

Communication

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## Gas-Phase Synthesis and Reactivity of a Gold Carbene Complex

Alexey Fedorov, Marc-Etienne Moret, and Peter Chen\*

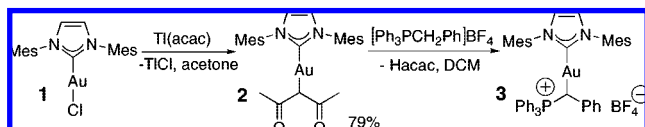
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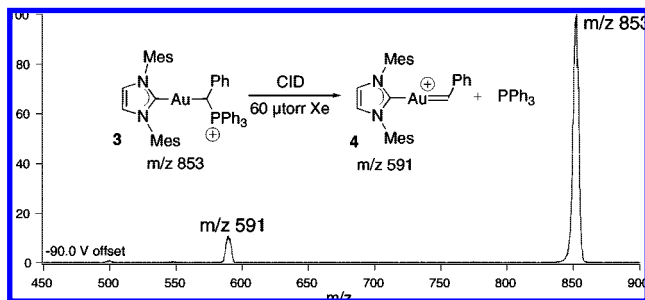
We report quantitative data for a gas phase synthesis of a NHC-supported benzylidene gold carbene and its characteristic reactions.

Given the remarkable progress in the catalytic transformations presumably involving gold carbenes and carbenoids,<sup>1</sup> demand for spectroscopic evidence of such species is very high. Indeed, besides a rather special case of the “bare” methyldiene gold carbene  $\text{Au}(\text{CH}_2^+)^2$  to the best of our knowledge there is no experimental data on the compounds of the general type  $\text{L}_n\text{Au}=\text{CHR}^+$ . We address this issue by the synthesis of a gold carbene directly in the mass-spectrometer from a labile precursor, where the reactive intermediate is stabilized by the interaction with a basic leaving group. Recently, Milstein and co-workers<sup>3</sup> have demonstrated the practical significance of such a transformation for the synthesis of late transition metal carbenes and this chemistry has been exploited for the early transition metals as well.<sup>4</sup> During mechanistic studies on the intermediates operating in the rhenium-catalyzed aldehyde olefination, we also discovered interconversion of the carbene and ylid complexes.<sup>5</sup>

### Scheme 1. Synthesis of the Gold-Ylide Adduct 3

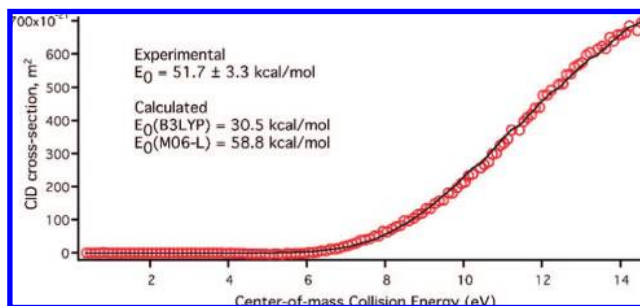


After some screening we found that the phosphonium ylide complex **3** (Scheme 1) could provide access to the desired carbene **4** (Figure 1). Adduct **3** was prepared in situ adopting an established procedure<sup>6</sup> and subjected to electrospray ionization tandem mass spectrometric (ESI-MS/MS) experiments using a modified TSQ-700 mass spectrometer (Finnigan MAT).<sup>7</sup>



**Figure 1.** Daughter-ion spectrum obtained after the mass-selection of **3** at  $m/z$  853 and collision-induced dissociation with xenon in the octopole collision cell exhibits the benzylidene complex **4** as the sole product.

Under a broad range of collision offsets and target gas (Xe) pressures in the collision chamber, the fragmentation of the cation **3** furnishes mainly a signal with  $m/z$  591 that corresponds to the  $\text{PPh}_3$  loss from the parent complex (Figure 1).



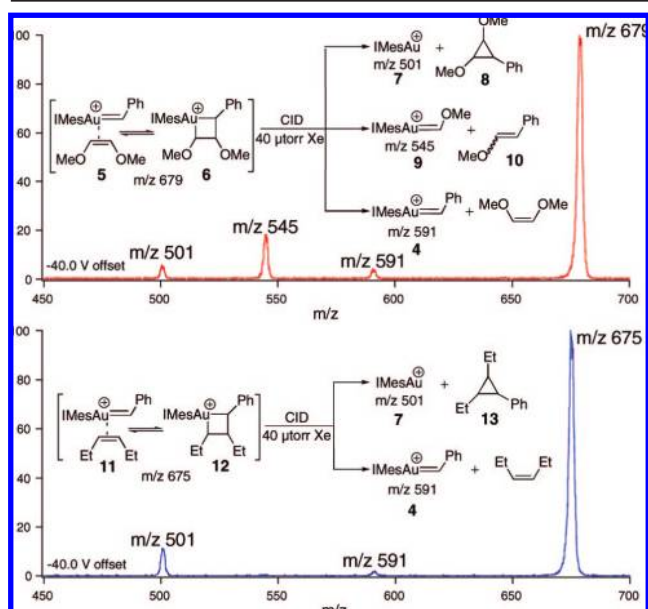
**Figure 2.** Energy resolved reactive cross-section measured for the loss of triphenylphosphine from **3**: extrapolation to zero pressure (red circles) and L-CID-fitted curve (black line).

