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Gold Catalysis

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On the Gold-Catalyzed Generation of Vinyl Cations from 1,5-Diynes

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Abstract: Conjugated 1,5-diynes bearing two aromatic units at the alkyne termini were converted in the presence of a gold catalyst. Under mild conditions, aryl-substituted dibenzopentalenes were generated. Calculations predict that aurated vinyl cations are key intermediates of the reaction. A bidirectional approach provided selective access to the angular annulated product in high yield, which was explained by calculations.

Divide systems are gaining importance as substrates for gold-catalyzed^[1] transformations. In most of these reactions, one of the alkynes in these systems is converted into a nucleophilic alkene/allene by initial intra- or intermolecular attack onto the π -activated triple bond. Subsequently, the reaction cascades are terminated by intramolecular reactions with the second alkyne, providing access to a diverse set of interesting organic scaffolds, often with complete atom economy.^[2]

Another type of reactivity is induced by dual gold catalysis. Instead of an external nucleophile, a gold acetylide directly attacks a π -activated alkyne to give rise to highly electrophilic intermediates, which can be used for fruitful follow-up chemistry (Scheme 1, left).^[3]

We demonstrated only recently that electrophilic species can also be generated when gold acetylides are reacted in the presence of appropriate leaving groups (Scheme 1, middle).^[4] In continuation of our studies on the gold-mediated generation of high-energy intermediates, we envisioned that instead of gold acetylides, non-terminal alkynes could also be applied as nucleophiles in combination with a second π -activated alkyne (Scheme 1, right). The resulting vinyl cation intermediates could then open up a new field of chemistry as their generation does not require the presence of at least one terminal alkyne in the diyne system as in dual gold catalysis.^[5] Earlier efforts by Müller and co-workers^[6a,b] with these substrates using stoichiometric amounts of PdCl₂, PtCl₂, PtCl₄, AuCl₃, AuCl, or Na[AuCl₄] all showed low selectivity

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Scheme 1. Diynes as precursors for high-energy intermediates. Left and middle: known vinylidene precursors; right: potential vinyl cation precursor, unknown.

(even worse, for gold "catalysts", a yield of only 1% was achieved, which corresponds to 0.02 turnovers, that is, a 50fold excess of gold with regard to the product formed); the authors proposed a radical mechanism and thus subsequently also investigated photochemical conversions without metal catalyst, which delivered a different product in 3% yield.^[6c] In 1991, Blum and Vollhardt succeeded in improving Müller's conditions, achieving a yield of 80% under quite forcing conditions (120°C) in a biphasic water/dichloromethane mixture with a phase-transfer catalyst and H₂[PdCl₄] (5 mol%) after 16 h; again, no mechanistic insight was obtained.^[6d] With respect to the substrate, a similar publication by Liu and co-workers^[6e] should be mentioned; while the authors assumed that a different mechanism is operating, they speculated about a possible mechanism involving vinyl cations only in a footnote. In the light of the results reported here, this mechanism should be re-investigated.

To study this hypothesis, we considered 1,2-di(arylalkynyl)arenes as ideal test systems. Gold vinylidenes by a dualcatalyzed pathway can easily be ruled out as no gold acetylide can be formed. Symmetric substrates circumvent the formation of regioisomeric products. The diphenyl-substituted system 1a was used for our initial experiments (Table 1). Among the other ligands tested (for the full Table, see the Supporting Information, Table S1), phosphorus-based ligands only gave poor yields (entry 1). No reaction took place with a nitrogen acyclic carbene (NAC) complex (entry 2), and changing to a more flexible Tedii (1-cyclopentadecyl-3-(2,6diisopropylphenyl)-2,3-dihydro-1H-imidazol-2-ylidene) Nheterocyclic carbene (NHC) ligand only delivered a moderate yield of 63 % (entry 3). As expected, no reaction occurred in the complete absence of a catalyst (entry 4) or with a silver(I) catalyst (entry 5). For reasons of practicality, we applied the air-stable and storable nitrile-stabilized [IPrAu(NCMe)]SbF₆ catalyst,^[7] which does not require in situ activation with







[a] Reactions were run on 3.6 μ mol scale in 0.7 mL [D₆]benzene for 24 h and were afterwards directly analyzed by ¹H NMR spectroscopy. Hexamethylbenzene was used as an internal standard. [b] If silica gel (50 mg) was added, the reactions were filtered through a short pad of glass wool prior to analysis. [c] Determined by NMR spectroscopy. Yields of isolated products (36 μ mol scale) given in parentheses.



