 Hz), 133.62, 132.01 (d, *J* = 7.5 Hz), 129.51, 129.14, 127.51, 126.74, 126.32 (d, *J* = 21.3 Hz), 126.04, 109.56 (d, *J* = 7.0 Hz), 35.57 (d, *J* = 22.0 Hz), 29.56. ^{31}P{^{1}H} NMR (C CD_2Cl_2, 283 MHz, –80 °C): δ 61.61. HRMS (APCI/APPI) calcd (found) for $C_{25}H_{32}AuP$: 560.1924 (560.1907).

[P(*t*-Bu)$_2$*o*-biphenyl]Au(η^1-C$_5$H$_4$Me) (3b). Reaction of (**P**)AuOTf with C_5H_4MeLi employing a procedure analogous to that used to synthesize **3a** gave **3b** in 63% yield as a pale brown solid. ^{1}H NMR (700 MHz, CD_2Cl_2, –80 °C): δ 7.75 (t, *J* = 7.21 Hz, 1H), 7.49 – 7.41 (m, 5H), 7.18 (s, 3H), 5.22 (s, 2H), 5.05 (s, 2H), 1.99 (s, 3H), 1.10 (d, *J* = 15.4 Hz, 18H). ^{13}C{^{1}H} NMR (176 MHz, CD_2Cl_2, –80 °C): δ 149.4 (d, *J* = 15.7 Hz), 143.4 (d, *J* = 5.7 Hz), 134.5, 134.3, 132.7 (d, *J* = 6.9 Hz), 130.2, 129.8, 128.3, 127.4, 127.3, 127.1, 109.0 (m), 107.0 (m), 36.5 (d, *J* = 21.4 Hz), 30.3 (br s), 16.2. ^{31}P{^{1}H} NMR (CD_2Cl_2, 283 MHz, –80 °C): δ 62.06. HRMS (APCI/APPI) calcd (found) for $C_{26}H_{34}AuP$: 574.2082 (574.2064).

[P(*t*-Bu)$_2$*o*-biphenyl]Au(η^1-C$_5$HMe$_4$) (3c). Reaction of (**P**)AuOTf with C_5HMe_4Li employing a procedure analogous to that used to synthesize **3a** gave **3c** in 60% yield as a brown solid. ^{1}H NMR (700 MHz, CD_2Cl_2, –80 °C): δ 7.82 (t, *J* = 7.85 Hz, 1H), 7.49 – 7.36 (m, 5H), 7.16 (m, 3H), 2.12 (d, *J* = 14.8 Hz, 1H), 1.73 (s, 6H), 1.68 (s, 6H), 1.21 (d, *J* = 14.8 Hz, 18H). ^{13}C{^{1}H} NMR (176 MHz, CD_2Cl_2, –80 °C): δ 148.86 (d, *J* = 16.5 Hz), 143.58 (d, *J* = 5.6 Hz), 134.58, 133.87, 132.17 (d, *J* = 7.7 Hz), 129.32, 128.94, 128.21, 128.02, 127.58, 126.77, 126.26 (d, *J* = 5.1 Hz), 126.10 (d, *J* = 3.0 Hz), 71.19 (d, *J* = 61.3 Hz), 36.41 (d, *J* = 19.5 Hz), 29.94, 14.17, 11.00. ^{31}P{^{1}H} NMR (CD_2Cl_2, 283 MHz, –80 °C): δ 64.14. HRMS (APCI/APPI) calcd (found) for $C_{29}H_{40}AuP$: 616.2553 (616.2533).

