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Experimental Evaluation of the Electron Donor Ability of a Gold Phosphine Fragment in a Gold Carbene Complex

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X-ray analysis of the gold cyclopropyl(methoxy)carbene complex [(P)AuC(OMe)(*c*-Pr)]⁺ SbF₆⁻ [P = P(*t*-Bu)₂*o*-biphenyl] and comparison to extant protonated cyclopropyl ketones indicates that electron donation from the (P)Au fragment to the electron-deficient C1 atom is similar to that provided by a cyclopropyl group.

Although gold(I) carbene complexes are commonly invoked as intermediates in a range of gold(I)-catalyzed transformations,¹⁻³ there remains considerable debate regarding the nature of the Au–C bond in these complexes.⁴⁻⁷ Unresolved issues include the relative contributions of the carbene (Au⁺=CR₂) and α -metallocarbenium ion (Au–CR₂⁺) forms (Figure 1, **A**) and more generally, the extent to which gold stabilizes the electron-deficient C1 atom.⁸⁻¹⁰ These ambiguities persist in large part due to the dearth of experimental information regarding the electronic structure of the Au–CR₂ bond.⁴⁻⁷ Fürstner concluded that stabilization of a γ,γ -dialkoxy allylic cation by a gold phosphine fragment in complexes **B** was “marginal” on the basis of C–C rotational barriers (Figure 1).^{5,11} However, as noted by Toste and Goddard,⁶ the influence of gold in complexes **B** is likely obscured by the combined effect of the two conjugated oxygen atoms. Rather, DFT calculations suggest that a tertiary allylic carbocation is stabilized to a similar extent by a (Me₃P)Au group and a methoxy group.⁶

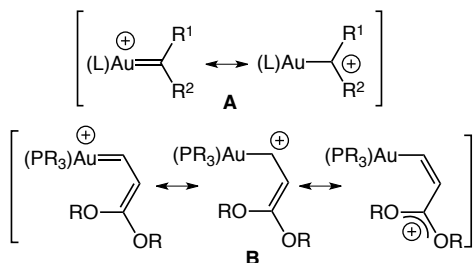


Figure 1. Mesomeric representations of gold(I) carbene complexes **A** and **B**.

Toward an experimental evaluation of Au \rightarrow C1 electron donation in a gold carbene complex, we were drawn to the large

body of experimental¹²⁻¹⁶ and theoretical^{17,18} work regarding the geometric perturbations of a cyclopropyl ring bound to a π -acceptor group. In the preferred bisected conformation,¹⁹ overlap of the occupied Walsh 3e' orbital with the empty p or π^* orbital of the acceptor leads to shortening of the C1–C2 and distal C3–C4 bonds with concomitant lengthening of the vicinal C2–C3/4 bonds that is commensurate with the extent of delocalization (Figure 2).^{14,17} We therefore reasoned that analysis of the bond lengths associated with the cyclopropyl group of a gold cyclopropylcarbene complex in comparison to appropriate reference compounds would reveal the relative electron density of C1 and, hence, the relative carbocation stabilizing ability of the (L)Au fragment.

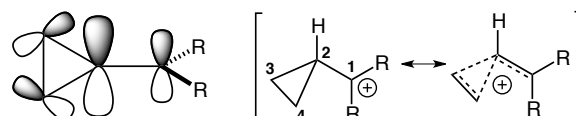
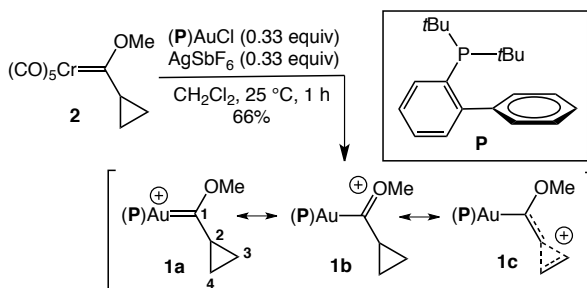


Figure 2. Orbital and resonance representations of the bisected cyclopropylcarbinyl cation

