ORGANOMETALLICS

Article

Cite This: Organometallics 2018, 37, 781−786

Role of σ,π-Digold(I) Alkyne Complexes in Reactions of Enynes

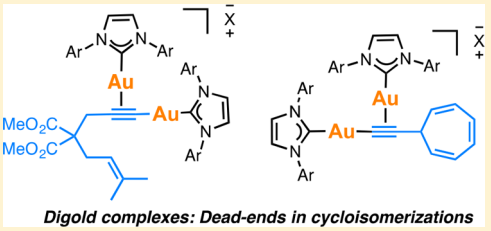
Sofia Ferrer[†] and Antonio M. Echavarren*[,†,‡]

[†]Institute of Chemical Research of Catalonia (ICIQ), Barcelona Institute of Science and Technology, Av. Països Catalans 16, 43007 Tarragona, Spain

[‡]Departament de Química Analítica i Química Orgànica, Universitat Rovira i Virgili, C/Marcel·li Domingo s/n, 43007 Tarragona, Spain

Supporting Information

ABSTRACT: Gold(I) acetylide and σ,π-digold(I) alkyne complexes derived from one prototypical 1,6-enyne and from 7-ethynyl-1,3,5-cycloheptatriene have been prepared and structurally characterized. Their possible role in gold(I)-catalyzed cycloisomerizations has been studied by experiment and by DFT calculations. Gold(I) acetylides are totally unproductive complexes in the absence of Brønsted acids. Similarly, no cyclizations were observed by heating σ,π-digold(I) alkyne digold(I) at least up to 130 °C. Theoretical studies provide a rationale for the much lower reactivity of digold species in reactions of enynes.

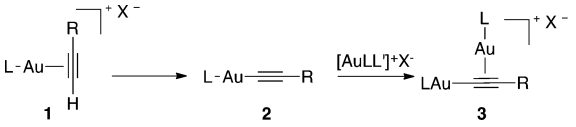


INTRODUCTION

Although digold(I) complexes have been known since the mid-1970s,[1] their relevance in homogeneous gold(I) catalysis has only been recognized recently.[2−4] They also display interesting luminescence properties and are important building elements for the design of supramolecular structures.[5] Alkenyl[6−9] and aryl[10−12] digold complexes with Au_2C three-center−two-electron bonds have been characterized.[13]

The vast majority of the gold(I)-catalyzed chemistry of alkynes under homogeneous conditions can be understood by the initial π coordination via ligand substitution to form π-alkyne gold(I) complexes **1**, which then react with carbo- or heteronucleophiles (Scheme 1).[14,15] Complexes of this type

Scheme 1. Formation of σ,π-Digold(I) Alkyne Complexes 3 from π-Gold(I) Alkyne Gold(I) Complexes 1

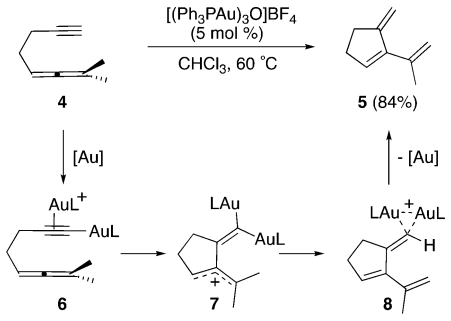


with nonterminal alkynes have been structurally characterized.[16−18] Alternatively, deprotonation of the terminal alkyne by the counterion X^- can generate σ-alkynyl gold(I) complexes **2**. Acetylides **2** react with **1** or with the initial catalyst [AuLL′]X to form finally σ,π-digold(I) alkyne digold(I) complexes **3**,[19−21] which are stable species that have been structurally characterized.[22−29] The facile formation of complexes **3** is a result of the stronger binding of gold(I) to acetylides **2** than to free alkynes.[30]

Digold complexes **3** are excellent catalysts in reactions of diynes in which one of the alkynes is a terminal one, by allowing the simultaneous formation of a nucleophilic σ-alkynyl gold(I) species and an electrophilic π-alkyne gold(I) species, which then react with each other in a dual-gold(I)-catalyzed process.[31−33]

The first example of the reaction of alkynes via σ,π-activation was proposed by Toste and Houk for the cycloisomerization of 1,5-allenynes catalyzed by $[(Ph_3PAu)_3O]BF_4$ (Scheme 2).[34]

Scheme 2. Proposed Role of *gem*-Diaurated Species in the Gold(I)-Catalyzed Cycloisomerization of 1,5-Allenynes



The experimental and computational data for the cyclization of allenynes such as **4** to form **5** suggested that σ,π-alkyne digold(I) intermediates **6** initiate a 5-*endo*-dig cyclization to form *gem*-diaurated species **7** and **8**, which give rise to **5** by protodeauration. This and related mechanisms have been recently reexamined by Fensterbank, Gandon, and Gimbert in the context of a broader study on the ligand and anion effects in the cycloisomerizations of allenynes.[35]

Although similar species have been observed in the cycloisomerization of 1,6-enynes by mass spectrometry under

Special Issue: Organometallic Chemistry in Europe

Received: September 2, 2017
Published: December 19, 2017

DOI: 10.1021/acs.organomet.7b00668
Organometallics 2018, 37, 781−786

electrospray ionization, the real involvement of digold complexes as intermediates in this reaction has been questioned.[36] Furthermore, a theoretical study on the gold(I)-catalyzed hydroamination of alkynes suggested that the nucleophilic attack takes place on π-alkyne gold(I) complexes **1**, rather than σ,π-digold(I) alkyne digold(I) complexes **3**.[37] On the other hand, digold complexes of type **3** have been proposed to be superior catalysts in several gold(I)-catalyzed transformations.[22]

