Carbenoids

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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(η^1-C_7H_7)] (**P** = P(tBu)$_2$(o-biphenyl)) with triphenylcarbenium tetrafluoroborate at −80 °C led to the isolation of the cationic gold cycloheptatrienylidene complex [(**P**)Au(η^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(*t*Bu)$_2$(*o*-biphenyl)). Unfortunately, the attempted synthesis

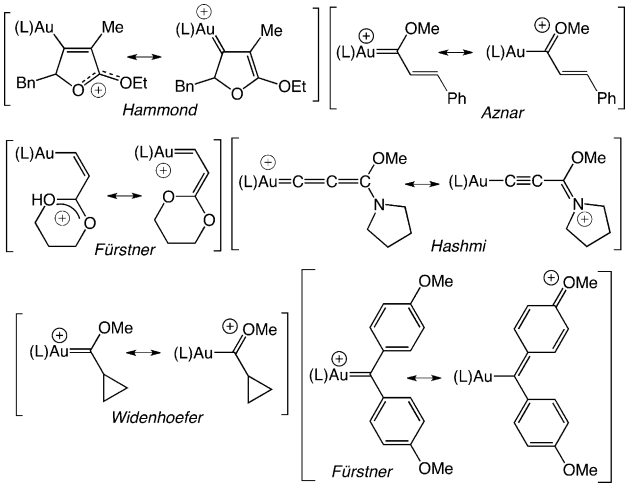
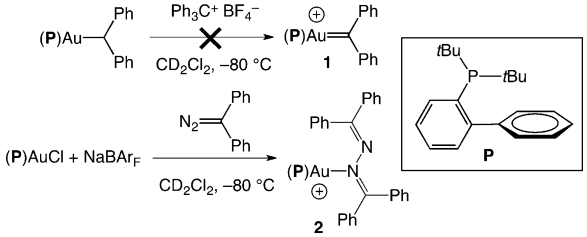


Figure 1. Representative cationic, heteroatom-stabilized gold carbenoid complexes (L = N-heterocyclic carbene or tertiary phosphine).[6–9]

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(η^1-C_7H_7)] (**3**; 10:4:3 mixture of isomers) at −80 °C led to the immediate formation (≤ 5 min) of an approximately 3:1 mixture of the desired gold

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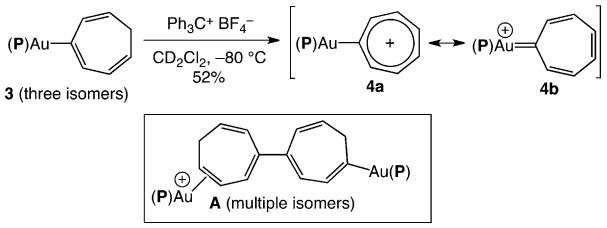
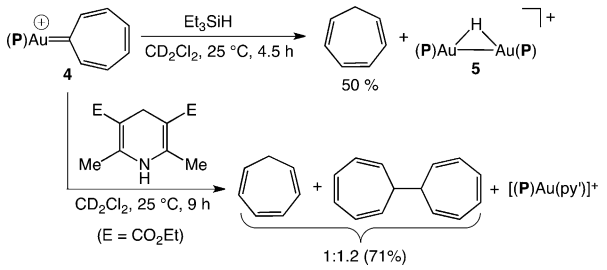
cycloheptatrienylidene complex $[(\mathbf{P})Au(\eta^1\text{-}C_7H_6)]^+ B(C_6F_5)_4^-$ ($\mathbf{4}\cdot B(C_6F_5)_4$) and an isomeric mixture of the bis(gold) bicycloheptatrienyl complexes $[\{(\mathbf{P})Au\}_2(\eta^1,\eta^2\text{-}C_{14}H_{13})]^+ B(C_6F_5)_4^-$ ($\mathbf{A}\cdot B(C_6F_5)_4$), which are presumably formed through the attack of unreacted **3** on $\mathbf{4}\cdot B(C_6F_5)_4$.[14,15] On the basis of this latter hypothesis, we reasoned that the formation of **A** could be mitigated through the slow addition of **3** to a solution of the triphenylcarbenium ion. Indeed, dropwise addition of a solution of **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 $[(\mathbf{P})Au(\eta^1\text{-}C_7H_6)]^+ BF_4^-$ (**4**) in 52% yield as a yellow microcrystalline solid (Scheme 2).



Scheme 2. Synthesis of gold cycloheptatrienylidene complex **4**.

