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σ – π -Diauration as an alternative binding mode for digold intermediates in gold(I) catalysis†

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Abstract

While investigating the gold(I)-catalyzed intramolecular hydroarylation of allenes, the structure of a digoldvinyl intermediate was verified. Instead of the previously proposed geminally diaurated binding mode for the digold when $L = PPh_3$, an alternative σ – π -diauration mode was observed with the bulkier ligand $L = P(o-Tol)_3$. Reactivity studies indicate the σ – π -mode has a disproportionate effect on protonolysis reactivity.

Introduction

Cationic gold complexes efficiently catalyze a broad variety of complex C–X (X = C, O, N) bond forming reactions, principally through the activation of C–C multiple bonds.¹ Early studies in gold(I) catalysis have principally focused on methodology development, though a movement to underpin such studies with targeted mechanistic investigations is emerging.^{2,3}

We have recently reported that in gold(I)-catalyzed intramolecular allene hydroarylation and hydroalkoxylation reactions (10 mol% $Ph_3PAuNTf_2$ (**4a**)⁴ and (2-biphenyl)^t $Bu_2PAuOTf$, respectively), most of the gold catalyst rests as a dinuclear species, the adduct of an expected monogold-vinyl intermediate and the cationic R_3PAu^+ catalyst (Scheme 1).^{5,6}

These species could easily be detected by *in situ* ³¹P NMR as two sharp signals in a 1 : 1 ratio, a consequence of the two diastereotopic P-ligands. In at least the hydroalkoxylation example, the digold intermediate was demonstrated to principally (but not exclusively) exist off-cycle.^{5b} In the hydroarylation reaction, both gold-vinyl intermediates **3a** and **5** were isolated and characterized by NMR; unfortunately, only **3a** could be confirmed by X-ray analysis. Intermediate **5** was proposed to contain a vinyl-bridged Au---Au⁺ unit that benefited from an aurophilic closed shell interaction (5–10 kcal mol⁻¹).^{5a} This structural proposal was primarily based on characteristic NMR data and reactivity that paralleled the seminal geminally diaurated gold-aryl complexes of Grandberg, Nesmeyanov, and Schmidbaur.⁷

The viability of geminally diaurated vinyl intermediates in gold-catalyzed reactions was recently reinforced by Fürstner and coworkers, who synthesized model complexes and provided structural evidence for hyperconjugated vinylic C(sp²) atoms (Fig. 1).⁸

†Electronic supplementary information (ESI) available: Experimental details and NMR data. CCDC 873041. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2sc21281a

Additionally supportive are more recently characterized geminally diaurated vinyl and aryl catalytic intermediates by Hashmi *et al.* in gold(i)-catalyzed alkyne functionalization reactions.⁹ In each case the geminally diaurated products are symmetric in nature.

In this work, we report the structural elucidation of a digold intermediate of catalysis that suggests an alternative binding mode for digold-vinyl intermediates in gold(i) catalysis: σ - π diauration. To the best of our knowledge this binding mode has not yet been reported in organogold-vinyl chemistry,¹⁰ though it has been recently described in gold(i)-acetylide chemistry by the groups of Widenhoefer, Russell, and Finze (Fig. 2).¹¹

Results and discussion

³¹P NMR spectroscopy proved to be an effective tool for investigating catalyst speciation during the conversion of allene **1** to **2** with various Ar₃PAuNTf₂ catalysts. As previously reported, most Ar₃PAuNTf₂ catalysts rested at a digold structure like **5**, as suggested by two sharp resonances in a 1 : 1 ratio at $\delta \approx 36$ ppm in the ³¹P NMR spectrum.

However, when 10 mol% of the sterically demanding catalyst (*o*-tolyl)₃PAuNTf₂ (**4b**) was employed, ³¹P NMR data revealed three broad signals at 22.6, 16.1, and -0.7 ppm in a 1 : 1 : 0.6 ratio (Fig. 3) during the conversion,¹² which contrasted previous observations. The signal at $\delta = -0.7$ ppm corresponded to **4b**. While the relative integration of the 22.6 and 16.1 ppm peaks suggested a digold structure, the broad asymmetric shape of the signals caused us to investigate this case more carefully.