We have isolated σ,π-digold(I) alkyne digold(I) complexes **3** in the intermolecular [2 + 2 + 2] cycloaddition of alkynes with oxoalkenes,[24] as well as in the synthesis of cyclobutenes by intermolecular [2 + 2] cycloaddition of alkynes with alkenes.[38] However, these isolated complexes were shown to lay outside of the main catalytic cycle. Actually, by a change in the counterion of the cationic catalyst from SbF_6^- to the softer anion BAr_4^{F-}, the formation of digold species could be minimized,[24] which had a positive effect on the overall yields of the [2 + 2] cycloaddition and other related processes.[39]

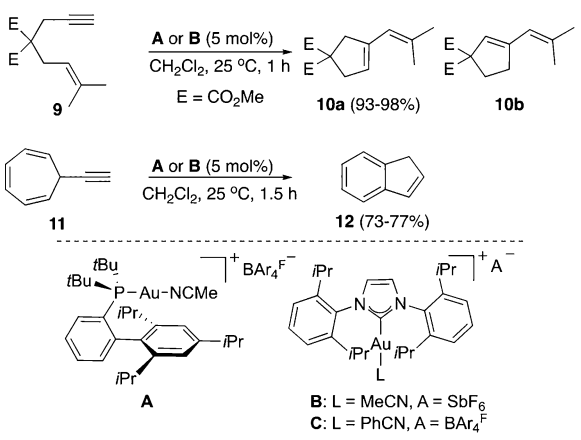
The active role displayed by σ,π-digold(I) alkyne digold(I) complexes in the gold(I)-catalyzed cycloisomerization of 1,5-allenynes (Scheme 2)[34] is in apparent contradiction with the proposal that these species are actually "dead ends" in reactions of cycloisomerizations of enynes and in the cyclobutene synthesis.[38] In order to shed light on the actual role played by σ,π-digold(I) alkyne complexes (**3**) in catalytic transformations of 1,*n*-enynes, we reinvestigated several gold(I)-catalyzed cycloisomerization reactions by isolating the corresponding gold(I) acetylides and digold complexes.

RESULTS AND DISCUSSION

Mechanistic studies of gold(I)-catalyzed cycloisomerizations of 1,*n*-enynes have been the benchmark for the understanding of the fundamental reactivity of alkynes and alkenes,[40−42] which have recently been extended to intermolecular systems.[39c] The gold(I)-catalyzed reaction of 1,6-enyne **9** at room temperature leads cleanly to diene **10a** by a single cleavage rearrangement using complex **A** or **B** (Scheme 3).[40] At longer reaction times, or using complex **C** as catalyst, mixtures of **10a** and **10b**, the products of double-bond isomerization, were obtained. We also examined the reaction of 7-ethynyl-1,3,5-cycloheptatriene (**11**), which reacts cleanly with **A** or **B** to give indene (**12**).[43]

Gold(I) acetylide **13** was easily prepared by deprotonation of 1,6-enyne with *n*-BuLi at −50 °C followed by reaction with IPrAuCl (Figure 1). Further reaction of **13** with **B** or **C** led to σ,π-digold(I) alkyne complexes **14a,b**. Complexes **15**−**17** and **18a,b** were similarly prepared from 7-ethynyl-1,3,5-cycloheptatriene (**11**). We also synthesized gold acetylide complex **19** from 3-methoxy-7-methylocta-5,6-dien-1-yne and IPrAuCl, although the corresponding digold complex could not be obtained in pure form by reaction with **B** or **C**.

Scheme 3. Cycloisomerizations of 1,6-Enyne 9 and 7-Ethynyl-1,3,5-cycloheptatriene 11



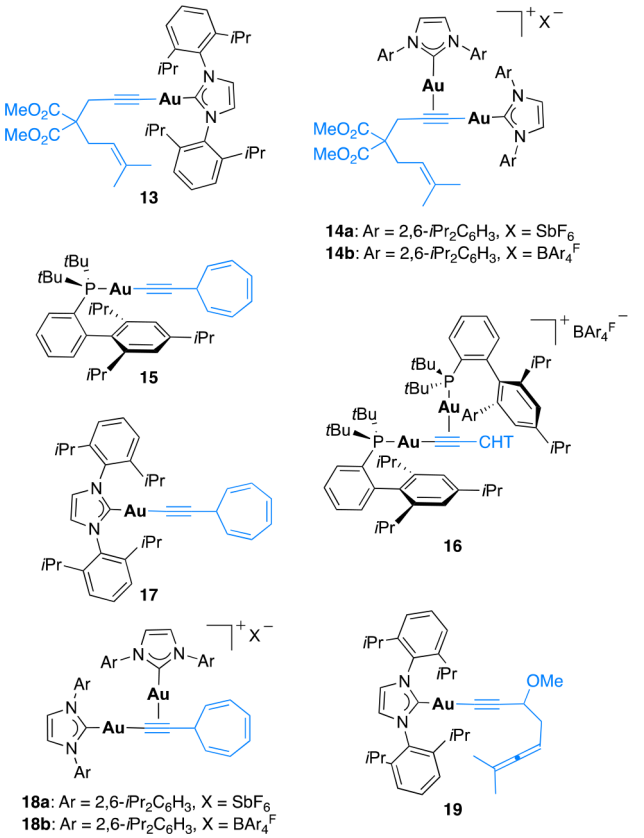


Figure 1. Acetylide gold(I) and σ,π-digold(I) alkyne complexes **13**−**19** (CHT = cycloheptatriene).

