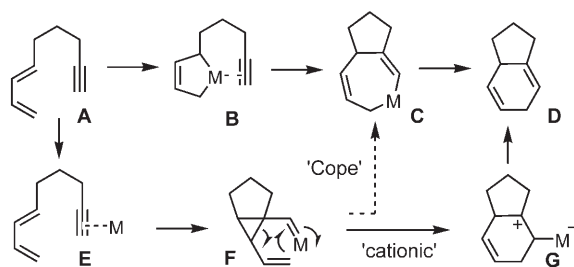


Cycloadditions

Two Manifolds for Metal-Catalyzed Intramolecular Diels–Alder Reactions of Unactivated Alkynes**

Alois Fürstner* and Christopher C. Stimson

The poor reactivity of unactivated alkynes as dienophiles has for a long time limited their use in Diels–Alder reactions.^[1] Only after the discovery of the remarkable catalytic effect of various transition-metal complexes could the synthetic potential of this transformation be exploited.^[2–4] Such cycloadditions of dienynes **A** are assumed to proceed via metallacyclic intermediates of type **B** and **C**, which are formed by oxidative cyclization, and subsequent insertion of the alkyne (Scheme 1).^[3] We speculated, however, that entirely different scenarios might also result in a net [4+2] cycloaddition, and present herein preliminary data to support this view.



Scheme 1. Different scenarios for metal-catalyzed Diels–Alder reactions of dienynes. Top: conventional pathway based on oxidative cyclization; bottom: novel electrophilic activation manifold.

Activation of the triple bond of **A** followed by attack of the diene's proximal alkene moiety should generate an electrophilic metal carbene **F** with a pendant vinyl group on its cyclopropyl ring.^[5] This species might undergo a "metalla-Cope" rearrangement with formation of **C** and proceed from there on; alternatively, one may envisage formation of cation **G** that releases cycloadduct **D** and regenerates the catalyst. The excellent performance of cationic gold complexes as carbophilic Lewis acids^[5] prompted us to probe this concept by exposing various dienynes to [(Ph₃P)Au]SbF₆ generated

in situ (Table 1). Whereas the parent compounds **1** decomposed (Table 1, entry 1), substrates with a nonterminal alkyne were converted into the corresponding 1,4-cyclohexadiene

Table 1: Gold-catalyzed cycloadditions;^[a] E = COOEt.

Entry	Substrate	Product	Yield
1			— ^[b] (X = CE ₂ , NTs, O)
2			75 % (X = CE ₂)
3			91 % (X = NTs)
4			40 % (X = C(SO ₂ Ph) ₂)
5			82 % ^[c]
6			81 % ^[c]
7			70 % (R = SnBu ₃)
8			63 % (R = CH ₂ OAc)

[a] [(Ph₃P)AuCl] (5 mol %), AgSbF₆ (5 mol %), CH₂Cl₂, RT. [b] Decomposition. [c] The product is partly aromatized in air (ca. 10%). Ts = toluene-4-sulfonyl.

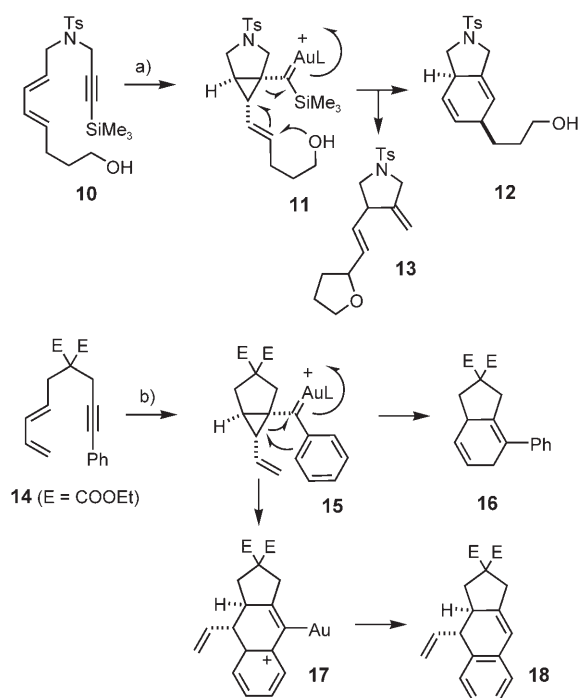
products in respectable yields. As silyl end groups on the alkyne are lost upon work-up,^[6] access to the unfunctionalized cycloadducts is secured (Table 1, entries 2–6).