The species **6** giving rise to the peaks at 22.6 and 16.1 ppm could be enriched by reacting **4b** with **1** in the presence of 2,6-di*tert*-butyl pyridine (DTBP), which inhibited protodemetalation.¹³ NMR data revealed that 2 equiv. of **4b** were required for complete consumption of **1** and that the reaction with **4b** (13–24 h) was significantly slower than with **4a** (30 min). We presume this rate difference is attributable to the more basic or encumbered nature of (*o*-CH₃-C₆H₄)₃P *versus* PPh₃.¹⁴

Slow evaporation of an enriched sample of **6** in CH₂Cl₂ layered with pentanes produced a mixture of single crystals suitable for X-ray diffraction analysis. NMR spectroscopy indicated that the crystals were a mixture of {(*o*-Tol)₃P}₂AuNTf₂ and **6** (see ESI†).¹⁵ Although these crystals were not visibly differentiable, the third mounting provided a single crystal of **6** that could be solved (Fig. 4).

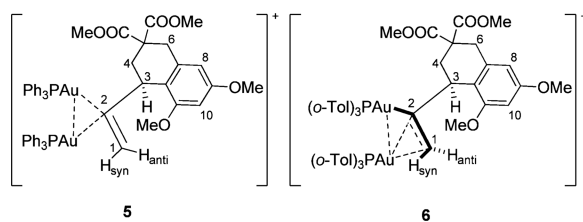
The structure of **6** revealed a geminal diauration binding mode different from that observed by Fürstner and Hashmi. Instead, the second gold cation interacted with the original gold-vinyl in a fashion best described as σ - π with the addition of a stabilizing aurophilic bond. The length of the Au2–C2 σ -bond [2.059(3) Å] (*c.f.* 2.050(2) Å for **3a**) and the sum of bond angles at C2 (359.4° *vs.* 359.9° in **3a**) indicated that the incorporation of a second gold cation did not significantly perturb the gold-vinyl component of the structure. Based on these structural parameters, the second gold atom (Au1 in Fig. 4) seemingly binds to the C1=C2 double bond independent of the gold vinyl (Au2) and actually closely resembles the cationic gold(i) π -alkene complexes published by Widenhoefer *et al.*¹⁶ The distances between Au1–C1 [2.275(3) Å] and Au1–C2 [2.287(3) Å] match the distances in other π -coordinated olefins, which have ranged from 2.167 to 2.365 Å. While no bond angle changes were noted on π -complexation, the C1=C2 double bond does become elongated in comparison to **3a** (1.369(5) Å *vs.* 1.324(4) Å).

The distance between Au1 and Au2 [3.13563(18) Å] suggested a stabilizing aurophilic bond, the demonstrated range for which is quite large [2.8 Å –3.5 Å].¹⁸ The Au1–Au2

distance in **6**, however, was intermediate between the short Fürstner and Hashmi geminally diaurated complexes [2.75 to 2.84 Å],^{8,9} and the longer Au–Au distances of the σ – π -diaurated acetylide complexes (3.41 to 3.62 Å).¹¹ Worth noting in the analogous σ – π -diaurated acetylide chemistry was a rapid interconversion of the two gold units through a process proposed to involve a geminally diaurated acetylide.^{11c}

Since crystallographic evidence for the structure of previously published digold **5** has not been forthcoming, the key ¹H NMR signals (600 MHz) of **6** and **5** were examined to draw comparisons to the binding mode in **5**. Specifically, protons H¹_{syn}, H¹_{anti}, and H³ revealed significant differences.