The structures of **13**, **14a,b**, **15**−**17**, and **18a,b** were confirmed by X-ray diffraction. The structures of the two representative complexes **15** and **16** are shown in Figure 2. For the gold(I) acetylide complexes **13**, **15**, and **17**, the C_1−Au and C≡C bond distances are 1.98−2.01 and 1.18−1.21 Å, respectively. In the case of σ,π-digold(I) alkyne complexes (**14a,b**, **16**, and **18a,b**) the C_1−Au (1.98−2.03 Å) and C≡C bond distances (1.21−1.23 Å) are similar. As expected, the second π-coordinated gold atom is symmetrically bonded to the alkyne: 2.25/2.20 Å for **14a**, 2.21/2.23 Å for **14b**, 2.22/2.25 Å for **16**, 2.20/2.20 Å for **18a**, and 2.21/2.20 Å for **18b**.

Mononuclear species **13**, **15**, and **17** were heated under refluxing conditions in $CDCl_3$. Gold(I) acetylide **13** remained unchanged, whereas **15** and **17** showed partial decomposition, although indene (**12**) could not be detected after 2 h. These results definitively confirm that gold(I) acetylides are not intermediates in these cycloisomerizations.

Digold complexes **14a,b**, **16**, and **18a,b** were heated from 25 to 130 °C in $CDCl_2CDCl_2$,[44a] and any reaction progress was monitored by ^1H, ^{31}P, and ^{19}F NMR. Complexes **14a** and **18a** with SbF_6^- as the counterion remained unchanged up to 130 °C. Complexes **14b**, **16**, and **18b** bearing the weakly coordinating counterion BAr_4^{F-} were stable up to 100 °C. At

DOI: 10.1021/acs.organomet.7b00668
Organometallics 2018, 37, 781−786

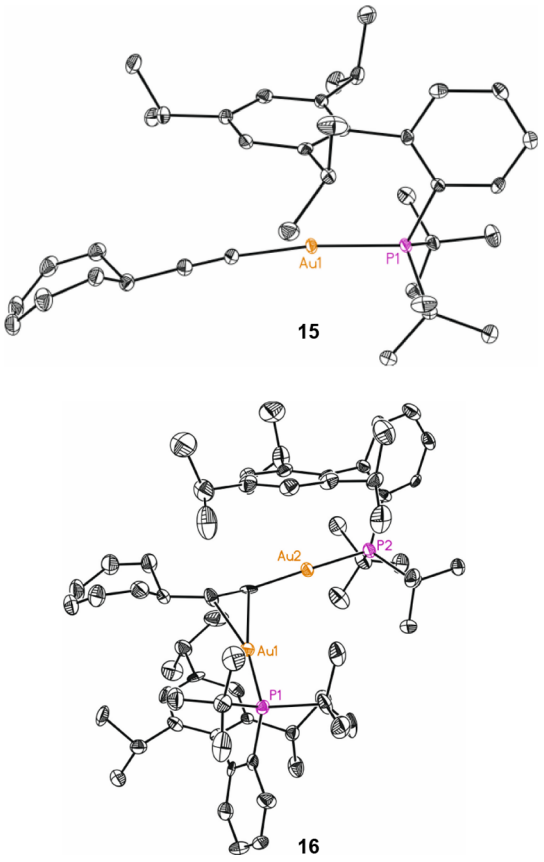


Figure 2. ORTEP plots (50% thermal ellipsoids) for gold(I) acetylide **15** and σ,π-alkyne digold(I) Complex **16**. The SbF_6^- anion of **16** is omitted for clarity.

this temperature, a slow conversion of the digold species into new gold complexes together with cyclization products were observed. In the case of **14b** at 130 °C, a mixture of the starting complex and two new gold species were formed in a 1:1.2:1.5 ratio, together with cyclization product **10a**, which was obtained in 58% yield (^{1}H NMR yield, using mesitylene as internal standard). From the reaction mixture, we obtained a crystalline compound, whose structure was determined by X-ray diffraction analysis as the symmetrical gold(I) complex **20** (Figure 3).[45]

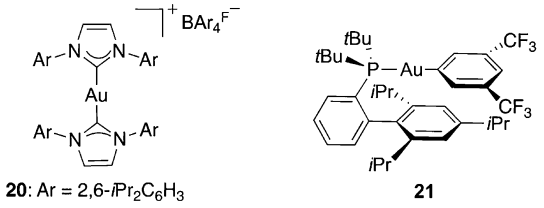


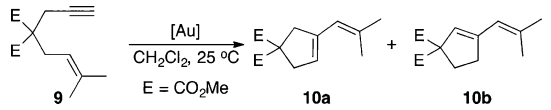
Figure 3. Complexes **20** and **21**.

