

Synthesis, Structure, and Reactivity of a Gold Carbenoid Complex That Lacks Heteroatom Stabilization**

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Abstract: Hydride abstraction from the neutral gold cycloheptatrienyl complex $[(P)Au(\eta^1-C_7H_7)]$ ($P = P(tBu)_2(o$ -biphenyl)) with triphenylcarbenium tetrafluoroborate at $-80^\circ C$ led to the isolation of the cationic gold cycloheptatrienylidene complex $[(P)Au(\eta^1-C_7H_6)]^+ BF_4^-$ in 52 % yield, which was characterized in solution and by single-crystal X-ray diffraction. This cycloheptatrienylidene complex represents the first example of a gold carbenoid complex that lacks conjugated heteroatom stabilization of the electron-deficient C1 carbon atom. The cycloheptatrienylidene ligand of this complex is reactive; it can be reduced by mild hydride donors, and converted to tropone in the presence of pyridine N-oxide.

Cationic gold carbenoid complexes have been widely proposed as reactive intermediates in a range of gold(I)-catalyzed transformations, including alkene cyclopropanation and enyne cycloaddition.^[1] Nevertheless, there remains considerable debate regarding the nature of these complexes,^[2–4] which is in large part due to the lack of direct experimental information regarding the structure and behavior of cationic gold carbenoid complexes.^[5] Rather, information regarding the nature of cationic gold carbenoid complexes was for many years restricted to indirect experimental evidence and computational studies.^[1–5] In 2008, Hammond reported the spectroscopic detection of a gold carbenoid/oxonium complex,^[6] and since then, a number of cationic gold carbenoid complexes have been isolated,^[7–10] including Fürstner's recent disclosure of a reactive dianisylcarbenoid complex (Figure 1).^[9] However, in all cases, these complexes rely on the conjugation of heteroatoms to the electron-deficient C1 carbon atom for stabilization. Herein, we report the synthesis, structure, and reactivity of a gold cycloheptatrienylidene complex, which represents the first gold carbenoid complex that lacks stabilizing, conjugated heteroatom groups.

Toward the synthesis of a gold carbenoid complex that lacks conjugated heteroatom groups, we initially targeted the gold diphenylcarbenoid complex $[(P)AuCPh_2]^+ SbF_6^-$ (**1**; $P = P(tBu)_2(o$ -biphenyl)). Unfortunately, the attempted synthesis

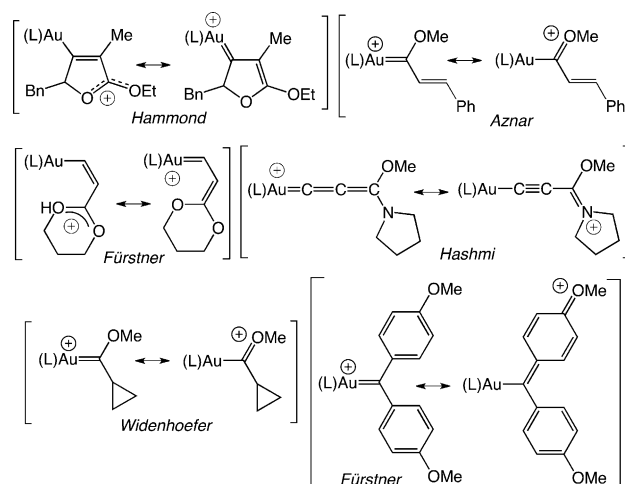
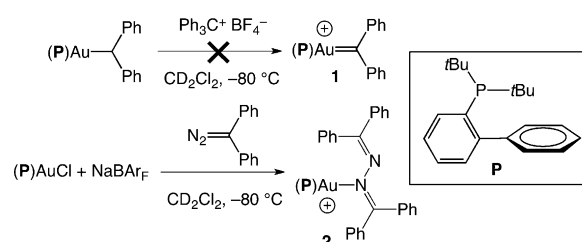