The proposed mechanism, which proceeds via an intermediate of type **F**, is consistent with the results shown in Scheme 2. Thus, compound **10** furnished cycloadduct **12** (68 %) and tetrahydrofuran **13** (15 %), which derives from the putative electrophilic carbene **11** by reaction with the tethered alcohol; such vinylogous alkoxy cyclizations have ample precedence in gold and platinum catalysis.^[7] Even more instructive is the conversion of substrate **14** into **16** and **18**, both of which again likely originate from the same intermediate **15**. Whereas evolution of this species along the pathway depicted in Scheme 1 affords cycloadduct **16**, competing attack of the phenyl ring onto the electrophilic carbene provides the companion product **18**. The latter course corroborates the view that gold cyclopropyl "carbenes"

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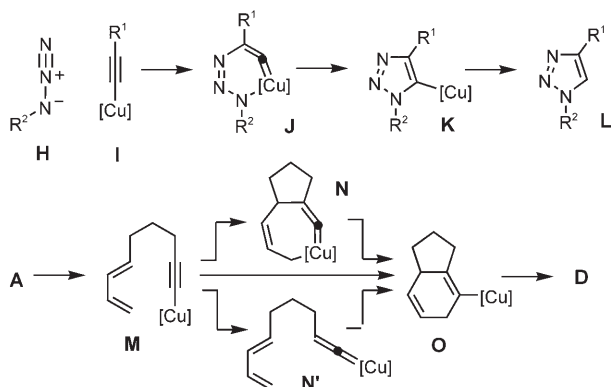
Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.



Scheme 2. a) [(Ph₃P)AuCl] (5 mol %), AgSbF₆ (5 mol %), CH₂Cl₂, **12** (68 %), **13** (15 %); b) [(Ph₃P)AuCl] (5 mol %), AgSbF₆ (5 mol %), CH₂Cl₂, 78 % (**16/18** ca. 3:4).

resemble “nonclassical cations” in behavior.^[5,8] Since similar compounds have previously been observed in enyne cycloisomerizations known to proceed via metal cyclopropyl carbenoids,^[9] the isolation of **18** provides strong evidence for the proposed “electrophilic” pathway.

We envisaged that yet another, entirely different, scenario might also allow unactivated alkynes to take part in Diels–Alder reactions. In analogy to the copper-catalyzed ligation of azides and terminal alkynes, which is thought to proceed from acetylide **I**, via the cyclic vinylidene **J**, to the vinylcopper species **K**,^[10] a similar pathway for dienynes can be conceived (Scheme 3). In fact, compound **1a** reacts with catalytic amounts of CuX in the presence of Et₃N in CH₂Cl₂ to give



Scheme 3. Tentative mechanism of copper-catalyzed azide cycloadditions^[10] and the envisaged Diels–Alder manifold involving analogous copper acetylide (–vinylidene) and –vinyl intermediates.

cycloadduct **2a** in high yield (Table 2). It is noteworthy that even one equivalent of CuI in the absence of the base did not lead to any significant rate acceleration over the thermal

Table 2: Optimization of the copper-catalyzed Diels–Alder reaction.

Entry	CuX	Base	T [°C]	t [h]	Yield [%]
1	–	Et ₃ N	70	18	25
2	CuI (100 %)	–	70	18	30
3	CuSO ₄ (10 %)	[a]	20	18	trace
4	CuCl (10 %)	Et ₃ N	20	6	75
5	CuI (10 %)	Et ₃ N	20	6	92
6	CuTC (10 %) ^[b]	–	20	6	95

[a] Sodium ascorbate. [b] CuTC = copper thiophene-2-carboxylate.

background reaction (Table 2, compare entries 1 and 2). This observation suggests that a copper acetylide must be generated for the cycloaddition to proceed. In line with this, copper thiophene-2-carboxylate^[11] was found to be an active catalyst since this particular salt can simultaneously act as a Cu^I source and as a base (Table 2, entry 6).