While proton H¹_{syn} appeared as a doublet in **5** (δ = 6.43 ppm, geminal coupling to H¹_{anti} with $J_{\text{HH}} = 3.0$ Hz), it appeared in **6** as an apparent quartet at δ = 6.14 ppm due to coupling to three spin ½ nuclei (two J_{PH} of 3.0 Hz each and one J_{HH} of 3.0 Hz to H¹_{anti}). H¹_{anti} resonated in the spectrum of **5** at δ = 5.90 ppm as an apparent doublet of triplets due to coupling to two diastereotopic phosphorus atoms (6.0 Hz and 3.0 Hz) and the geminal proton H¹_{syn} (3.0 Hz). In contrast, proton H¹_{anti} in **6** appeared at δ = 5.81 ppm as a doublet of doublets with measurable coupling to only one phosphorus atom (9.6 Hz) and the geminal proton H¹_{syn} (3.0 Hz). The allylic proton H³ (δ = 4.50 ppm) in **5** appeared as a multiplet, but could be deconvoluted into equal couplings to the two diastereotopic phosphorus atoms and the two protons at C⁴ (each 7.8 Hz). In **6** H³ appeared as a quartet at δ = 4.21 ppm, coupling to only *one* phosphorus atom and the two protons at C⁴ (7.8 Hz).¹⁹ The σ – π -bonding mode thus creates an environment where one P-ligand is distinctly different as noted through J_{PH} coupling to H¹_{syn}, H¹_{anti}, and H³, the σ -gold presumably being more coupled into the spin system than the π -gold.



Reactivity similarities and differences between **5** and **6** were also noted.²⁰ Like **5**, compound **6** was found to have one gold unit readily abstracted by the addition of P(*o*-Tol)₃ or NBU₄Br to form gold-vinyl **3b**²¹ and {(*o*-Tol)₃P}₂AuNTf₂ or (*o*-Tol)₃PAuBr, respectively. Similarly, conc. HCl led to immediate protodemetalation to **2**, though like **5** digold **6** was acetic acid stable.

Where their reactivity diverged, however, was in the reaction with non-coordinating strong acids like HNTf₂. For example, on reacting with ~40 equiv. of HNTf₂ **5** reacted in 5 min to give **2**, while complete consumption of **6** (to multiple decomposition products) with ~60 equiv. HNTf₂ took nearly 11 h. This difference in acid sensitivity indicated that the σ – π -binding mode significantly diminishes the propensity for protonolysis. The stability of **6** towards Brønsted acids is not entirely unreasonable given the direct engagement of the π -unit in coordinating the second (*o*-Tol)₃PAu⁺ unit. The hypothesis that the protonolysis occurs by direct π attack onto the C=C double bond is in line with reports by Blum²² and Fürstner,⁸ and related similar observations by Widenhoefer with σ – π -diaurated acetylene complexes.^{11c}