Figure 1. Representative cationic, heteroatom-stabilized gold carbenoid complexes ($L = N$ -heterocyclic carbene or tertiary phosphine).^[6–9]

of **1** either through hydride abstraction from a gold diphenylmethane precursor or through the reaction of a mixture of $[(P)AuCl]$ and $AgSbF_6$ with diphenyldiazomethane failed to form detectable quantities of **1**, with the latter reaction giving only the hydrazine complex **2** (Scheme 1).^[11,12] Fürstner likewise noted the failure to generate complex **1** through transmetalation from Group 6 diphenylcarbenoid complexes.^[8]



Scheme 1. Attempted synthesis of gold diphenylcarbenoid complex **1**.

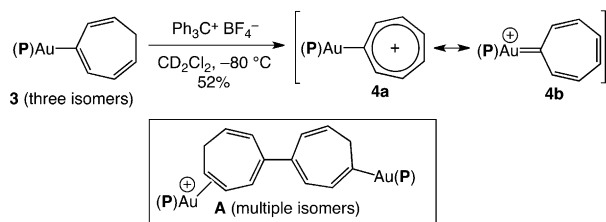
In an effort to impart greater stability in a heteroatom-free gold carbenoid complex, we sought to exploit the potential aromatic stabilization of the cycloheptatrienylidene ligand.^[13] An initial experiment was encouraging, and the treatment of a solution of triphenylcarbenium tetra(perfluorophenyl)borate in CD_2Cl_2 with the neutral gold cycloheptatrienyl complex $[(P)Au(\eta^1-C_7H_7)]$ (**3**; 10:4:3 mixture of isomers) at $-80^\circ C$ led to the immediate formation (≤ 5 min) of an approximately 3:1 mixture of the desired gold

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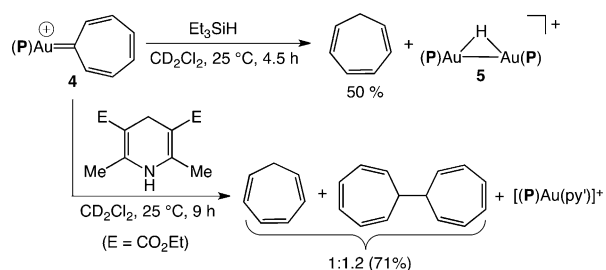
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cycloheptatrienyliene complex $[(\mathbf{P})\text{Au}(\eta^1\text{-C}_7\text{H}_6)]^+ \text{B}(\text{C}_6\text{F}_5)_4^-$ ($\mathbf{4}\cdot\text{B}(\text{C}_6\text{F}_5)_4$) and an isomeric mixture of the bis(gold) bicycloheptatrienyl complexes $[(\mathbf{P})\text{Au}]_2(\eta^1, \eta^2\text{-C}_{14}\text{H}_{13})^+ \text{B}(\text{C}_6\text{F}_5)_4^-$ ($\mathbf{A}\cdot\text{B}(\text{C}_6\text{F}_5)_4$), which are presumably formed through the attack of unreacted $\mathbf{3}$ on $\mathbf{4}\cdot\text{B}(\text{C}_6\text{F}_5)_4$.^[14,15] On the basis of this latter hypothesis, we reasoned that the formation of $\mathbf{A}$ could be mitigated through the slow addition of $\mathbf{3}$ to a solution of the triphenylcarbenium ion. Indeed, dropwise addition of a solution of $\mathbf{3}$ in CH_2Cl_2 over 30 minutes to a solution of triphenylcarbenium tetrafluoroborate in CH_2Cl_2 at -80°C led to the isolation of pure $[(\mathbf{P})\text{Au}(\eta^1\text{-C}_7\text{H}_6)]^+ \text{BF}_4^-$ ($\mathbf{4}$) in 52% yield as a yellow microcrystalline solid (Scheme 2).



Scheme 2. Synthesis of gold cycloheptatrienyliene complex $\mathbf{4}$.