The intervention of a copper acetylide **M** is also consistent with the observation that only terminal alkynes participate in such cycloadditions, whereas end-capped substrates are recovered unchanged (Table 3, entries 4 and 5). This inherent limitation notwithstanding, the scope of the reaction is broad: it encompasses different tethers and tolerates various functional groups including free hydroxy groups, silyl ethers, esters, sulfonamides, sulfones, and even alkyl halides (Table 3). Moreover, substrates with 1,4-disubstituted dienes give the corresponding *cis*-configured bicycles with excellent selectivity (Table 3, entries 7–9, see below).

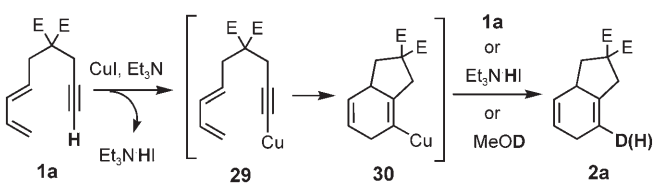
The same reaction conditions also allowed a series of formal hetero-Diels–Alder reactions^[12] to be performed under equally mild conditions (Table 3, entries 10–15).^[13] Therefore, this novel protocol constitutes an alternative to the ruthenium-based methodology previously used to prepare annelated [3,4-*c*]pyrans of this type.^[14] The mildness of the new method greatly contributes to the success, because such cyclic bis-enol ethers are highly sensitive and must be handled with great care under acid-free, non-oxidative conditions.

Although these results seem to imply copper acetylides as reactive intermediates, further evidence for the proposed mechanism was sought. To this end, substrate **1a** was treated with CuI/Et₃N (1 equiv) in rigorously dried MeOD (Scheme 4). The fact that the resulting product had incorporated a deuterium label (**[D]-2a**) is consistent with a vinylcopper species **30** intervening. However, non-negligible amounts of **H-2a** were also produced (**[D]-2a/H-2a** ca. 4:1), despite considerable efforts to exclude all traces of adventitious water. This result indicates that the generated ammonium salt Et₃N·HI reenters the scene and likely plays a pivotal role in closing the catalytic cycle if the reaction is performed

Table 3: Copper-catalyzed Diels–Alder and hetero-Diels–Alder reactions of unactivated dienyynes;^[a] E = COOEt.

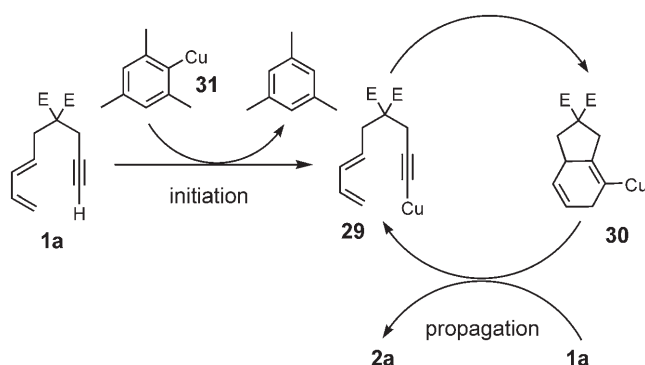
Entry	Substrate	Product	Yield ^[b]
1			92 % (X = CE ₂)
2			95 % (X = NTs)
3			76 % (X = C(SO ₂ Ph) ₂)
4			0 % (R = Me)
5			0 % (R = SiMe ₃)
6			80 %
7			95 % (X = OH)
8			69 % (X = OTBS)
9			92 % (X = I)
10			83 % (R = H)
11			70 % (R = Me)
12			67 % (R = Ph)
13			100 % ^[c]
14			100 % (R = H) ^[c]
15			100 % (R = Ph) ^[c]

[a] All reactions were performed with CuI (10 mol %) and Et₃N (1 equiv) in CH₂Cl₂ at RT. [b] Yields of isolated product. [c] GC yield, see text for more details. TBS = *tert*-butyldimethylsilyl.



Scheme 4. Deuteration experiment which indicates that a vinylcopper intermediate may react with different proton sources to close the catalytic cycle; 90 % ([D]-**2a**/H-**2a** ca. 4:1).