a silver salt, and gave the best yield (entry 6). The structure of the product was unambiguously assigned by X-ray singlecrystal structure analysis.^[8] A preparative reaction delivered the product in 74% yield. The product was the expected dibenzopentalene **2a** (Figure 1), and is thus structurally strongly related to the dibenzopentalene derivatives obtained from terminal alkynes by dual catalysis.^[3f] However, the



Figure 1. Solid-state molecular structures of **2a** and **2o**. Thermal ellipsoids set at 50% probability.

presence of the second aryl substituent in the vinyl cation intermediate leads to an aryl-substituted product in this case. This clearly underlines the fact that aside from gold acety-lides, non-terminal alkynes can also serve as nucleophiles in diyne cyclizations, giving rise to high-energy intermediates with potential for fruitful follow-up chemistry. The obtained dibenzopentalene scaffold has been known for over 100 years,^[9] but π -extended pentalenes, in particular, came into the focus of materials science only recently.^[10] The most

advanced strategies towards these synthetically challenging targets are based on transition-metal-catalyzed processes. Mostly, the target compounds are obtained by homocoupling reactions of ortho-alkynylaryl bromides or aryl acetylenes under Pd or Ni catalysis.[11] Unsymmetrically substituted systems can be obtained either through the use of tinsubstituted precursors^[12a] or by C-H activation strategies,^[12b] but all of these reactions require temperatures of at least 100°C, and often other, non-desirable additives have to be used. Di(arylalkynyl)arenes have also been used as precursors for dibenzopentalene systems. One strategy uses substoichiometric amounts of platinum catalysts at high temperatures (our results suggest that the dibenzopentalenes in fact slowly decompose at such elevated temperatures; for examples, see the Supporting Information, Table S1, entries 15-18),^[6] and only recently, Erker and co-workers showed that stoichiometric amounts of strongly electrophilic $B(C_6F_5)_3$ are also capable of initiating a related transformation that is intrinsically accompanied by a shift of one of the aromatic moieties at the boron center.^[13] Nevertheless, owing to the increasing demand for pentalene derivatives as new potent compounds for organic electronics, a simple method for the preparation of these compounds at room temperature and under open-flask conditions is highly desirable. To evaluate the applicability of the gold-catalyzed approach, several divne systems were synthesized and subjected to the optimized reaction conditions (Table 2).

First we varied the substituents at the aromatic system (Table 2). Electron-donating substituents in the para or meta position were tolerated well, and the corresponding products could be isolated in good to moderate yields (2b-2e). For the ortho-substituted arene 2 f, the yield dropped significantly. Electron-withdrawing substituents led to yields of around 20% (2g-2i); we assume that the decreased nucleophilicity of the aromatic moieties in these substrates slows down the formation of the desired product so that unwanted side reactions of the vinyl cation dominate; in addition, the stability of the vinyl cation is decreased by this substituent, which again accelerates side reactions. Among the applied heteroaromatic systems, a benzothiophene turned out to be a suitable substrate (2j) whereas in the case of methylthiophene, the formed product (visible by TLC) turned out to be unstable during isolation. Then we focused on variations of the aromatic backbone of the diyne system. All of the tested backbones could be converted with good efficiency regardless of whether electron-donating (2m, 2n) or electron-withdrawing substituents (20, 2p; Figure 1) were present. A substrate with a naphthyl backbone was also successfully converted, giving rise to the π -extended pentalene **2q** in acceptable yield.

A clean reaction was observed with tetrayne **3**; out of the two conceivable regioisomers, only the angular annulated **4a** was obtained in remarkable yield considering the complexity of the obtained carbon scaffold (Scheme 2). The connectivity of the obtained product was confirmed by X-ray single-crystal structure analysis (Figure 2). The reason for the selectivity is probably an unfavorable interaction in intermediate **II**; Scheme 2 also shows the two different intermediates **IIa** and **IIb**. As clearly visible from the optimized geometries, in **IIb** (which would lead to the non-observed **4b**), there is

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2

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Table 2: Substrate scope.^[a]



[a] On 20–25 μ mol scale in technical-grade benzene (c = 0.1 M) using 5 mol% of [IPrAuNCMe]SbF₆. The reactions were stopped after TLC analysis showed complete conversion (typically 0.5 to 7 h). [b] Owing to the rather poor solubility of the starting material in benzene, 1,2-dichloroethane was used instead.

a repulsion between the IPr ligand on the vinylgold intermediate and the phenyl substituent on the already formed dibenzopentalene substructure. This unfavorable interaction is probably also present in the corresponding alkyne π -complexes. To explore all factors contributing to this very useful selectivity, we are currently conducting a full-scope computational study that considers all steric and electronic parameters directing the selectivity.