We targeted the cyclopropyl(methoxy)carbene complex [(P)AuC(OMe)(*c*-Pr)]⁺ SbF₆⁻ [**1**; P = P(*t*-Bu)₂*o*-biphenyl] for structural analysis on the expectation that a single C1-oxygen atom would sufficiently stabilize the complex to allow isolation, but would not obscure the effects of Au \rightarrow C1 electron donation. Employing a modified version of the procedure reported by Aznar,²⁰ slow addition of a 1:1 suspension of (P)AuCl and AgSbF₆ to a solution of (CO)₅CrC(OMe)(*c*-Pr) (**2**) (3 equiv) in CH₂Cl₂ led to isolation of analytically pure **1** in 66% yield as a thermally stable white solid (Scheme 1).²¹ In the ¹³C NMR spectrum of **1**, the C1 resonance appeared as a phosphorus-coupled doublet at δ 303.9 (J_{CP} = 99 Hz), which is significantly more deshielded than are the C1 atoms of Fürstner's dialkoxy carbene complexes **B** (δ 213–215)⁵ and is typical of an electrophilic carbene complex.^{21,22} Likewise, the cyclopropyl C2 [δ 35.6 (d, J_{CP} = 5.6 Hz)] and C3/C4 (δ 19.2) resonances are deshielded relative to a neutral cyclopropyl ketone (δ ~20, ~10), pointing to contribution of the bisected cyclopropylcarbinyl cation **1c**.

However, the C2 cyclopropyl resonance of **1** is more shielded than are those of group 6 and 8 cyclopropyl(methoxy)carbene carbonyl complexes (δ 41.5 - 44.3),²² pointing to greater stabilization of the C1 carbon atom of **1** relative these related carbene complexes.



Scheme 1. Synthesis of gold cyclopropyl(methoxy)carbene complex **1**.

Slow diffusion of hexanes into a CH_2Cl_2 solution of **1** at 4 °C gave colorless crystals suitable for X-ray analysis (Figure 3). Complex **1** adopts a near-linear conformation about gold with a P–Au–C1 angle of 177.6° and with the carbene ligand oriented such that O1–C1–C2 plane is perpendicular to the plane that reflects the *tert*-butyl C6 and C10 atoms. The cyclopropyl ring adopts an *s-cis* orientation relative to the methoxy group and within the cyclopropyl(methoxy) ligand of **1**, the C1–O1 bond length (1.285 Å) lies between the values expected for a C=O double and C(sp²)–O single bond,^{23,24} consistent with contribution of oxocarbenium form **1b**. Importantly, the C2–C3 and C2–C4 bonds are ~0.073 Å longer than is the C3–C4 bond (Δd)²⁵ and the C1–C2 bond is ~0.03 Å shorter than is that of a neutral cyclopropyl ketone,¹³ which together point to contribution of the bisected cyclopropylcarbinyl cation form **1c**.¹²⁻¹⁹ Also worth noting is that the Au–C1 bond of **1** is ~0.085 Å shorter than is that of the neutral gold acyl complex $(\text{Ph}_3\text{P})\text{AuC}(\text{O})\text{Ph}$.²⁶

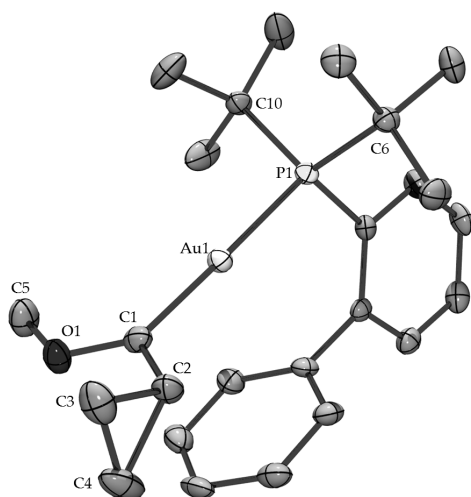


Figure 3. ORTEP diagram of **1**. Ellipsoids are shown at the 50% probability level with counterion and hydrogen atoms omitted for clarity. Selected bond distances (Å) and bond angles (deg) for **1**: Au1–C1 = 2.032(4), Au1–P1 = 2.314(1), C1–O1 = 1.285(4), C1–C2 = 1.448(5), C2–C3 = 1.537(5), C2–C4 = 1.534(5), C3–C4 = 1.462(6), O1–C5 = 1.455(4), P1–Au1–C1 = 177.6(1), O1–C1–C2 = 113.2(3), O1–C1–Au1 = 125.9(3), C2–C1–Au1 = 120.8(3).