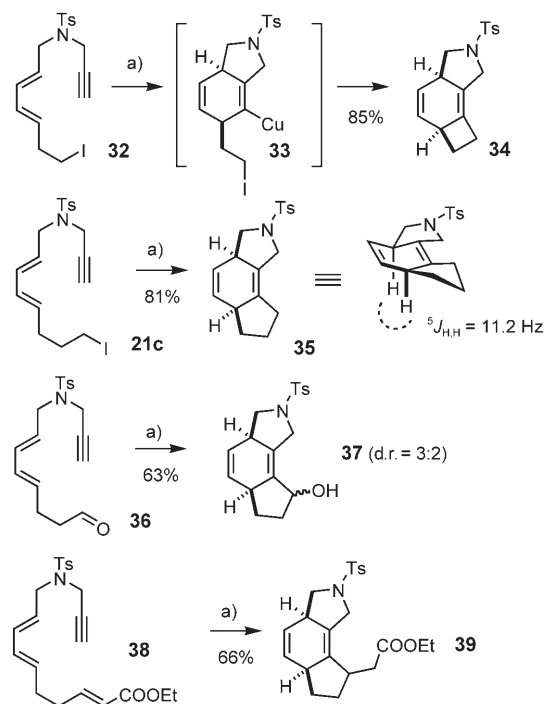
in aprotic media. Alternatively, one may envisage that the substrate itself serves as a proton source, as its terminal alkyne should be acidic enough to react with **30**, release the product, and thereby regenerate the catalytically competent intermediate **29**. To probe this possibility, **1a** was treated with mesitylcopper (**31**)—one of the few thermally robust organo-copper species that can be readily isolated in pure form (Scheme 5).^[15] In this case, formation of the copper acetylide generates mesitylene which cannot react with any organo-copper intermediate later in the catalytic cycle. In fact, **31** turned out to be exceptionally active, thus allowing the



Scheme 5. Proposed catalytic cycle upon the use of mesitylcopper (**31**).

cycloaddition to be performed at -78°C . Since catalytic amounts of **31** suffice to reach complete conversion, a proton transfer from the substrate's terminal alkyne to the putative vinylcopper intermediate must occur, which allows the overall reaction to be separated into an “initiation” and a “propagation” phase.

This analysis suggests that it might be possible to outperform this rapid proton transfer with other electrophiles. In fact, a series of intramolecular trapping experiments gave excellent results and led to tricyclic products by an unprecedented copper-mediated [4+2] cycloaddition/alkylation cascade (Scheme 6). Primary iodides, an aldehyde, as well as an enoate were found to be suitable as electrophilic partners.^[16] The products were obtained with excellent levels of stereo-selectivity, with the lateral rings being invariably fused in a 1,4-*cis* manner to the core, as evident from pertinent NMR



Scheme 6. Copper-mediated Diels–Alder/alkylation cascade; a) mesitylcopper (**31**, 1 equiv), THF, $-78^{\circ}\text{C} \rightarrow \text{RT}$.

data and from the structure of **35** in the solid state (Figure 1).^[17–19] These trapping experiments provide compelling evidence for the intervention of a vinylcopper species of

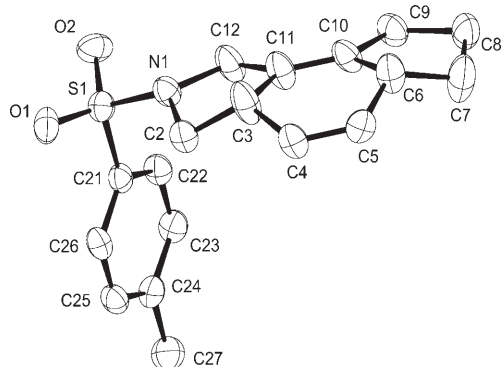


Figure 1. One of the two independent molecules of **35** in the solid state. Anisotropic displacement parameters are drawn at the 50% probability level.

type **O** (Scheme 3), and hence exclude metallacycles of type **B** that are usually invoked in [4+2] cycloadditions catalyzed by low-valent-metal complexes.^[3] Although we concede that the mechanism of this novel copper-catalyzed Diels–Alder protocol deserves further study in the laboratory and in silico, in particular to clarify if the conversion of **M** into **O** proceeds directly or involves vinylidenes of type **N** or **N'**, all the available data imply that a reaction mechanism beyond that of conventional schemes is operative.