{[P(*t*-Bu)$_2$*o*-biphenyl]Au}$_2$(η^1,η^1-1,3-C$_5$H$_5$)}$^+$ NTf$_2^-$ (4a). A solution of **3a** (15 mg, 4.5 × 10^{-2} mmol) and (**P**)AuNTf$_2$ (21 mg, 4.5 × 10^{-2} mmol) in CD_2Cl_2 (600 μL) was added to NMR tube, shaken, and cooled to –80 °C. ^{31}P NMR analysis of the solution revealed quantitative (≥98%) formation of **4a**. Slow diffusion of hexanes into the resulting solution at –20 °C for 12 h gave **4a** (34 mg, 95%) as yellow-brown crystals. ^{1}H NMR (700 MHz, CD_2Cl_2, –80 °C): δ 7.74 (t, *J* = 7.60 Hz, 2H), 7.55-7.41 (m, 10H), 7.24-7.12 (m, 6H), 5.43 (s, 5H), 1.07 (d, *J* = 15.8 Hz, 36H). ^{13}C{^{1}H} NMR (176 MHz, CD_2Cl_2, –80°C): δ 148.11 (d, *J* = 14.3 Hz), 142.52 (d, *J* = 6.8 Hz), 133.17, 132.15 (d, *J* = 7.7 Hz), 130.08, 129.27, 127.94, 126.74 (d, *J* = 28.9 Hz), 124.56, 124.31, 118.9 (q, J_{CF} = 320 Hz), 107.95, 35.84 (d, *J* = 24.0 Hz), 29.49. ^{31}P{^{1}H} NMR (CD_2Cl_2, 283 MHz, –80 °C): δ 60.15.

{[P(*t*-Bu)$_2$*o*-biphenyl]Au}$_2$(η^1,η^1-1,3-C$_5$H$_4$Me)}$^+$ NTf$_2^-$ (4b). A solution of **3b** (15 mg, 4.4 × 10^{-2} mmol) and (**P**)AuNTf$_2$ (20 mg, 4.3 × 10^{-2} mol) in CD_2Cl_2, (600 μL) was added to NMR tube, shaken, and cooled to –80 °C. ^{31}P NMR analysis of the solution revealed quantitative (≥97%) formation of **4b**. Slow diffusion of hexanes into the resulting solution at –20 °C for 12 h gave **4b** (27 mg, 96%) as yellow-brown crystals. ^{1}H NMR (700 MHz, CD_2Cl_2, –80 °C): δ 7.74 (t, *J* = 7.8 Hz, 2H), 7.53 – 7.41 (m, 10H), 7.22-7.13 (m, 6H), 5.13 (s, 2H), 4.80 (s, 2H), 1.94 (s, 3H), 1.08 (d, *J* = 15.5 Hz, 36H). ^{13}C{^{1}H} NMR (176 MHz, CD_2Cl_2, –80 °C): δ 148.9 (d, *J* = 14.7 Hz), 143.3 (d, *J* = 6.5 Hz), 141.7, 133.9, 132.8 (d, *J* = 7.8 Hz), 130.8, 129.9, 128.7, 127.5 (d, *J* = 6.2 Hz), 127.2, 125.2 (d, *J* = 42.9 Hz), 119.58 (q, J_{CF} = 321 Hz), 103.7 (m), 103.6 (m), 36.7 (d, *J* = 23.7 Hz), 30.2 (br s), 15.7. ^{31}P{^{1}H} NMR (CD_2Cl_2, 283 MHz, –80 °C): δ 60.44.

{[P(*t*-Bu)$_2$*o*-biphenyl]Au}$_2$(C$_5$HMe$_4$)}$^+$ NTf$_2^-$ (4c). A solution of **3c** (15 mg, 0.02 mmol) and (**P**)AuNTf$_2$ (19 mg, 0.02 mmol) in CD_2Cl_2, (600 μL) was added to NMR tube, shaken, and cooled to –80 °C. ^{31}P NMR analysis of the solution revealed formation of **4c** which constituted >90% of the reaction mixture. ^{1}H NMR (700 MHz, CD_2Cl_2, –80 °C): δ 7.76 (t, *J* = 7.89 Hz, 2H), 7.47 (s, 10H), 7.12 (s, 6H), 3.18 (s, 1H), 1.79 (s, 6H), 1.56 (s, 6H), 1.08 (d, *J* = 15.4 Hz, 36H). ^{13}C{^{1}H}NMR (176 MHz, CD_2Cl_2, –80 °C): δ 148.35 (d, *J* = 14.6 Hz), 142.58 (d, *J* = 6.3 Hz), 134.29, 133.47, 132.40 (d, *J* = 7.6 Hz), 130.08, 129.07, 127.89, 126.93, 126.65, 124.44, 124.21, 118.9 (q, J_{CF} = 320 Hz), 116.21, 85.07 (t, *J* = 17.0 Hz), 36.54 (d, *J* = 23.3 Hz), 29.51, 15.31, 12.00. ^{31}P{^{1}H} NMR (CD_2Cl_2, 283 MHz, –80 °C): δ 60.41.