Complex $\mathbf{4}$ was thermally stable and characterized by NMR spectroscopy and single-crystal X-ray diffraction. The ^1H NMR spectrum of $\mathbf{4}$ displayed a 1:1:1 ratio of vinylic resonances at $\delta = 9.02$, 8.79, and 8.64 ppm, which were shifted downfield relative to the alkene protons of $\mathbf{3}$ ($\delta \leq 7.9$ ppm), consistent with a contribution of the aromatic canonical form $\mathbf{4a}$ (Scheme 3). In the ^{13}C NMR spectrum of $\mathbf{4}$, the C1



Scheme 3. Reaction of $\mathbf{4}$ with hydride donor reagents.

carbenoid resonance appeared as a phosphorus-coupled doublet at $\delta = 225.5$ ppm ($J_{\text{CP}} = 101.8$ Hz), which is similar to the C1 resonances of cationic cyclopentadienyl Group 8 dicarbonyl ($\delta = 224\text{--}242$ ppm)^[14] and neutral Pd^{II} η^1 -cycloheptatrienyliene complexes ($\delta = 224\text{--}229$ ppm),^[16] and slightly downfield of the C1 resonance of the cationic Pt^{II} complex $[\text{trans}(\text{PPh}_3)_2\text{PtBr}(\eta^1\text{-C}_7\text{H}_6)]$ ($\delta = 210$ ppm).^[17]

Vapor diffusion of diethyl ether into a concentrated solution of $\mathbf{4}$ in acetonitrile at 25°C provided crystals of $\mathbf{4}\cdot 0.25\text{CH}_3\text{CN}$ suitable for X-ray analysis (Figure 2).^[18] Complex $\mathbf{4}$ adopts a near-linear conformation about gold with a P–Au–C1 angle of 177.2° and with the cycloheptatrienyliene ligand positioned perpendicular to the plane that reflects the

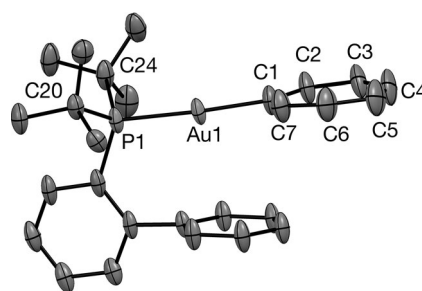
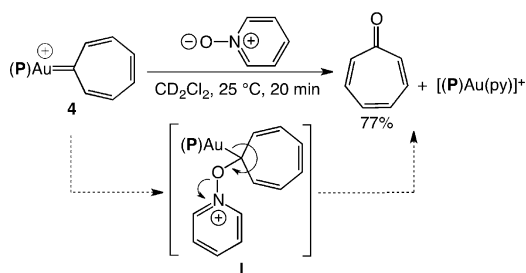


Figure 2. ORTEP diagram of $\mathbf{4}\cdot 0.25\text{CH}_3\text{CN}$. One of two crystallographically independent molecules is depicted with ellipsoids shown at the 50% probability level with counterion and hydrogen atoms omitted for clarity. Selected bond distances (Å) and bond angles (deg) for $\mathbf{4}\cdot 0.25\text{CH}_3\text{CN}$: Au1–C1 = 2.035(6), Au1–P1 = 2.3008(13), C1–C7 = 1.406(9), C2–C3 = 1.385(9), C3–C4 = 1.396(11), C4–C5 = 1.327(11), C5–C6 = 1.418(11), C6–C7 = 1.392(9), P1–Au1–C1 = 177.0(2), C7–C1–C2 = 123.3(6), C7–C1–Au1 = 118.9(5), C2–C1–Au1 = 117.8(5).

atoms C20 and C24 of the *tert*-butyl group. The mean C–C–C bond angle of the cycloheptatrienyliene ring is $128.5 \pm 1.9^\circ$, which is not significantly different from that of a regular heptagon (128.6°). The carbene carbon atom deviates most significantly from the mean with a C7–C1–C2 angle of $123.3(6)^\circ$, which is closer to the idealized value for an sp^2 -hybridized carbon atom than to that of a regular heptagon, which may suggest a contribution of the gold carbene form $\mathbf{4b}$.^[14] Unfortunately, any systematic deviations in the C–C bond distances within the cycloheptatrienyliene ligand that would be indicative of carbene contributor $\mathbf{4b}$ are obscured by the relatively large standard deviations associated with these bond lengths.