Experimental Section

Representative procedure (Table 3, entry 2): NEt_3 (70 μL , 0.51 mmol) was added to a solution of **1b** ($\text{X} = \text{NTs}$) (140 mg, 51 μmol)^[20] and CuI (9.7 mg, 0.51 mmol) in CH_2Cl_2 (2 mL) to give a cloudy yellow solution. After stirring the reaction mixture for 16 h, it was concentrated, and the residue purified by flash chromatography (hexanes/ EtOAc , 85:15) to give **2b** as a white solid (133 mg, 95%). M.p. 110–112 °C; ^1H NMR (400 MHz, CDCl_3): δ = 7.68 (d, J = 8.3 Hz, 2H), 7.28 (d, J = 8.3 Hz, 2H), 5.74 (dddd, J = 10.0, 3.5, 2.7, 1.2 Hz, 1H), 5.63 (ddq, J = 10.0, 2.1, < 1 Hz, 1H), 5.52 (m, 1H), 3.98 (ddt, J = 13.2, 2.6, 1.7 Hz, 1H), 3.80 (ddd, J = 8.8, 8.0, < 1 Hz, 1H), 3.69 (dq, J = 13.2, 1.6 Hz, 1H), 2.94 (m, 1H), 2.63 (dd, J = 11.4, 8.8 Hz, 1H), 2.59 (m, 2H), 2.39 ppm (s, 3H); ^{13}C NMR (100 MHz, CDCl_3): δ = 143.4, 134.8, 133.7, 129.6, 127.5, 126.7, 123.1, 117.1, 52.8, 50.7, 37.8, 26.6, 21.5 ppm; for the full data set, see the Supporting Information.

Copper-catalyzed Diels–Alder/alkylation cascade: A solution of substrate **21c** ($\text{X} = \text{I}$, 30 mg, 68 μmol) in THF (1 mL) was added to a solution of copper mesitylene (15 mg, 82 μmol) in THF (1 mL) at –78 °C. The resulting mixture was warmed to room temperature and stirred for 16 h to give a cloudy dark brown solution. Water (0.5 mL) was added and the mixture diluted with Et_2O (20 mL). The organic layer was washed with water (2 $\times$ 10 mL), dried (MgSO_4), and evaporated to dryness, before purifying the residue by flash chromatography (hexanes/ EtOAc , 4:1) to give **35** as a clear oil which solidified upon standing (17 mg, 81%). ^1H NMR (400 MHz, CDCl_3): δ = 7.70 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 5.84 (dt, J = 9.6, 2.3 Hz, 1H), 5.61 (ddd, J = 9.6, 2.8, 1.9 Hz, 1H), 3.92 (dddt, J = 13.8, 3.6, 2.2, 1.8 Hz, 1H), 3.85 (dd, J = 9.0, 8.2 Hz, 1H), 3.62 (ddm, J = 13.8, 1.8 Hz, 1H), 3.03 (dddt, 1H, J = 11.2, 8.0, 3.0, 1.6 Hz), 2.69 (m,

1H), 2.53 (dd, J = 11.2, 9.0 Hz, 1H), 2.40 (s, 3H), 2.17 (dddd, J = 16.6, 10.0, 2.6, 2.4 Hz), 2.08 (dddm, J = 16.4, 9.2, 8.8 Hz, 1H), 2.01 (dtm, J = 11.8, 6.9 Hz, 1H), 1.76 (dddd, J = 12.7, 8.8, 7.1, 2.8, 1.5 Hz, 1H), 1.64 (dddd, J = 12.9, 11.7, 10.0, 9.2, 6.6 Hz, 1H), 1.03 ppm (dq, J = 12.0, 7.4 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ = 143.4, 135.3, 133.9, 130.5, 129.7, 127.4, 124.7, 124.1, 52.6, 49.0, 42.0, 39.6, 32.2, 27.4, 24.0, 21.5 ppm; for the full data set, see the Supporting Information.

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