Conclusions

In conclusion, a σ - π -binding mode was observed as a digold intermediate in the hydroarylation of allenes when a bulky P-ligand was utilized. Based on the broad and asymmetric signal shapes of **6** in the ^{31}P NMR spectrum and the contrasting sharp resonances with less bulky catalysts, different coupling constants in the ^1H NMR spectra, and most importantly different reactivity with excess HNTf_2 it is proposed that the σ - π -diaurated structure of **6** does not resemble the binding mode of previously isolated **5**, and that the latter better reflects the cyclopropyl-stabilized digold-vinyl structure of Fürstner and the examples by Hashmi. It does, however, represent another bonding scheme for how *bone fide* catalytic intermediates can become sequestered into polynuclear aggregates and affect catalysis efficiency and speciation.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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12. Complex **4b** catalyzed the reaction but at a rate that is slower than **4a**.
13. Intermediate **6** could not be isolated in pure form. Only an enriched sample could be prepared. Impurities, such as DTBP, DTBP·HNTf₂ or $\{(o\text{-CH}_3\text{-C}_6\text{H}_4)_3\text{P}\}_2\text{AuNTf}_2$, were not successfully removed.
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15. It is important to note that single crystals of **6** and of $\{(o\text{-CH}_3\text{-C}_6\text{H}_4)_3\text{P}\}_2\text{AuNTf}_2$ were obtained simultaneously. The third crystal picked gave a dataset by X-ray diffraction for compound **6**. The formation of $\{(o\text{-CH}_3\text{-C}_6\text{H}_4)_3\text{P}\}_2\text{AuNTf}_2$ could imply decomposition *via* homo-coupling as observed by Fürstner for a geminally diaurated cyclopropyl-vinyl complex. However, analysis of the decomposed mixture was not conclusive to determine the mass balance.
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17. See the ESI† for the supplementary crystallographic data for **6**.
18. The potential energy surface for Au–Au interactions is rather flat for the approach of two gold atoms, see: ref. 7*a*.
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21. Gold-vinyl **3b** was not isolated, but was strongly implicated based on characteristic chemical shifts and coupling constants of vinyl protons.
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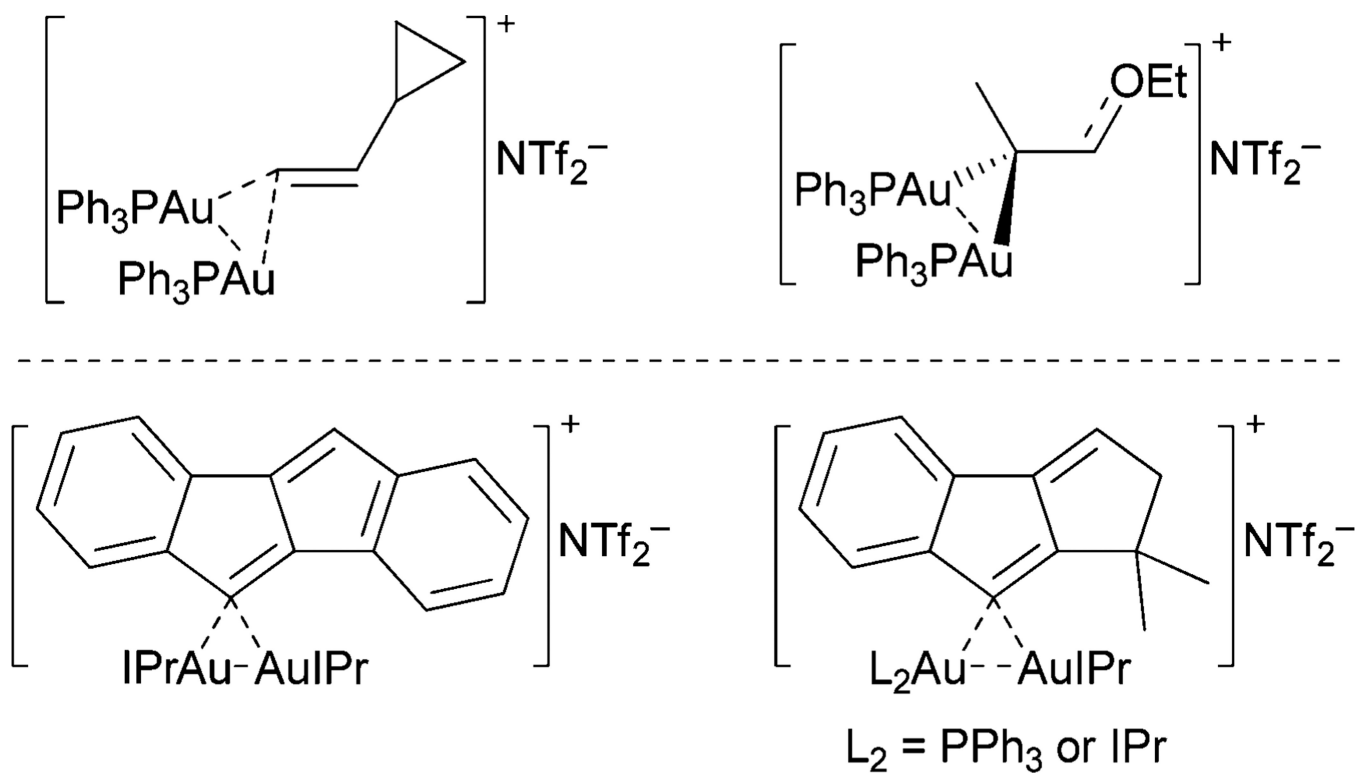


Fig. 1.
Structurally characterized geminally diaurated vinyl-complexes by Fürstner (top) and Hashmi (bottom).