Equilibrium binding affinity of gold cyclopentadienyl complexes to (P)Au$^+$. A solution of **3a** (6 mg, 0.01 mmol) and [(**P**)Au(NCPh)]$^+$ SbF$_6^-$ (**5**; 9 mg, 0.01 mol) in CD_2Cl_2 (600 μL) containing benzonitrile (~55 mM) was added to an NMR tube, mixed thoroughly, and placed in the probe of an NMR spectrometer precooled at –80°C. ^{31}P NMR analysis of the solution showed quantitative conversion of **5** to **4a**. Assuming that ≥ 5% of **5** would have been detected in solution, a lower limit for the equilibrium constant for the conversion of **3a** and **5** to **4a** and NCPh of K_{eq} = [**4a**][NCPh]/[**3a**][**5**] ≥400 was determined assuming [NCPh] = [**4a**]. Employing similar procedures and assumptions, equilibrium constants for the conversion of **3b** and **5** to **4b** (K_{eq} = [**4b**][NCPh]/[**3b**][**5**] ≥ 400) and for the conversion of **3c** and **5** to **4c** (K_{eq} = [**4c**][NCPh]/[**3c**][**5**] = 8.63) were determined.

Equilibrium binding affinity of cyclopentadienes to (P)Au$^+$. A solution of cyclopentadiene (1.5 μL, 0.02 mmol) and [(**P**)Au(NCPh)]$^+$ SbF$_6^-$ [**5**; 15 mg, 0.02 mmol] in CD_2Cl_2 (600 μL) was added to an NMR tube, mixed thoroughly, and placed in the probe of an NMR spectrometer precooled at –80°C. ^{31}P NMR analysis of the solution revealed a 1.0:4.7 mixture of [(**P**)Au(η^2-C$_5$H$_6$)]$^+$ SbF$_6^-$(**6a**) and **5**; **6a** was characterized in solution by ^{1}H and ^{31}P NMR spectroscopy and by analogy to known cationic (**P**)Au(η^2-1,3-diene) complexes.[32,33] An equilibrium constant for the conversion of **5** to **6a** of K_{eq} = [**6a**][NCPh]/[C$_5$H$_6$][**5**] = 0.043 ± 0.008 was determined assuming [C$_5$H$_6$] = [**5**] and [NCPh] = [**6a**]. Employing a similar procedure and assumptions, an equilibrium constant for the reaction of methylcyclopentadiene with **5** of K_{eq} = [(**6b**)][NCPh]/[C$_5$H$_5$Me][**5**] = 0.22 ± 0.02 was determined where **6b** = [(**P**)Au(η^2-C$_5$H$_5$Me)]$^+$ SbF$_6^-$. ^{31}P NMR analysis of an equimolar solution of **5** and 2,4,5,6-tetramethylcyclopentadiene revealed no detectable formation of [(**P**)Au(η^2-C$_5$H$_2$Me$_4$)]$^+$ SbF$_6^-$(**6c**). Assuming ≥ 5% of **6c** would have been detected in solution, an upper limit for the

equilibrium constant for the reaction of $C_5H_2Me_4$ with **5** of K_{eq} = [(**6c**)][NCPh]/[$C_5H_2Me_4$][**5**] ≤ 2.4×10^{-3} was determined

For (P)Au(π-C_5H_6) (6a):[33] ^{1}H NMR (CD_2Cl_2, 700 MHz, –80 °C): δ 7.93-7.01 (m), 6.80 (br s, 2H), 5.79 (br s, 2H), 3.25 (d, J = 25.7 Hz, 1H), 3.14 (d, J = 26.1 Hz, 1H) 1.27 (d, J = 16.7 Hz, 18H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 283 MHz, –80 °C): δ 62.95.