We conducted quantitative determination of  $\text{PPh}_3$  dissociation energy from collision-induced dissociation (CID) energy-resolved cross sections measurements under near single-collision conditions and compared the experimental value with calculated results (Figure 2). Extrapolation to zero-pressure and subsequent analysis with the L-CID program<sup>8</sup> afforded the value for  $E_0 = 51.7 \pm 3.3$  kcal/mol assuming that the loss of the  $\text{PPh}_3$  from **4** occurs via a loose transition state.<sup>9</sup>

Density functional theory (DFT) calculations at the B3LYP level yielded a binding energy of 30.5 kcal/mol, that is, about 20 kcal/mol lower than the experimental value.

This discrepancy could be explained by the inaccurate treatment of the dispersive interaction contribution to the binding energy by DFT. To check this hypothesis, we performed the same calculations using the recently developed M06-L functional, which has been shown to perform well for transition metal thermochemistry and noncovalent interactions.<sup>10</sup> The M06-L calculations gave a binding energy of 58.8 kcal/mol, in acceptable agreement with the experiment, thus confirming the importance of dispersion forces for fragments of this size.

Taking into account that mass alone does not provide a definitive structural assignment, we investigated whether **4** reacts like a carbene complex. Carbene **4** was generated during the spray process by applying a hard tube lens voltage. Introduction of olefins into the 24-pole rf ion guide led to the formation of new signals in the spectrum.<sup>7</sup> An ion with  $m/z$  679 (**5** or **6**) that arises when *cis*-dimethoxyethylene is introduced into the ion guide region gives three further signals upon mass-selection and collision with xenon (Figure 3). Importantly, the signal with  $m/z$  545 is assigned<sup>7</sup> to the Au carbene **9** thus demonstrating metathesis-type reactivity unprecedented for gold. The pathway leading to the methoxy-group-stabilized carbene **9** is the preferred reaction manifold. Interestingly, the cyclopropanation reaction, which is often observed in the solution for gold carbenoids,<sup>11</sup> also operates in the gas phase: the signal with  $m/z$  501 corresponding to the monocoordinated species **7** is consistent with benzylidene transfer to the  $\text{C}=\text{C}$  double bond. This pathway becomes preferred upon changing the substituents at



**Figure 3.** Daughter-ion spectrums produced by mass selection of adducts **5/6** and **11/12** formed by gas phase reaction of **3** with *cis*-dimethoxyethylene and *cis*-3-hexene, respectively. The observed fragments indicate that both olefin metathesis and cyclopropanation take place.

the olefin from methoxy to an alkyl. Switching to the *cis*-3-hexene completely shuts off the metathesis channel and cyclopropanation becomes the favored pathway (Figure 3).

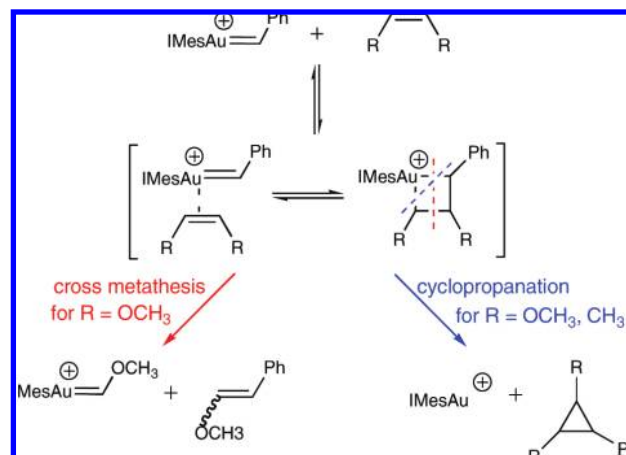
It is highly desirable to develop a convenient cyclopropanation strategy based on the easily available phosphonium ylids.<sup>12</sup>

The current study sheds light on the possibility to use gold ylid complexes for such a purpose. Solution-phase results as well as dependence of the cyclopropanation versus metathesis ratio on the electronic and steric effects of the substituents (Scheme 2) explored by gas-phase methods will be reported in due course.

In conclusion, we report a first example of the mass spectrometric characterization of the benzylidene gold carbene. The measured activation energy for its formation is in agreement with the value predicted by DFT calculations using the M06-L functional. The chemical nature of the synthesized carbene is clearly demonstrated by its characteristic reactivity with olefins, including cross-metathesis and cyclopropanation.

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**Scheme 2.** Competing Cyclopropanation and Metathesis Channels



**Supporting Information Available:** Experimental procedures, computational details, energies, reference mass spectra, as well as the energy-resolved collision-induced cross-section spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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