Extending the work of Allen¹³ and Childs,¹⁴⁻¹⁶ analysis of the bond lengths of monosubstituted cyclopropanes **3-7** bound to a π -acceptor group (Table 1) reveals a correlation ($r = -0.91$) between the difference in the C2–C3/4 and C3–C4 bond lengths (Δd)²⁵ and the C1–C2 bond length (Figure 4). When arranged in this manner, the electron density of C1 increases from top left to lower right. Carbene complex **1** fits this correlation, allowing estimation of the C1 electron density of **1** relative to these reference compounds, most importantly the protonated cyclopropyl ketones $\text{R}(c\text{-Pr})\text{COH}^+$ [R = Me (**3a**), Ph (**3b**), *c*-Pr (**3c**)].¹⁴⁻¹⁶ Because Olah found no significant difference in the C=O bond polarization of protonated and methylated ketones,²⁷ the C1 electron density in compounds **1** and **3** directly reflects the electron donor ability of the C1 substituent. This comparison indicates that the carbocation stabilizing ability of the (P)Au fragment exceeds that of a methyl or phenyl group, but is similar to that of a cyclopropyl group.²⁸⁻³⁰

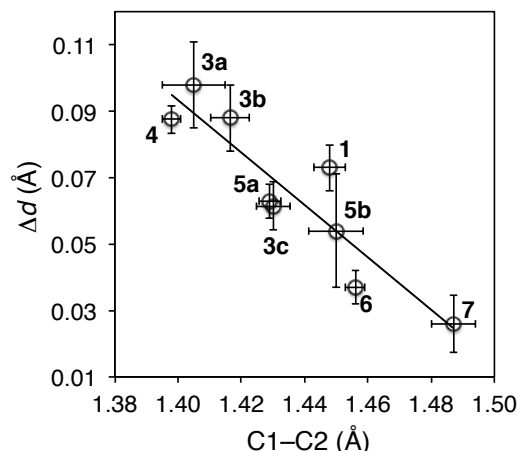


Figure 4. Correlation between Δd and the C1–C2 bond lengths for cyclopropanes bound to a π -acceptor group.²⁵

Table 1. Relevant bond distances (Å) for cyclopropanes bound to a π -acceptor group determined by X-ray crystallography.

compound	C1–C2 ^{a,b}	Δd ^{b,c}	compound	C1–C2 ^{a,b}	Δd ^{b,c}
1	1.448(5)	0.073(7)			
			R = Me (3a) ^d	1.405(10)	0.098(13)
			R = Ph (3a) ^{e,f}	1.417(6)	0.087(10)
			R = <i>c</i> -Pr (3c) ^{g,g}	1.432(5)	0.062(7)
				1.455(3)	0.037(5)
			6 ^{g,i}	1.455(3)	0.037(5)
			7 ^k	1.487(7)	0.026(9)

^aNumbering system follows that of **1**. ^bError limits determined from published e.s.d.s and standard propagation of error. ^c $\Delta d = 1/2[d(\text{C2–C3}) + d(\text{C2–C4})] - d(\text{C3–C4})$. ^dThis work. ^eReference 14. ^fReference 13. ^gAverage of two crystallographically independent molecules. ^hAverage of two crystallographically independent cyclopropyl groups. ⁱReference 31. ^jReference 32. ^kReference 34.

In summary, we have synthesized the gold cyclopropyl(methoxy)carbene complex **1**, which represents both the first example of a gold cyclopropylcarbene complex and the first structurally characterized transition metal cyclopropylcarbene complex. Comparison of the bond lengths associated with the bisected cyclopropyl(methoxy)carbene ligand of **1** to those of protonated cyclopropyl ketones **3** indicate that the relative carbocation stabilizing ability of the (P)Au fragment exceeds that of a methyl or phenyl group and is similar to that of a cyclopropyl group. Extending these results to other gold carbene complexes, although the extent of Au → C1 donation will vary as a function of the electron demand of C1, the inherent carbocation stabilizing ability of the (P)Au group vis-à-vis Me, Ph, and *c*-Pr, will remain invariant provided the system is not levelled by strong electron donor groups.³⁵

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† Electronic Supplementary Information (ESI) available: Experimental methods and spectroscopic and X-ray crystallographic data. See DOI: 10.1039/c000000x/

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