CHEMISTRY
A EUROPEAN JOURNAL

DOI: 10.1002/chem.201102852

Cascade Pericyclic Reactions of Alleno-Acetylenes: Facile Access to Highly Substituted Cyclobutene, Dendralene, Pentalene, and Indene Skeletons

Corinna M. Reisinger, Pablo Rivera-Fuentes, Samuel Lampart, W. Bernd Schweizer, and François Diederich*[a]

Cascade reactions are valuable tools for building complex molecular architectures with high efficiency, selectivity, and atom economy. These processes have a proven record in the preparation of natural products and biologically relevant molecules.[1] In a similar manner, cascade transformations would greatly benefit the field of advanced materials science, where they offer opportunities for rapid and divergent synthetic elaboration, thereby expanding the chemical space for functional materials.

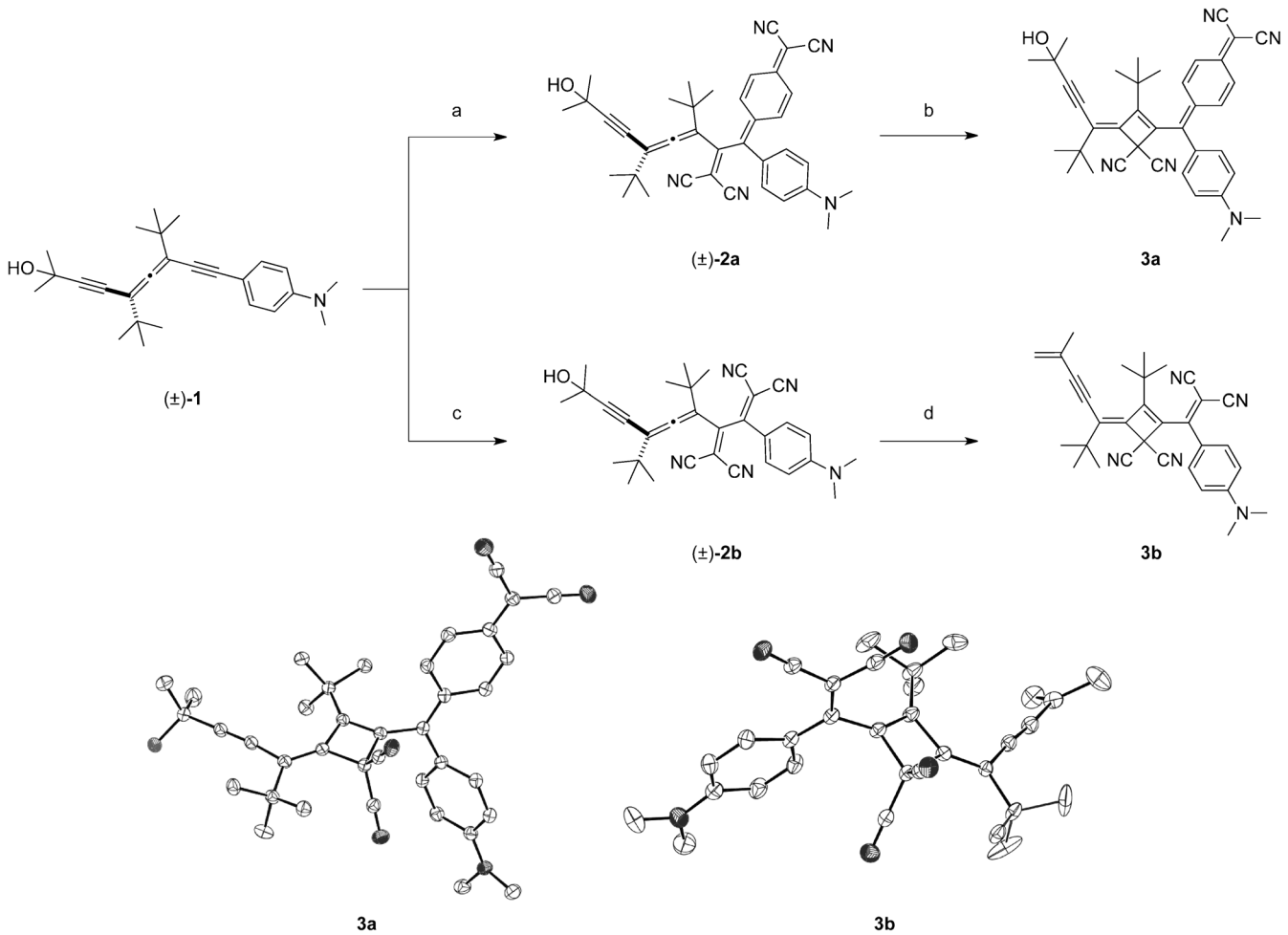
Allenes are particularly interesting candidates for the development of cascade reactions, given the diversity and specificity of their reaction modes.[2] Our interest in alleno-acetylenic scaffolding prompted us to introduce allenes as building blocks in the construction of three-dimensional chiral carbon-rich structures. To be able to prepare stable alleno-acetylenic chromophores, the 1,3-di-*tert*-butyl-1,3-diethynylallene (DEA) moiety was developed.[3] The introduction of *tert*-butyl substituents provides steric hindrance to the allene core, reducing its reactivity considerably. Taking advantage of the kinetic stability of these alleno-acetylenic scaffolds, we were able to resolve their enantiomers,[4] and use them to build enantiopure chiral push–pull chromophores,[4,5] macrocycles,[6] and helical foldamers.[7] Here, we explore the potential of the allene core of DEAs to participate in cascade pericyclic reactions, which lead to highly substituted complex carbon skeletons in a one-pot fashion, with excellent chemo-, regio-, and stereoselectivities.[8]