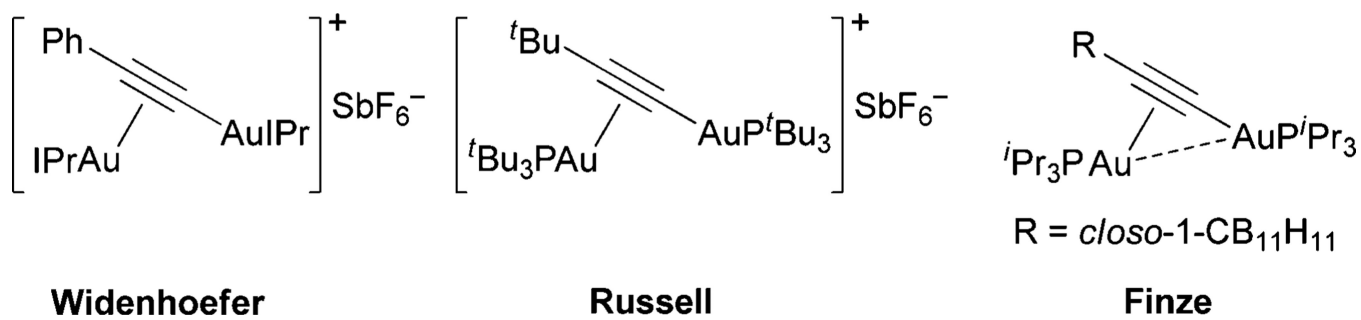


Fig. 2. Representative examples of known σ - π -diaurated gold-acetylide complexes.

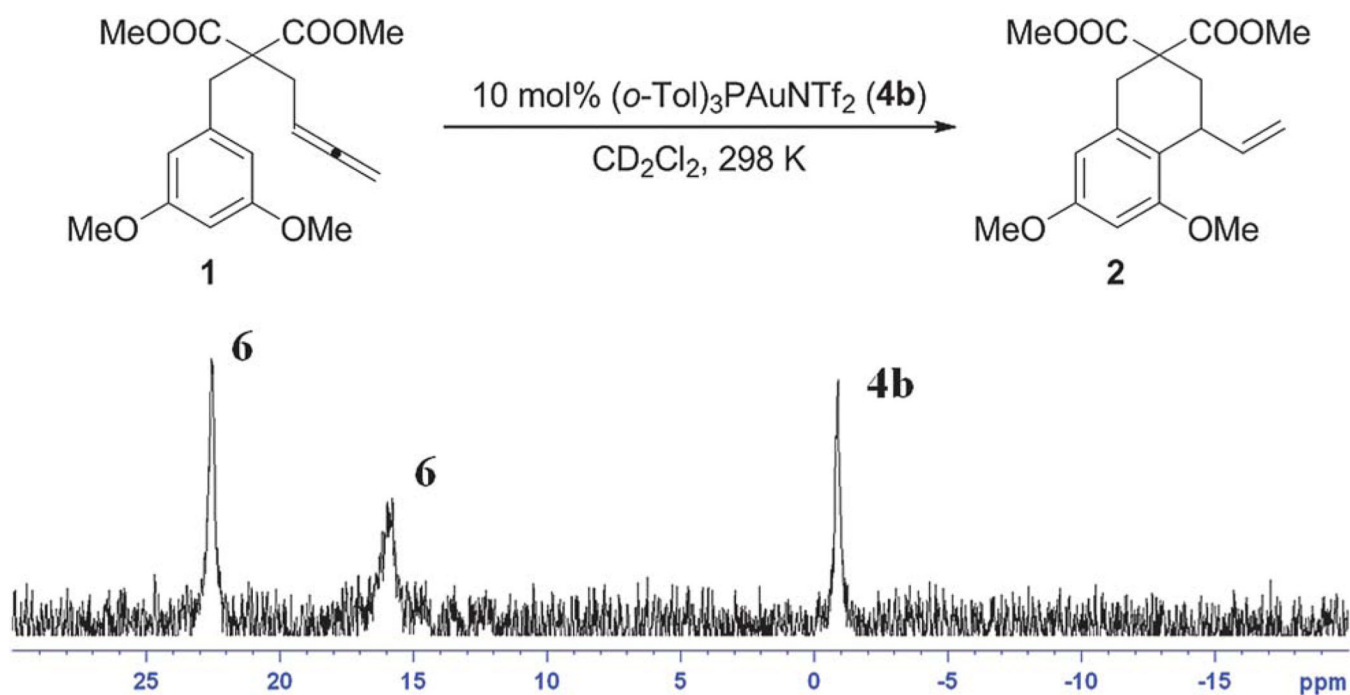


Fig. 3. ^{31}P NMR data of the catalytic reaction of **1** with 10 mol% **4b**. Two broad and asymmetrically shaped signals were detected at $\delta = 22.6$ and 16.1 ppm. The signal at $\delta = -0.7$ ppm for **4b** did not disappear as catalysis progressed.