In the case of **16**, a 1:8 ratio between starting digold complex and a new gold species was observed at 130 °C, together with indene (**12**), which was formed in 40% NMR yield. The major product was determined by X-ray diffraction to be complex **21**, arising by transmetalation from the tetrakis[3,5-bis-(trifluoromethyl)phenyl]borate (BAr_4^{F-}) counterion to the gold cation. In fact, gold(I) is known to be able to heterolytically cleave the C−B bond of BAr_4^F, leading to the aryl transfer from boron to gold.[46]

The presence of cyclization products **10a** and **12** in the thermolysis of **14b** and **16** suggests two possible pathways. One is the aryl transfer from the BAr_4^{F-} to σ-coordinated gold to form LAuAr complexes together with alkynyl borates, which undergo cyclization promoted by the second, π-coordinated gold center. Hydrolysis of the C−B bonds could take place at the enynes or the final products by reaction with water present in the solvent. The other involves first a protodeauration of the σ-coordinated gold with the water present in the solvent, leading to the corresponding alkyne species and subsequent aryl transfer from the BAr_4^{F-} to this gold to form LAuAr complexes. The alkynes could then undergo cyclization promoted by the second π-coordinated gold center. Similar results were obtained when digold complexes **14b** and **16** were heated in $CDCl_3$[44b] under refluxing conditions for 1 h.

We also studied the catalytic activity of the isolated gold(I) acetylide and digold complexes in the cyclizations of substrates **9** and **11** (Tables 1 and 2). Gold(I) acetylide **13** was not

Table 1. Cycloisomerization of 1,6-Enyne 9 with Complexes 13a,b and 14a,b

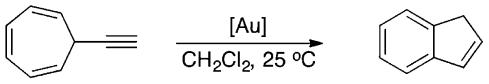


entry	[Au] (amt (mol %))	additive (amt (mol %))	time (h)	**10a**:**10b** yield (%)[a]
1	**13** (5)		24	
2	**13** (5)	$HSbF_6{\cdot}6H_2O$ (5)	8	21:34
3	**14a** (2.5)		1	11:0[b]
4	**14a** (2.5)		2	15:0[b]
5	**14a** (2.5)		24	79:0
6	**14a** (5)	$HSbF_6{\cdot}6H_2O$ (5)	8	23:33
7	**14b** (3)		24	51:0
8	**14b** (5)	$HSbF_6{\cdot}6H_2O$ (5)	8	21:34

[a]Yields determined by ^{1}H NMR using mesitylene as internal standard. [b]An 84−87% of enyne **1** was recovered.

catalytically active (Table 1, entry 1), although addition of $HSbF_6{\cdot}6H_2O$, which cleaves the Au−C bond, generates a catalytically active cationic gold(I) species (Table 1, entry 2).[3b,24] On the other hand, digold complexes **14a**, were

Table 2. Cycloisomerization of Cycloheptatriene 11 with Complexes 17 and 18a,b



entry	[Au] (amt (mol %))	Aadditive (amt (mol %))	time (h)	**12** yield (%)[a]
1	**17** (5)		24	
2	**17** (5)	$HSbF_6{\cdot}6H_2O$ (5)	8	61
3	**18a** (2)		24	40
4	**18a** (3)		24	46
5	**18a** (5)	$HSbF_6{\cdot}6H_2O$ (5)	8	50
6	**18b** (2)		24	37
7	**18b** (5)	$HSbF_6{\cdot}6H_2O$ (5)	8	48

[a]Yields determined by ^{1}H NMR using mesitylene as internal standard.

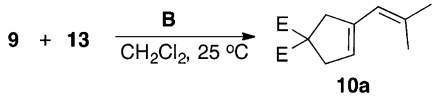
DOI: 10.1021/acs.organomet.7b00668
Organometallics 2018, 37, 781−786

moderately active in the cycloisomerization of **9**. However, even under the best conditions (Table 1, entry 5), the reaction required 24 h to furnish **10a** in 79% yield, while catalyst **A** or **B** provided **10a** in higher yields (93−98%) after just 1 h.

Very similar results were obtained in the reaction of **11** to give indene (**12**) (Table 2). Again, gold(I) acetylide **17** was catalytically inactive (Table 2, entry 1), whereas in the presence of a strong Brønsted acid (Table 2, entry 2) or using digold complexes **18a,b** (Table 2, entries 3−7), indene (**12**) was obtained. Nevertheless, all of these reactions are slower than those catalyzed by **A** or **B** (1.5 h, 25 °C, Scheme 3).

We also performed experiments by first mixing 1,6-enyne **9** with 3 mol % of gold acetylide **13** in CD_2Cl_2, followed by addition of 3 mol % of catalyst **B** (Table 3). After 15 min, only

Table 3. Competition Studies between 1,6-Enyne 9 and Gold Acetylide 13



entry	amt of **B** (mol %)	time	**10a** yield (%)[a]
1	3	15 min	trace
2	3	20 h	45[b]
3	6	15 min	95

[a]Yields determined by ^{1}H NMR using mesitylene as internal standard. [b]A 51% yield of enyne **9** was recovered.