The cycloheptatrienyliene ligand of $\mathbf{4}$ underwent reduction in the presence of mild hydride donors. For example, the treatment of $\mathbf{4}$ with triethylsilane (2.4 equiv) in CD_2Cl_2 at room temperature for 4.5 hours led to the formation of free cycloheptatriene in 50% yield and the bis(gold) hydride complex $[(\mathbf{P})\text{Au}]_2(\mu\text{-H})^+ \text{BF}_4^-$ ($\mathbf{5}$) as the exclusive phosphine-containing species. This outcome is consistent with the initial reduction of the cycloheptatrienyliene ligand of $\mathbf{4}$ followed by protodemetalation of $\mathbf{3}$ to form free cycloheptatriene and the cationic gold fragment $[(\mathbf{P})\text{Au}]^+$, which reacts with HSiEt_3 to form $\mathbf{5}$ (Scheme 3).^[19] Similarly, the treatment of $\mathbf{4}$ with the Hantzsch ester gave a 1:1.2 mixture of free cycloheptatriene and free 7,7'-bicycloheptatriene in 71% combined yield as exclusive organic products, and $[(\mathbf{P})\text{Au}(\text{py}')^+]^2 \text{BF}_4^{2-}$ ($\text{py}' = \text{dimethyl pyridine-3,5-dicarboxylate}$) as the sole phosphine-containing species (Scheme 3). This outcome is consistent with the initial reduction of $\mathbf{4}$ followed by either protodeauration of $\mathbf{3}$ to form free cycloheptatriene, or the attack of $\mathbf{3}$ on $\mathbf{4}$ to form $\mathbf{A}$, followed by protodeauration to form free bis(cycloheptatriene).^[15] Interestingly, no reduction of $\mathbf{4}$ was observed in the presence of substituted cycloheptatrienes such as *p*-anisylcycloheptatriene.

We also investigated the reactivity of $\mathbf{4}$ toward nucleophiles. Complex $\mathbf{4}$ reacts rapidly with triethylamine or ethyl vinyl ether below room temperature to form intractable mixtures of products. In contrast, treatment of $\mathbf{4}$ (21 mM) with pyridine *N*-oxide (1.2 equiv) in CD_2Cl_2 at 25°C for 20 minutes



Scheme 4. Reaction of **4** with pyridine *N*-oxide.

led to a selective oxygen atom transfer to form tropone in 77 % yield and $[(\text{P})\text{Au}(\text{py})]^+ \text{BF}_4^-$ as the exclusive phosphine-containing species (Scheme 4). This outcome is consistent with a nucleophilic attack at the C1 atom of **4** followed by elimination from intermediate **I**.^[20]

In summary, we have synthesized the gold cycloheptatrienylidene complex **4** through hydride abstraction from the neutral gold cycloheptatrienyl complex **3**. Complex **4** represents the first example of a gold carbenoid complex lacking heteroatom-stabilizing groups in conjugation with the C1 carbon atom. Downfield shifts of the cycloheptatrienylidene protons of **4** relative to the cycloheptatrienyl protons of **3** in the ^1H NMR spectra point to the contribution of the tropylium canonical form **4a**, whereas the compressed C7–C1–C2 bond angle (123.3°) of the cycloheptatrienylidene ligand of **4** relative to the mean C–C–C bond angle ($128.5 \pm 1.9^\circ$) may suggest a contribution of gold carbene form **4b**. The cycloheptatrienylidene ligand of **4** is reactive; it can be reduced by mild hydride donors such as triethylsilane and Hantzsch ester, and converted to free tropone in the presence of pyridine *N*-oxide.

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