

Gold Complexes

Generation and Structural Characterization of a Gold(III) Alkene Complex**

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Gold complexes are effective catalysts for a range of organic transformations including the coupling of alkenes and alkynes to other organic fragments.^[1-10] A key step in these catalytic reactions is assumed to be the coordination of a C-C multiple bond to the gold center.^[1,2,6] Although various catalytic cycles involving Au^{III} π complexes have been proposed,^[2,6,11,12] no Au^{III} alkene,^[13] alkyne, allene, or arene complexes have been conclusively detected and characterized.^[1,6,14,15] In 1964, Chalk proposed the generation of $[C_{0}H_{12} \cdot AuCl_{3}]$,^[16] based solely on an IR spectrum and elemental analysis of mixtures containing two species.^[14,15] Since then several groups have attempted to prepare olefin complexes of Au^{III} chlorides and bromides, but clear identification of an Au^{III} alkene complex has been elusive. $^{[14,\,15,\,17-21]}$ Gas phase calculations of $AuCl_3$ and ethylene suggest that the alkene binding is exothermic.^[22,23] In contrast, Au^I alkene complexes have been known for some time with several examples reported^[16,24-32] and in part reviewed.[1-3,33-35]

Recent interest in the characterization of potential Au^{III} intermediates has resulted in the isolation of both an Au^{III} hydride^[36] and an Au^{III} vinyl^[37] complex. Herein, we describe the preparation of the first crystallographically characterized Au^{III} alkene complex and discuss the factors that contribute to

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the stability of this unusual molecule, in which the Au center is directly bonded solely to carbon atoms.

The cyclometalated tolylpyridine (tpyH) complex $[(tpy)AuMe_2]$ (1, Scheme 1) was prepared as recently described.^[38] Addition of triflic acid (HOTf, ca. 2.2 equiv) to



Scheme 1. Protonation of $[(tpy)AuMe_2]$ **1** at low temperature followed by addition of cod to generate $[(cod)AuMe_2^+][X^-]$ (**3**-X; X = OTf or BArf). BArf=tetrakis[3,5-bis(trifluoromethyl)phenyl]borate.

a CD₂Cl₂ solution of **1** at -78 °C followed by warming to -40 °C yielded the Au^{III} dimethyl species [(tpyH)AuMe₂-(OTf)] (**2**).^[39] Selective protonolysis of the Au–C(sp²) bond, as has been observed in other Au^{III} complexes,^[40] is confirmed by the two inequivalent AuMe groups, the absence of methane, and the symmetry of the tolyl group. NOE interactions between the protons of one AuMe group and aromatic protons of tpyH suggest that tpyH is coordinated to Au as a monodentate ligand in **2** through the N atom. Triflate presumably occupies the fourth site of the square plane around the Au^{III} center.

Addition of 1,5-cyclooctadiene (cod, 1 equiv) to the solution of **2** at -78 °C followed by slow warming to 0 °C resulted in the gradual consumption of cod with concomitant formation of the Au^{III} alkene complex [(cod)AuMe₂⁺][OTf⁻] (**3**-OTf; Scheme 1) in 85% yield from **1** (NMR, internal standard). The byproduct is tolylpyridinium triflate, tpyH₂OTf, formed by reaction of HOTf with tpyH liberated from the Au center upon coordination of cod.

The ¹H NMR spectrum of **3**-OTf at 0 °C consists of a single AuMe resonance at $\delta = 1.71$, a pair of multiplets for the CH₂ groups in the backbone of the bound cod at $\delta = 2.75$ and 2.99, and a broad singlet for the vinylic protons of the bound cod at $\delta = 6.39$, which is 0.8 ppm higher than the signal of free cod in CD₂Cl₂ at $\delta = 5.56$. Although vinylic protons typically shift to lower δ values on binding to a metal center,^[41] as seen in the Au¹ complex [(HB{3,5-(CF₃)₂pz}₃)Au(C₂H₄)],^[31] there are also examples of shifts to higher δ values with especially electrondeficient metals, such as Ag¹ in [(HB{3,5-(CF₃)₂tz}₃)Ag (C_2H_4)] (pz = pyrazolyl, tz = triazolyl).^[42] The signal of the ethylene protons of this Ag complex appears 0.3 ppm higher than that of free ethylene. Notably, the ¹³C resonance for the bound ethylene shifts to lower values by 13.6 ppm. In **3**-OTf the ¹³C signal of the cod sp² carbon atoms is also shifted to a higher δ value, 134 ppm when compared to free cod at δ = 129. Further support for the binding of cod to gold is a through-space NOE interaction (700 MHz, 233 K) between the vinylic protons of the bound cod and the AuMe groups.