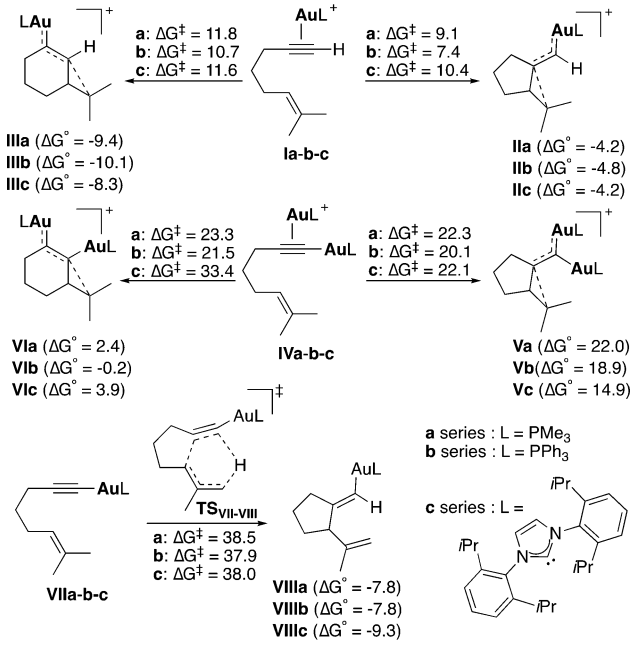
traces of product **10a** together with digold complex **18a** were formed (Table 3, entry 1), suggesting a higher affinity of the gold(I) for the gold acetylide species, in accordance with the precedents.[30,36] After 20 h (Table 3, entry 2) product **10a** was formed in 45% yield. At this stage, addition of an extra 3 mol % of catalyst **B** led to a very fast conversion, affording **10a** in 95% yield (Table 3, entry 3). In the case of ethynylcycloheptatriene (**11**), after addition of 3 mol % of gold acetylide **17** and 3 mol % of catalyst **B**, **12** was obtained in 78% yield, along with digold complex **18a**, which suggests that the ligand exchange between the catalyst **B** and **11** is faster than that between catalyst **B** and gold acetylide **17**.

Computational Results. DFT calculations (M06, 6-31G(d) (C, H, P, N) and SDD (Au), CH_2Cl_2) were performed in order to compare the energy barriers for the previous gold(I)-catalyzed cycloisomerizations.[47] In all cases, the calculations were performed with three different ligands: L_1 = trimethylphosphine, L_2 = triphenylphosphine, and L_3 = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.

The gold(I)-catalyzed cycloisomerization of 1,6-enynes can proceed by two pathways, leading to five- or six-membered rings.[14,40,41] The 5-*exo*-dig cyclization of **Ia−c** leads to intermediates **IIa−c**, whereas **IIIa−c** are formed in a 6-*endo*-dig process that is less favorable kinetically (Scheme 4). In most cases slightly higher energy barriers were observed for the cyclization with the more electron donating carbene ligand L_3, which reduces the electrophilicity of AuL^+.

The cyclization in digold complexes **IVa−c** has a considerably higher energy barrier (5-*exo*-dig, L_1 22.3 kcal/mol, L_2 20.1 kcal/mol, L_3 22.1 kcal/mol; 6-*endo*-dig, L_1 23.3 kcal/mol, L_2 21.5 kcal/mol, L_3 33.4 kcal/mol), leading to *gem*-diaurated species **Va−c** and **VIa−c** in thermodynamically unfavorable reactions. These results are consistent with the experimental data and clearly show that digold species are

Scheme 4. Cycloisomerizations of Monogold (Ia−c) and Digold 1,6-Enyne (IVa−c) Complexes[a,b]



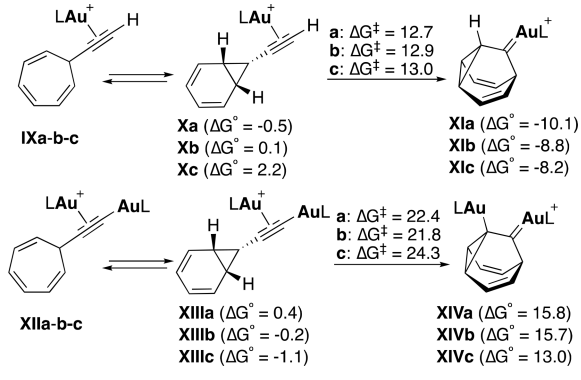
[a]Free energies in kcal/mol. [b]The energy of $TS_{IVc\text{-}VIc}$ was calculated by freezing the following distance: *d*(C8−C55).[48]

incompetent in the cycloisomerization process. Gold acetylides **VIIa−c** can only evolve by an ene reaction, via 1,5-hydrogen transfer trough $TS_{VII\text{-}VIII}$, leading to **VIIIa−c** (Scheme 4). Nevertheless, this transformation shows prohibitively high energy barriers (ca. 38 kcal/mol).

Calculations also show higher energy barriers for the reaction of digold complexes **XIIa−c** in comparison with the reaction of monogold species **IXa−c** (Scheme 5). These reactions actually proceed by cycloisomerization of the norcaradiene complexes **Xa−c**, which are in tautomeric equilibrium with the cycloheptatrienes.

The same reactivity pattern is reproduced in the reaction of 1,5-allenynes (Scheme 6).[34,35] Thus, much higher barriers were found in the first step of the reaction through digold complexes **XVIIIa−c** in comparison to that initiated by the cyclization of **XVa−c** to **XVIa−c**. However, in this case, the second step actually makes the digold pathway more favorable, in

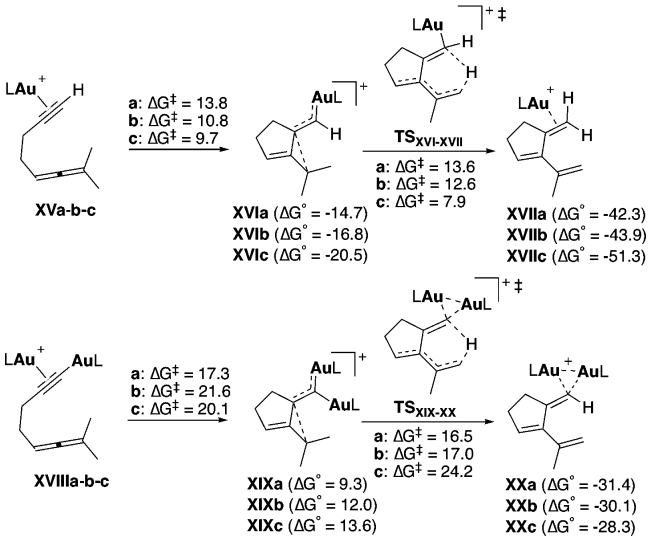
Scheme 5. Cycloisomerizations of Monogold (IXa−c) and Digold Cycloheptatriene (XIIa−c) Complexes[a]



[a]Free energies in kcal/mol.