Complex **4** was thermally stable and characterized by NMR spectroscopy and single-crystal X-ray diffraction. The ^{1}H NMR spectrum of **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 **3** ($\delta \leq 7.9$ ppm), consistent with a contribution of the aromatic canonical form **4a** (Scheme 3). In the ^{13}C NMR spectrum of **4**, the C1



Scheme 3. Reaction of **4** with hydride donor reagents.

carbenoid resonance appeared as a phosphorus-coupled doublet at $\delta = 225.5$ ppm ($J_{CP} = 101.8$ Hz), which is similar to the C1 resonances of cationic cyclopentadienyl Group 8 dicarbonyl ($\delta = 224$–242 ppm)[14] and neutral Pd^{II} η^1-cycloheptatrienylidene complexes ($\delta = 224$–229 ppm),[16] and slightly downfield of the C1 resonance of the cationic Pt^{II} complex [*trans*-$(PPh_3)_2PtBr(\eta^1\text{-}C_7H_6)$] ($\delta = 210$ ppm).[17]

Vapor diffusion of diethyl ether into a concentrated solution of **4** in acetonitrile at 25 °C provided crystals of $\mathbf{4}\cdot 0.25\,CH_3CN$ suitable for X-ray analysis (Figure 2).[18] Complex **4** adopts a near-linear conformation about gold with a P-Au-C1 angle of 177.2° and with the cycloheptatrienylidene ligand positioned perpendicular to the plane that reflects the

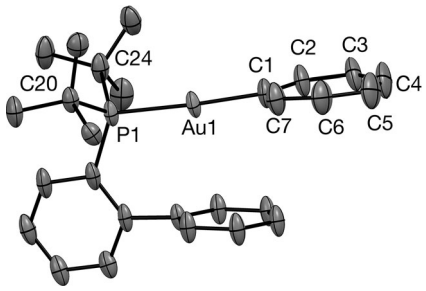
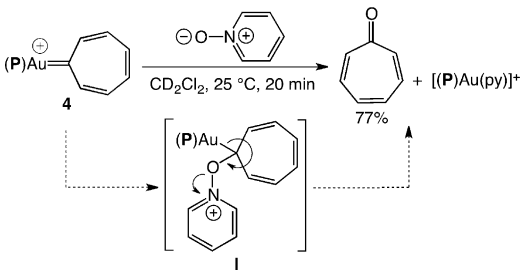


Figure 2. ORTEP diagram of $\mathbf{4}\cdot 0.25\,CH_3CN$. One of two crystallographically independent molecules is depicted with ellipsoids shown at the 50% probability level with counterion and hydrogen atoms omitted for clarity. Selected bond distances (Å) and bond angles (deg) for $\mathbf{4}\cdot 0.25\,CH_3CN$: 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 cycloheptatrienylidene ring is 128.5 ± 1.9°, 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)°, 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 **4b**.[14] Unfortunately, any systematic deviations in the C–C bond distances within the cycloheptatrienylidene ligand that would be indicative of carbene contributor **4b** are obscured by the relatively large standard deviations associated with these bond lengths.

The cycloheptatrienylidene ligand of **4** underwent reduction in the presence of mild hydride donors. For example, the treatment of **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 $[\{(\mathbf{P})Au\}_2(\mu\text{-}H)]^+ BF_4^-$ (**5**) as the exclusive phosphine-containing species. This outcome is consistent with the initial reduction of the cycloheptatrienylidene ligand of **4** followed by protodemetalation of **3** to form free cycloheptatriene and the cationic gold fragment $[(\mathbf{P})Au]^+$, which reacts with $HSiEt_3$ to form **5** (Scheme 3).[19] Similarly, the treatment of **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 $[(\mathbf{P})Au(py')]^+ BF_4^-$ (py′ = dimethyl pyridine-3,5-dicarboxylate) as the sole phosphine-containing species (Scheme 3). This outcome is consistent with the initial reduction of **4** followed by either protodeauration of **3** to form free cycloheptatriene, or the attack of **3** on **4** to form **A**, followed by protodeauration to form free bis(cycloheptatriene).[15] Interestingly, no reduction of **4** was observed in the presence of substituted cycloheptatrienes such as *p*-anisylcycloheptatriene.

We also investigated the reactivity of **4** toward nucleophiles. Complex **4** reacts rapidly with triethylamine or ethyl vinyl ether below room temperature to form intractable mixtures of products. In contrast, treatment of **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 $[(\mathbf{P})Au(py)]^+ BF_4^-$ 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 ^{1}H 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 ± 1.9°) 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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