The stability of **3**-OTf at ambient temperature in solution is somewhat limited. After 12 h at 25 °C, the concentration of **3**-OTf (initially ca. 14 mM) decreased by approximately 50 % even with a cod concentration of 40 mM in CD₂Cl₂. Attempts to obtain crystals from reaction mixtures containing **3**-OTf and excess HOTf invariably led to isolation of tpyH₂OTf.

In an effort to isolate crystals of the Au^{III} alkene complex, the reaction was repeated using 0.9 equivalent of HOTf to suppress the formation of tpyH₂OTf in the reaction mixture. However, the subsequent addition of as much as 50 equivalents of cod resulted in only approximately 30% yield of the desired 3-OTf (NMR, internal standard). In addition, the reaction mixture contained 2 (ca. 20%) and a new species (ca. 20%) that was subsequently identified as $[(tpyH)_2AuMe_2^+]$ -[OTf⁻] (4-OTf) by comparison to an independently prepared and crystallographically characterized sample.^[39,43] Upon addition of tpyH (ca. 6 equiv) to the equilibrium mixture above, the composition of the reaction mixture changed to < 5% yield of **3**-OTf, approximately 20% of **2**, and approximately 60% of 4-OTf. These observations suggest that 2, 3-OTf, 4-OTf, free cod, and free tpyH are in equilibrium, that is, cod and tpyH compete for coordination sites at the Au^{III} moiety. Importantly, the ¹H NMR resonances of 3-OTf remain unchanged regardless of whether the other species present in the reaction mixture are tpyH2OTf (resulting from excess acid) or 2 and 4-OTf (less than 1 equiv of acid). From this observation we infer that 3-OTf does not have an associated tpyH ligand in solution. All attempts to obtain crystals from reaction mixtures without excess HOTf resulted only in crystals of 4-OTf.^[39]

When approximately one equivalent of $[{3,5-(CF_3)_2-C_6H_3}_{4}B^-][(Et_2O)_2H^+]$ (HBArf·2 OEt₂)^[44] was used for the protonolysis of **1** in CD₂Cl₂, followed by addition of 15 equivalents of cod, $[(cod)AuMe_2^+][BArf^-]$ (**3**-BArf) was generated in approximately 70% yield (NMR, internal standard). The ¹H NMR chemical shifts for the AuMe groups and the vinylic and CH₂ protons of bound cod in **3**-BArf appear within 0.2 ppm of the corresponding resonances in a spectrum of **3**-OTf. The solution containing **3**-BArf was layered with pentane and left in a freezer at -35°C, resulting in small crystalline demispheres suitable for X-ray diffraction. The structure of the cation of **3**-BArf is shown in Figure 1.^[43]

Compound 3-BArf crystallized in the monoclinic space group $P2_1/c$ with the Au cation sitting in a pocket formed by the aryl groups of several BArf⁻ anions.^[43] The Au-C_{cod} bonds are rather long for a metal alkene complex, 2.389 Å (avg.). The cation is nearly C_2 symmetric (not crystallographically imposed). Interestingly, each cod C=C bond is asymmetrically bonded to Au such that one Au-C bond is significantly longer



Figure 1. Two ORTEP views of the Au^{III} cation in the 100 K solid-state structure of **3**-BArf with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Au(1)–C(1) 2.049(4), Au(1)–C(2) 2.055(4), Au(1)–C(3) 2.371(4), Au(1)–C(4) 2.415(4), Au(1)–C(7) 2.362(4), Au(1)–C(8) 2.406(4), C(3)–C(4) 1.348(5), C(7)–C(8) 1.364(5); C(3)-Au(1)-C(4) 32.71(13), C(7)-Au(1)-C(8) 33.23(12), C(7)-Au(1)-C(4) 77.86(13), C(3)-Au(1)-C(8) 77.87(13), C(1)-Au(1)-C(2) 85.0(2).