DOI: 10.1021/acs.organomet.7b00668
Organometallics 2018, 37, 781−786

Scheme 6. Cycloisomerizations of Monogold (XVa−c) and Digold 1,5-Allenyne (XVIIIa−c) Complexes[a,b]



[a]Free energies in kcal/mol. [b]The energy of $TS_{XVIIIc-XIXc}$ was calculated by freezing the following distances: *d*(C1−C79) and *d*(C1−C80).[49]

agreement with a previous theoretical study employing PH_3 as ligand.[34] Thus, the second step for the monogold pathway (**XVIa−c** to **XVIIa−c**) has much higher barriers (28−29 kcal/mol) in comparison to that of the digold pathway (**XIXa−c** to **XXa−c**), which only requires from around 5 to 10 kcal/mol. In this case aurophilic interactions are observed that could lower the energy of the transition states. Therefore, since both **XVa−c** and **XVIIIa−c** would be in equilibrium, the system will evolve almost exclusively through digold species **XIXa−c** and **XXa−c**. Products **XXa−c** possess strong aurophilic interactions and thus displace the reaction toward the products.

CONCLUSIONS

We have prepared gold(I) acetylides and *σ,π*-digold(I) alkyne digold(I) complexes from substrates that undergo isomerization reactions under mild conditions in the presence of gold(I) catalysts. Gold(I) acetylides are unproductive complexes in cycloisomerization reactions, unless a strong Brønsted acid is added to cleave the Au−C bond leading to a cationic gold(I) complex. Well-characterized digold(I) complexes are very robust and fail to cyclize on heating in solution up to 100−130 °C. These results confirm that these digold(I) species are not catalytic intermediates; rather, these complexes are "dead ends" in catalytic reactions of enynes, in full agreement with previous studies.[36,38] Only in the case of cationic digold(I) complexes with BAr_4^{F-} as the counterion were cyclization products observed by heating at 100 °C, although the observed reactivity is due to the decomposition of the complexes by transmetalation with the tetraarylborate that results in the transfer of one of the aryls from boron to gold.

Theoretical studies fully support the experimentally observed inertness of *σ,π*-digold(I) alkyne complexes in intramolecular reactions with alkenes. *σ*-Coordination by a second gold(I) raises the energy of the C−C bond formation by ca. 10−20 kcal/mol in the nucleophilic attack of the alkene to the *π*-activated alkyne. Finally, *σ,π*-digold(I) alkyne complexes were shown to be only moderate catalysts in intramolecular reactions of enynes, being less efficient than cationic complexes bearing nitriles as weakly coordinating ligands.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00668.

All procedures, characterization data for new compounds, and full details on the theoretical calculations (PDF)

Cartesian coordinates for the calculated structures (XYZ)

Accession Codes

CCDC 1572064−1572073 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*aechavarren@iciq.es.

ORCID

Antonio M. Echavarren: 0000-0001-6808-3007

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We thank the European Research Council (Advanced Grant No. 321066), Agencia Estatal de Investigación (AEI)/FEDER, UE (CTQ2016-75960-P), AEI-Severo Ochoa Excellence Accreditation 2014−2018 (SEV-2013-0319), the AGAUR (2014 SGR 818), and CERCA Program/Generalitat de Catalunya for financial support. We thank the ICIQ X-ray diffraction unit. We also thank Yahui Wang for preliminary experiments on the synthesis of **17** and **18** and M. Elena de Orbe for helpful discussions.

REFERENCES

(1) (a) Nesmeyanov, A. N.; Perevalova, E. G.; Grandberg, K. I.; Lemenovskii, D. A.; Baukova, T. V.; Afanassova, O. B. *J. Organomet. Chem.* **1974**, *65*, 131−144. (b) Porter, K. A.; Schier, A.; Schmidbaur, H. *Organometallics* **2003**, *22*, 4922−4927.

(2) Braun, I.; Asiri, A. M.; Hashmi, A. S. K. *ACS Catal.* **2013**, *3*, 1902−1907.

(3) Gómez-Suárez, A.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2012**, *51*, 8156−8159.

(4) (a) Seidel, G.; Lehmann, C. W.; Fürstner, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 8466−8470. (b) Hooper, T. N.; Green, M.; Russell, C. A. *Chem. Commun.* **2010**, *46*, 2313−2315. (c) Brown, T. J.; Widenhoefer, R. A. *Organometallics* **2011**, *30*, 6003−6009. (d) Brown, T. J.; Widenhoefer, R. A. *J. Organomet. Chem.* **2011**, *696*, 1216−1220.

(5) Lima, J. C.; Rodriguez, L. *Chem. Soc. Rev.* **2011**, *40*, 5442−556.

(6) (a) Weber, D.; Gagné, M. R. *Org. Lett.* **2009**, *11*, 4962−4965. (b) Weber, D.; Tarselli, M. A.; Gagné, M. R. *Angew. Chem., Int. Ed.* **2009**, *48*, 5733−5736. (c) Brown, T. J.; Weber, D.; Gagné, M. R.; Widenhoefer, R. A. *J. Am. Chem. Soc.* **2012**, *134*, 9134−9137. (d) Weber, D.; Gagné, M. R. *Chem. Sci.* **2013**, *4*, 335−338.