For (P)Au(π-C_5H_5Me) (6b): ^{1}H NMR (CD_2Cl_2, 700 MHz, –80 °C): δ 7.93-7.02 (m), 6.40 (s, 1H), 6.31 (s, 1H), 5.37 (s, 1H), 3.06 (d, J = 12.5 Hz, 2H), 2.05 (s, 3H), 1.21 (d, J = 16.67 Hz, 18H). ^{31}P{^{1}H} NMR (CD_2Cl_2, 283 MHz, –80 °C): δ 63.08.

Protodeauration of 3a, 3b, and 3c. Acetic acid (12 μL, 0.20 mmol) was added to an NMR tube containing a solution of **3a** (12 mg, 0.020 mmol) in CD_2Cl_2 (600 μL) at –80°C. The contents of the tube were mixed thoroughly and placed in the probe of an NMR spectrometer precooled at –80°C. A ^{31}P NMR spectrum recorded within 45 s revealed complete consumption of **3a** to form a 1:13 mixture of **4a** and (**P**)AuOAc as the only phosphorus-containing species; (**P**)AuOAc was identified by comparison to an authentic sample. The ^{1}H NMR spectrum recorded immediately thereafter revealed formation of a ~36:1 mixture of free cyclopentadiene and **4a** as the exclusive cyclopentadiene containing species. Assuming that ≥10% of unreacted **3a** would have been observed in the initial ^{31}P NMR spectrum and the protodeauration of **3a** obeys pseudo first-kinetics, we set a lower limit for the observed rate constant for protodeauration of **3a** of $k_{obs} \geq 5 \times 10^{-2}$ s^{-1}. Employing similar procedures and assumptions, we set lower limits for the observed rate constant for protodeauration of **3b** and **3c** of $k_{obs} \geq 5 \times 10^{-2}$ s^{-1}. Protodeauration of **3b** formed (**P**)AuOAc and methylcyclopentadiene, which comprised >95% of the organic and organometallic reaction products, respectively. Protodeauration of **3c** formed a 1.0:3.3:0.67 mixture of **4c**:(**P**)AuOAc: $C_5H_2Me_4$.

(P)AuOAc. A solution of (**P**)AuCl (50 mg, 0.09 mmol) and AgOAc (16 mg, 0.09 mmol) in CH_2Cl_2 (3 mL) was stirred at room temperature for ~1 hr. The solution was filtered and concentrated under reduced pressure to give (**P**)AuOAc (43 mg, 83%) as a white solid. ^{31}P{^{1}H} NMR (CD_2Cl_2, 283 MHz, –80 °C): δ 53.90.

Protodeauration of 4a, 4b, and 4c. In three separate experiments, acetic acid (13 μL, 0.23 mmol) was added to a solution of **4a**, **4b**, or **4c** (~0.02 mmol) in CD_2Cl_2 (600 μL) at –80 °C. The contents of the tube were mixed thoroughly and placed in the probe of an NMR spectrometer precooled at –80°C. ^{31}P and ^{1}H NMR analysis of the solutions recorded after 1 h revealed no detectable consumption of **4**. Assuming that ≥10% consumption of **4** would have been observed in the ^{31}P NMR spectrum and protodeauration of **4** obeys pseudo first-order kinetics, we can set an upper limit for the observed half-life for protodeauration of $k_{obs} \leq 3 \times 10^{-5}$ s^{-1}.

Computational methods. All DFT calculations were performed employing the Gaussian 16 program.[35] The B3LYP method[36] was used to locate all relevant conformations. The def2-TZVPP basis set was applied for all the nonmetallic atoms and def2ECP pseudopotential with the corresponding def2-TZVPP basis set was applied for gold. All the stationary points were optimized in the gas-phase and frequency calculations were performed at the same level to evaluate the thermal corrections at 298 K without scaling. Conformational energies based on the geometry structures obtained at the B3LYP level were calculated using the def2-TZVPP basis set for nonmetallic atoms and def2ECP pseudopotential with the corresponding def2-TZVPP basis set for gold.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Synthetic procedures, computational details, and scans of NMR spectra

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