than the other (2.362(4) vs. 2.406(4) and 2.371(4) vs. 2.415(4) Å, respectively). The C=C bond lengths in **3**-BArf are 1.348(5) and 1.364(5) Å. Several cationic Au^I alkene complexes have been recently structurally characterized.^[24-30,32] Their Au–C_{alkene} bond lengths are in the range of 2.098(5)^[24]–2.37(1)^[30] Å, and the C=C distances are in the range of 1.319^[26]–1.409(4)^[25] Å. It is noteworthy that the two long Au–C_{cod} distances in the cationic Au^{II} complexes.^[24-30,32] Furthermore, the C=C distances in **3**-BArf are essentially in the middle of the range seen for these Au^I complexes, thus indicating some back-bonding from Au^{III} to the C=C bonds, despite the strong *trans* influence of the two methyl groups.

The Au–C_{cod} bonds in **3**-BArf are also considerably longer than the Pt–C_{cod} bonds in the isoelectronic Pt^{II} complex [(cod)PtMe₂], and the C=C distances are significantly shorter in the Au complex than in the Pt analogue (Table 1), thereby hinting at reduced back-bonding from d(M) to π^* (cod) orbitals when Au^{III} is compared to Pt^{II}. The Au–C_{Me} bond lengths in **3**-BArf are 2.049(4) and 2.055(4) Å, quite typical for cationic Au^{III}Me₂ fragments with relatively weak donor ligands *trans* to the methyl groups.^[45,46]

The structures of $[(cod)AuMe_2^+]$ and $[(cod)PtMe_2]$, optimized at the DFT level with the hybrid PBE0 functional and quasi relativistic effective core potential (ECP) for Au (see computational details^[47]), indispensable for representing the structures and reactivity of Au complexes,^[57,58] are in excellent agreement with the solid-state structures (Table 1 and the Supporting Information). In particular, the calculations reproduce very well the nonequivalence of the two M-C_{cod} bond lengths to the same C=C, and the larger difference between these distances for Au versus Pt. For $[(cod)AuMe_2^+]$, the distances differ by 0.052 Å, but for [(cod)PtMe₂] they differ by only 0.024 Å. In relation to this, the olefinic carbon atoms C3, C4, C7, and C8 are not coplanar; the calculated dihedral angles C3-C4-C7-C8 are 13.7° and 11.6° for Au^{III} and Pt^{II}, respectively. These calculated values are in excellent agreement with the solidstate values of 13.4° and 12.7°, which show that these structural features are not due to crystal packing or to the counteranion in the case of Au^{III}, since the geometries were

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	Table 1:	Selected	geometrical	parameters	for	[(cod)AuMe ₂ +],	
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[(cod)PtMe_2], and free cod, and distortion energies of the cod ligand.^[a] See Figure 1 for atom labels.

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	[(cod)Au	Me ₂ [⊤]]	[(cod)PtMe ₂]		cod		
	Exp. ^[b]	Theo. ^[c]	Exp. ^[d]	Theo. ^[c]	Exp. ^[e]	Theo. ^[c]	
Distances [Å]							
M–C1 ^[f]	2.049(4)	2.055	2.040(11)	2.057	-	-	
M–C2 ^[f]	2.055(4)	2.055	2.072(11)	2.057	-	_	
M–C3 (d ₁) ^[f]	2.362(4)	2.390	2.204(11)	2.211	-	_	
M–C4 (d ₂) ^[f]	2.406(4)	2.442	2.255(12)	2.235	-	_	
$\Delta(d_2-d_1)$	0.044	0.052	0.051	0.024	-	_	
M–C7 (d ₃) ^[f]	2.371(4)	2.390	2.224(11)	2.211	-	_	
M–C8 (d ₄) ^[f]	2.415(4)	2.442	2.230(11)	2.235	-	_	
$\Delta(d_4-d_3)$	0.044	0.052	0.006	0.024	-	-	
$\Delta(avg.)^{[g]}$	0.044	0.052	0.029	0.024	-	-	
C3–C4	1.364(5)	1.366	1.348(17)	1.385	1.340(3)	1.335	
C7–C8	1.348(5)	1.366	1.361(17)	1.385	1.340(3)	1.335	
Angles [°]							
C3-C4-C7-C8	13.4	13.7	12.7	11.6	20.2	23.6	
C4-C5-C6-C7	46.5	44.4	34.5	36.7	63.8	61.2	
C8-C9-C10-	42.6	44.4	33.1	36.7	63.8	61.2	
C3							
E [kcal mol ⁻¹]							
Distortion	_	4.7	_	12.7	_	0.0	
E ^[h]							
=							