(7) Seidel, G.; Lehmann, C. W.; Fürstner, A. *Angew. Chem., Int. Ed.* **2010**, *49*, 8466−8470.

(8) (a) Hashmi, A. S. K.; Braun, I.; Nösel, P.; Schädlich, J.; Wieteck, M.; Rudolph, M.; Rominger, F. *Angew. Chem., Int. Ed.* **2012**, *51*, 4456−

4460. (b) Hashmi, A. S. K.; Wieteck, M.; Braun, I.; Nösel, P.; Jongbloed, L.; Rudolph, M.; Rominger, F. *Adv. Synth. Catal.* **2012**, *354*, 555−562. (c) Nösel, P.; Lauterbach, T.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Chem. - Eur. J.* **2013**, *19*, 8634−8641.
(9) (a) Zhdanko, A.; Maier, M. E. *Chem. - Eur. J.* **2013**, *19*, 3932−3942. (b) Zhdanko, A.; Maier, M. E. *Chem. - Eur. J.* **2014**, *20*, 1918−1930.
(10) Weber, D.; Jones, T. D.; Adduci, L. L.; Gagné, M. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 2452−2456.
(11) Chen, Y.; Chen, M.; Liu, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 6181−6186.
(12) Heckler, J. E.; Zeller, M.; Hunter, A. D.; Gray, T. G. *Angew. Chem., Int. Ed.* **2012**, *51*, 5924−5928.
(13) Gómez-Suárez, A.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2012**, *51*, 8156−8159.
(14) Echavarren, A. M.; Muratore, M. N.; López-Carrillo, V.; Escribano-Cuesta, A.; Huguet, A.; Obradors, C. *Org. React.* **2017**, *92*, 1−288.
(15) (a) Jiménez-Núñez, E.; Echavarren, A. M. *Chem. Rev.* **2008**, *108*, 3326−3350. (b) Obradors, C.; Echavarren, A. M. *Acc. Chem. Res.* **2014**, *47*, 902−912. (c) Dorel, R.; Echavarren, A. M. *Chem. Rev.* **2015**, *115*, 9028−9072.
(16) Shapiro, N.; Toste, F. *Proc. Natl. Acad. Sci. U. S. A.* **2008**, *105*, 2779−2782.
(17) Brown, T. J.; Widenhoefer, R. A. *J. Organomet. Chem.* **2011**, *696*, 1216−1220.
(18) (a) Das, A.; Dash, C.; Yousufuddin, M.; Celik, M. A.; Frenking, G.; Dias, H. V. R. *Angew. Chem., Int. Ed.* **2012**, *51*, 3940−3943. (b) Das, A.; Dash, C.; Celik, M. A.; Yousufuddin, M.; Frenking, G.; Dias, H. V. R. *Organometallics* **2013**, *32*, 3135−3144.
(19) Brooner, R. E. M.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 11714−11724.
(20) Halliday, C. J. V.; Lynam, J. M. *Dalton Trans.* **2016**, *45*, 12611−12626.
(21) Ranieri, B.; Escofet, I.; Echavarren, A. M. *Org. Biomol. Chem.* **2015**, *13*, 7103−7118.
(22) (a) Grirrane, A.; García, H.; Corma, A.; Álvarez, E. *ACS Catal.* **2011**, *1*, 1647−1653. (b) Grirrane, A.; García, H.; Corma, A.; Álvarez, E. *Chem. - Eur. J.* **2013**, *19*, 12239−12244. (c) Grirrane, A.; Álvarez, E.; García, H.; Corma, A. *Chem. - Eur. J.* **2017**, *23*, 2792−2801.
(23) Brown, T. J.; Widenhoefer, R. A. *Organometallics* **2011**, *30*, 6003−6009.
(24) Obradors, C.; Echavarren, A. M. *Chem. - Eur. J.* **2013**, *19*, 3547−3551.
(25) Gómez-Suárez, A.; Dupuy, S.; Slawin, A. M. Z.; Nolan, S. P. *Angew. Chem., Int. Ed.* **2013**, *52*, 938−942.
(26) Ciano, L.; Fey, N.; Halliday, C.; Lynam, J. M.; Milner, a.; Nimesh Mistry, L. M.; Pridmore, N. E.; Townsend, N. S.; Whitwood, N. C. *Chem. Commun.* **2015**, *51*, 9702−9705.
(27) Espada, J. M. F.; Campos, J.; López-Serrano, J.; Poveda, M. L.; Carmona, E. *Angew. Chem., Int. Ed.* **2015**, *54*, 15379−15384.
(28) Jašíková, L.; Roithová, J. *Organometallics* **2013**, *32*, 7025−7033.
(29) See also: Halter, O.; Plenio, H. *Chem. Commun.* **2017**, *53*, 12461.
(30) Jašíková, L.; Roithová, J. *Organometallics* **2013**, *32*, 7025−7033.
(31) Review: Asiri, A. M.; Hashmi, A. S. K. *Chem. Soc. Rev.* **2016**, *45*, 4471−4503.