In a mechanistic experiment, deuterated substrate 1r was prepared and subjected to the standard reaction conditions (Scheme 3). After the reaction, approximately 45% of 2rshowed deuterium incorporation at the vinylic position while no exchange was observed for all of the remaining aromatic hydrogen atoms. The deuterium labeling of the vinylic position strongly indicates that a gold atom was bound to that position during the reaction. The fact that only less than half of the vinylic positions were deuterated indicates an electrophilic attack of the vinyl cation at the π -system; the corresponding σ -complex then eliminates a D⁺, which partially exchanges for H⁺ with residual H₂O or the benzene in



Scheme 2. A bidirectional approach for the facile and constitutionalisomer-selective synthesis of π -extended pentalenes.



Figure 2. Solid-state molecular structure of **4a**. Thermal ellipsoids set at 50% probability.



Scheme 3. Conversion of $[D_{10}]$ -1 r into dibenzopentalene 2r.

solution. Insertion into the C–H σ -bond and subsequent 1,2-shifts would have led to complete intramolecular transfer of the deuterium without D/H exchange.

A computational study was conducted for the transformations of **1a**, **1e**, and **1i**; these substrates were chosen to

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Scheme 4. Mechanistic picture for the transformation of 1 into 2 obtained by calculations.

include the electronic parameters of the arene moiety into our considerations. We thus obtained a mechanistic picture (Scheme 4) and thermodynamic data for the intermediates (see the Supporting Information). Our mechanistic proposal^[14] starts with π -coordination of a cationic gold fragment to one of the alkyne units of 1, leading to alkyne complex I. Complex I is transformed into its valence tautomer II, the postulated vinyl cation, in an endergonic process. Our calculations predict an activation energy of 10–15 kcalmol⁻¹ for this process depending on the substitution pattern of the diyne. This rather low barrier is comparable with the barrier found for the valence isomerization processes of molecules such as bullvalenes that fluctuate at room temperature.^[15] Vinyl cation **II** is then trapped by an irreversible nucleophilic attack of the proximate anyl substituent onto the electrophilic cationic vinyl carbon atom, which generates a strongly resonance-stabilized cationic species III. As the calculated energies of both transition states are in the same range (TS I vs. TS II), we cannot unequivocally determine with the applied methods which of the two steps is turnover-limiting for the formation of 2. The calculations show that the formation, the trapping, and the stability of the vinyl cation intermediate are enhanced by an electron-donating paramethoxy substituent whereas an electron-withdrawing paratrifluoromethyl substituent has the opposite effect. These findings are qualitatively in line with our experimental finding of a dramatically increased reaction time for the formation of 2i. After the formation of III, rearomatization to the arene system and subsequent irreversible protodeauration (a process that was not explicitly included into this computational study owing to its obvious complexity) lead to IV; after ligand exchange, product 2 is released with subsequent regeneration of I.

In conclusion, we have shown that the use of non-terminal 1,5-diynes in combination with cationic gold complexes enables the generation of highly reactive vinyl cations.

These can be exploited for the synthesis of unsymmetrically substituted dibenzopentalenes, interesting targets for materials science as demonstrated by a bidirectional approach to a dibenzopentalene with extended conjugation in one step. First quantum-chemical calculations indicate a rapidly interconverting valence tautomer equilibrium between the gold alkyne complex and the vinyl cation. Further studies on the exploitation of diyne-derived vinyl cations in organic synthesis are ongoing in our laboratories.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: extended π -systems \cdot gold catalysis \cdot high-energy intermediates \cdot pentalenes \cdot vinyl cations

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On the Gold-Catalyzed Generation of Vinyl Cations from 1,5-Diynes



Positive intermediates: The combination of non-terminal 1,5-diynes with cationic gold complexes enables the generation of highly reactive vinyl cations that can be used for the synthesis of unsymmetrically

substituted dibenzopentalenes. Quantum-chemical calculations indicate a fast valence tautomer equilibrium between a gold alkyne complex and the vinyl cation.

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