[a] Distances [Å], angles [°], energies (kcal mol⁻¹). [b] X-ray structure reported in this work. [c] DFT (PBE0) calculations;^[47] [d] Data from X-ray structure.^[54] An earlier determined structure, for which the cif file is not available, gives a Δ (avg.) of 0.024 Å,^[55] [e] Data from gas-phase electron diffraction structure;^[56] [f] M=Au, Pt; [g] Mean value of Δ (d₂-d₁) and Δ (d₄-d₃); [h] Energy difference, *E*(bound)–*E*(free), between optimized free cod and cod in the confirmations calculated in [(cod)AuMe₂⁺] and [(cod)PtMe₂], respectively.

fully optimized in the gas phase and in the absence of a counteranion. To determine the origin of these features, free cod was optimized at the same level of theory. In free cod, the C3-C4-C7-C8 dihedral angle is 23.6°, showing that the two C=C bonds are distinctively nonparallel. It thus appears that the two C=C bonds become increasingly parallel upon coordination and more so for PtII than AuIII. This trend is attributed to the preference for a staggered conformation of the -CH2CH2- backbone of cod. In free cod where no constraints are present, the two -CH₂CH₂- units are fully staggered as indicated by the dihedral angles C4-C5-C6-C7 and C8-C9-C10-C3 of 61.2°, associated with the dihedral angle C3-C4-C7-C8 of 23.6°. Coordination of the metal to the two C=C bonds, which forces the two double bonds to be more parallel, also forces the -CH₂CH₂- linkers to assume a more eclipsed conformation. The effect is smaller for Au^{III} than Pt^{II} as shown by the C4-C5-C6-C7 and C8-C9-C10-C3 dihedral angles of 45° and 35° (avg.), respectively. The -CH2CH2- backbone never reaches a fully eclipsed conformation and the two C=C bonds never become coplanar, which leads to nonequivalent M-C bond lengths.

Distorting the cod ligand from its preferred conformation to its conformations in the metal complexes has an energy cost of 4.7 kcalmol⁻¹ and 12.7 kcalmol⁻¹ for Au^{III} and Pt^{II}, respectively. The electronic effect that compensates for this distortion energy is the back donation from the metal to the two π^* orbitals as shown by an NBO (natural bond orbital) analysis. The four orbitals containing the 8 d electrons were identified amongst the NLMOs (natural localized molecular orbitals). The d_{z^2} and $d_{x^2-y^2}$ orbitals appear as lone pairs located on the metal center, with no significant contribution from the ligands (see the Supporting Information). In contrast, the d_{xz} and d_{yz} orbitals are involved in the $d \rightarrow \pi^*$ back donation from the metal center to the C=C bond of cod. This interaction is weaker in $[(cod)AuMe_2^+]$, where the contribution from the $\pi^*(C=C)$ (see the Supporting Information) is 2.2% with the d_{xz} and 2.8% with the d_{yz} . The corresponding numbers for [(cod)PtMe₂] are 9.5% with the d_{xz} and 12 % with the d_{yz} . The difference between Au and Pt is apparent in the graphical representation of these NLMOs (Figure 2) and is consistent with the greater distortion (more



Figure 2. NLMOs (with orbital phases in green/red) associated with the metal $d \rightarrow \pi^*(cod)$ back donation.

eclipsed) of the -CH₂CH₂- backbones of cod in the Pt complex and the increasing elongation of the C=C bonds (1.335 Å in free cod, 1.366 Å in [(cod)AuMe₂⁺], and 1.385 Å in [(cod)PtMe₂]). These results show that, compared to Pt, the metal $d \rightarrow \pi^*$ (C=C) back donation is weaker, but still significant, in [(cod)AuMe₂⁺], thus stabilizing this unprecedented Au^{III} bis(alkene) complex.

In summary, we have successfully characterized the first Au^{III} alkene complex, including the crystal structure of [(cod)AuMe₂⁺][BArf⁻]. This unambiguous demonstration of the existence of Au^{III} alkene complexes validates their inclusion in mechanistic proposals and will allow for further work to better understand mechanisms that potentially involve Au^{III} alkene complexes. Reactivity studies of **3**-OTf along with improved synthesis of this and other Au^{III} complexes with π -bound ligands are currently under investigation.

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