(32) Leading references: (a) Ye, L.; Wang, Y.; Aue, D. H.; Zhang, L. *J. Am. Chem. Soc.* **2012**, *134*, 31−34. (b) Hashmi, A. S. K.; Braun, I.; Rudolph, M.; Rominger, F. *Organometallics* **2012**, *31*, 644−661. (c) Hashmi, A. S. K.; Lauterbach, T.; Nösel, P.; Vilhelmsen, M. H.; Rudolph, M.; Rominger, F. *Chem. - Eur. J.* **2013**, *19*, 1058−1065. (d) Hashmi, A. S. K.; Wieteck, M.; Braun, I.; Nösel, P.; Jongbloed, L.; Rudolph, M.; Rominger, M. *Adv. Synth. Catal.* **2012**, *354*, 555−562. (e) Hansmann, M. M.; Rudolph, M.; Rominger, F.; Hashmi, A. S. K. *Angew. Chem., Int. Ed.* **2013**, *52*, 2593−2598. (f) Wang, Y.; Yepremyan, A.; Ghorai, S.; Todd, R.; Aue, D. H.; Zhang, L. *Angew. Chem., Int. Ed.* **2013**, *52*, 7795−7799. (g) Larsen, M. H.; Houk, K. N.; Hashmi, A. S. K. *J. Am. Chem. Soc.* **2015**, *137*, 10668−10676.
(33) Odabachian, Y.; Le Goff, X. F.; Gagosz, F. *Chem. - Eur. J.* **2009**, *15*, 8966−8970.
(34) Cheong, P. H.-Y.; Morganelli, P.; Luzung, M. R.; Houk, K. N.; Toste, F. D. *J. Am. Chem. Soc.* **2008**, *130*, 4517−4526.
(35) Jaroschik, F.; Simonneau, A.; Lemière, G.; Cariou, K.; Agenet, N.; Amouri, H.; Aubert, C.; Goddard, J.-P.; Lesage, D.; Malacria, M.; Gimbert, Y.; Gandon, V.; Fensterbank, L. *ACS Catal.* **2016**, *6*, 5146−5160.
(36) Simonneau, A.; Jaroschik, F.; Lesage, D.; Karanik, M.; Guillot, R.; Malacria, M.; Tabet, J.-C.; Goddard, J.-P.; Fensterbank, L.; Gandon, V.; Gimbert, Y. *Chem. Sci.* **2011**, *2*, 2417−2422.
(37) Mazzone, G.; Russo, N.; Sicilia, E. *J. Chem. Theory Comput.* **2015**, *11*, 581−590.
(38) Homs, A.; Obradors, C.; Leboeuf, D.; Echavarren, A. M. *Adv. Synth. Catal.* **2014**, *356*, 221−228.
(39) (a) Ranieri, B.; Obradors, C.; Mato, M.; Echavarren, A. M. *Org. Lett.* **2016**, *18*, 1614−1617. (b) de Orbe, E.; Echavarren, A. M. *Org. Synth.* **2016**, *93*, 115−126. (c) de Orbe, M. E.; Amenós, L.; Kirillova, M. S.; Wang, Y.; López-Carrillo, V.; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2017**, *139*, 10302−10311.
(40) (a) Nieto-Oberhuber, C.; Muñoz, M. P.; Buñuel, E.; Nevado, C.; Cárdenas, D. J.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2402−2406. (b) Nieto-Oberhuber, C.; López, S.; Muñoz, M. P.; Cárdenas, D. J.; Nevado, C.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2005**, *44*, 6146−6148.
(41) Escribano-Cuesta, A.; Pérez-Galán, P.; Herrero-Gómez, E.; Sekine, M.; Braga, A. A. C.; Maseras, F.; Echavarren, A. M. *Org. Biomol. Chem.* **2012**, *10*, 6105−6111.
(42) (a) Brooner, R. E. M.; Brown, T. J.; Widenhoefer, R. A. *Angew. Chem., Int. Ed.* **2013**, *52*, 6259−6261. (b) Brooner, R. E. M.; Robertson, B. D.; Widenhoefer, R. A. *Organometallics* **2014**, *33*, 6466−6473. (c) Harris, R. J.; Widenhoefer, R. A. *Chem. Soc. Rev.* **2016**, *45*, 4533−4551. (d) Kim, N.; Brooner, R.; Widenhoefer, R. A. *Organometallics* **2017**, *36*, 673−678.
(43) McGonigal, P.; de León, C.; Wang, Y.; Homs, A.; Solorio-Alvarado, C. R.; Echavarren, A. M. *Angew. Chem., Int. Ed.* **2012**, *51*, 13093−13096.
(44) (a) $CDCl_2CDCl_2$ contains ca. 5% of water, which corresponds to ca. 2 equiv of water with respect to the substrates. (b) $CDCl_3$ contains 5−5.5% of water.
(45) Collado, A.; Bohnenberger, J.; Oliva-Madrid, M.-J.; Nun, P.; Cordes, D. B.; Slawin, A. M. Z.; Nolan, S. P. *Eur. J. Inorg. Chem.* **2016**, *2016*, 4111−4122.
(46) (a) Weber, S. G.; Zahner, D.; Rominger, F.; Straub, B. F. *Chem. Commun.* **2012**, *48*, 11325−11327. (b) Lenker, H. K.; Gray, T. G.; Stockland, R. A., Jr. *Dalton Trans.* **2012**, *41*, 13274−13276.
(47) Additional calculations using B3LYP are included in the Supporting Information.
(48) The value of this distance was taken from the optimized geometry using a simplified ligand (Me instead of *i*Pr) and B3LYP as the functional.
(49) The values of these distances were taken from the optimized geometry using a simplified ligand (Me instead of *i*Pr) and B3LYP as the functional.

DOI: 10.1021/acs.organomet.7b00668
Organometallics 2018, 37, 781−786