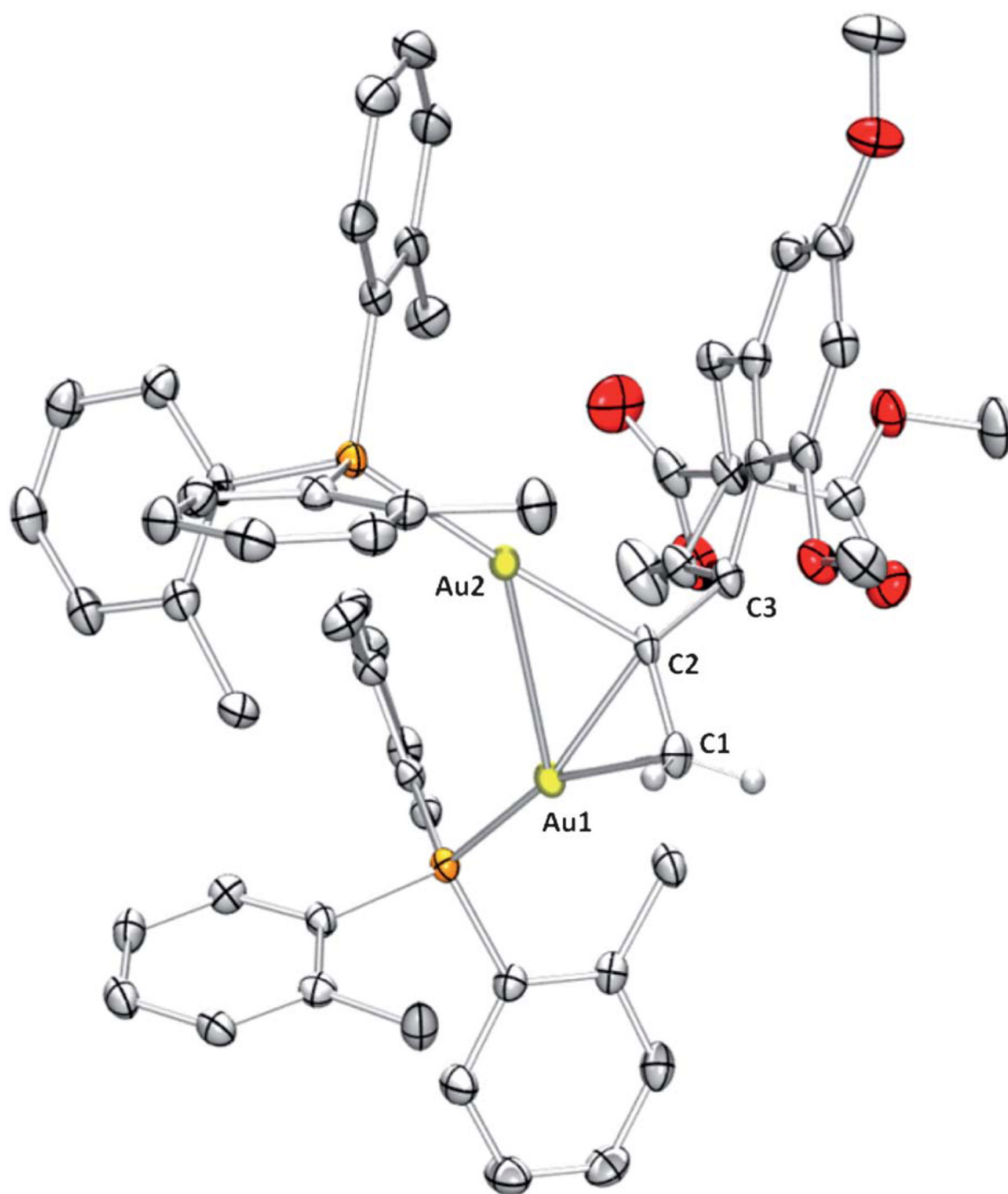
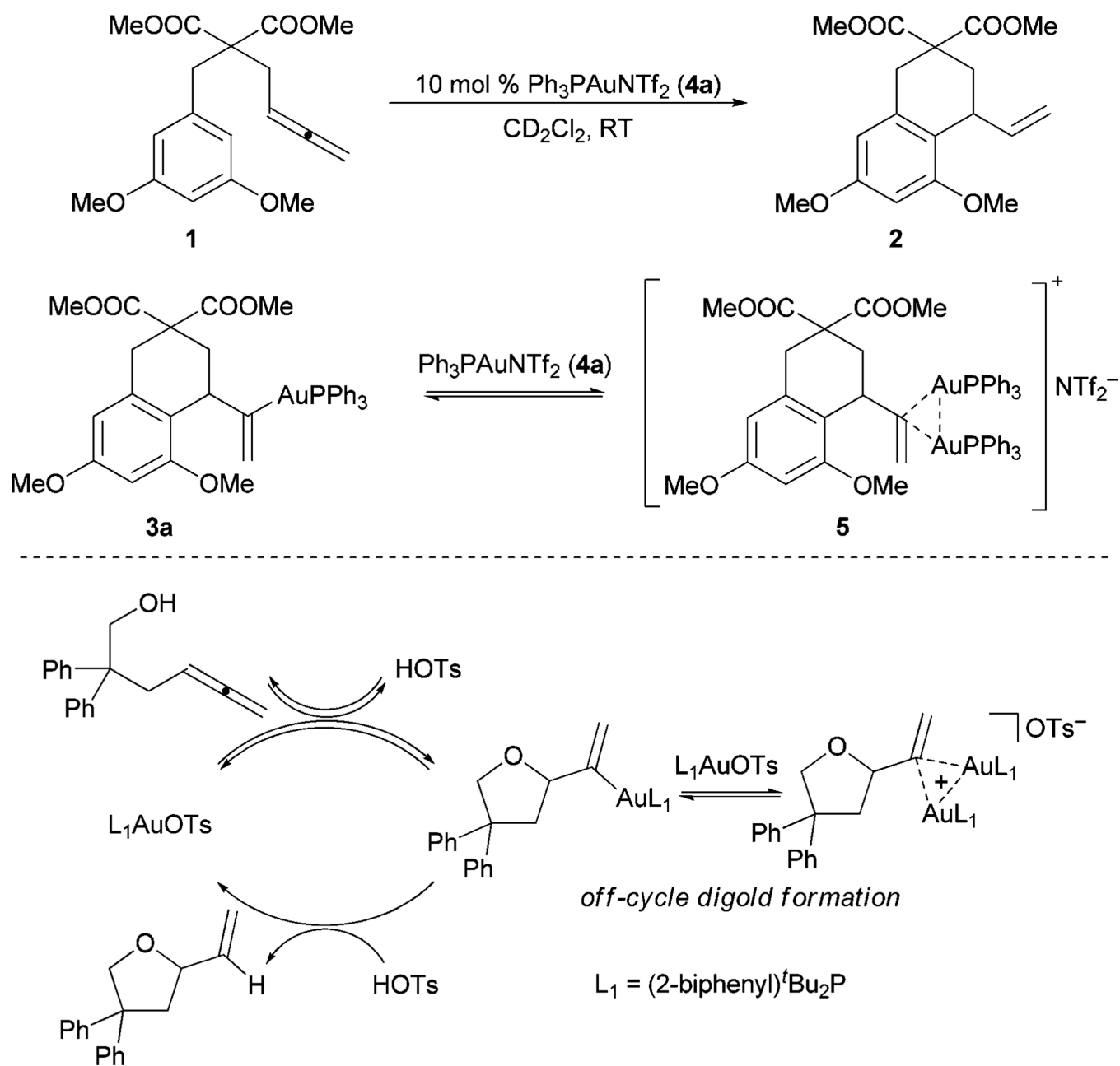


Fig. 4. ORTEP diagram of **6** with 50% probability ellipsoids; most hydrogen atoms, CH_2Cl_2 , and the NTf_2^- anion are omitted for clarity. Key bond lengths [\AA] include: Au1–Au2 [3.13563(18)], Au2–C2 [2.059(3)], Au1–C1 [2.275(3)], Au1–C2 [2.287(3)], and C1–C2 [1.369(5)].¹⁷

**Scheme 1.**

Digold resting states in the gold(i)-catalyzed intramolecular allene hydroarylation (top) and hydroalkoxylation (bottom) reactions.