We first investigated the reaction between racemic DEA (±)-**1** and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ) and 1,1,2,2-tetracyanoethene (TCNE), to give butadienes (±)-**2a** and (±)-**2b**, respectively, by a formal [2+2] cycloaddition, followed by cycloreversion (CA/CR).[9] While the reaction with TCNE proceeded cleanly at room temperature,[4] we noticed that when the reaction with TCNQ was carried out at 40 °C, a significant amount of a by-product was formed. Isolation and characterization of this compound showed that adduct (±)-**2a** undergoes a 4π electrocyclization (EC) between the allene core and the proximal dicyanovinyl moiety, to give cyclobutene **3a** (Scheme 1). In a similar way, butadiene (±)-**2b** could be transformed into cyclobutene **3b**, in which water was eliminated from the acetonide protecting group. The molecular structures of cyclobutenes **3a** and **3b** were unambiguously assigned by X-ray diffraction studies (Scheme 1; for details, see the Supporting Information).[10] The triple CA/CR/EC cascade also produced dicyanocyclobutenes **18** and **19** (see Scheme SI1 in the Supporting Information) in high yield (82–87%) with the acetonide protecting group replaced by an iPr$_3$Si substituent. We found that addition of 10 equivalents of trifluoroacetic acid (TFA) accelerates the reaction and increases the yields significantly. It can be inferred that TFA protonates the aniline nitrogen, quenching the intramolecular charge-transfer interaction, and in turn making the dicyanoolefin more electron-deficient, and hence more reactive.[2a] Concomitantly, protonation may also lead to a conformational change that favors the electrocyclization. The TCNQ- and TCNE-derived dicyanocyclobutenes feature interesting opto-electronic properties that are currently further exploited. Thus, the intense intramolecular charge-transfer (CT) band of **3a** appears at 649 nm ($\varepsilon = 30400\ M^{-1}cm^{-1}$), whereas the corresponding band of **3b** has $\lambda_{max} = 471$ nm ($\varepsilon = 39300\ M^{-1}cm^{-1}$). The CA/CR steps display identical chemo- and regioselectivity as reported before.[9b] Additionally, the 4π EC reaction is stereoselective, giving a single isomer (*E*) of the exocyclic double bond of the formed cyclobutene. Theoretical calculations (see the Supporting Information) showed that the energy of the (*Z*)-configured product is 5.5 kcal mol^{-1} higher than that of the (*E*)-configured isomer, thus revealing that the latter is thermodynamically favored.

In an attempt to prepare DEA (±)-**5a**, bearing a 1,1-dimethylhomoallyl appendage, by Pd-catalyzed S_N2'-reaction of bispropargylic ester (±)-**4** (for preparation, see the Supporting Information) with acetylenic nucleophiles,[4] another cascade transformation was discovered (Scheme 2A). Significant amounts of a by-product were detected from the very first runs, which after isolation and characterization was identified as the buta-1,3-diene **6a**. Heating pure (±)-**5a** in 1,2-dichloroethane induced the clean formation of buta-1,3-diene **6a** in high yield and as a single double-bond (*E*) isomer (NOE correlations). This experiment demonstrates that compound **6a** arises from the in situ thermal rearrangement of allene (±)-**5a**. The transformation of allene (±)-**5a**

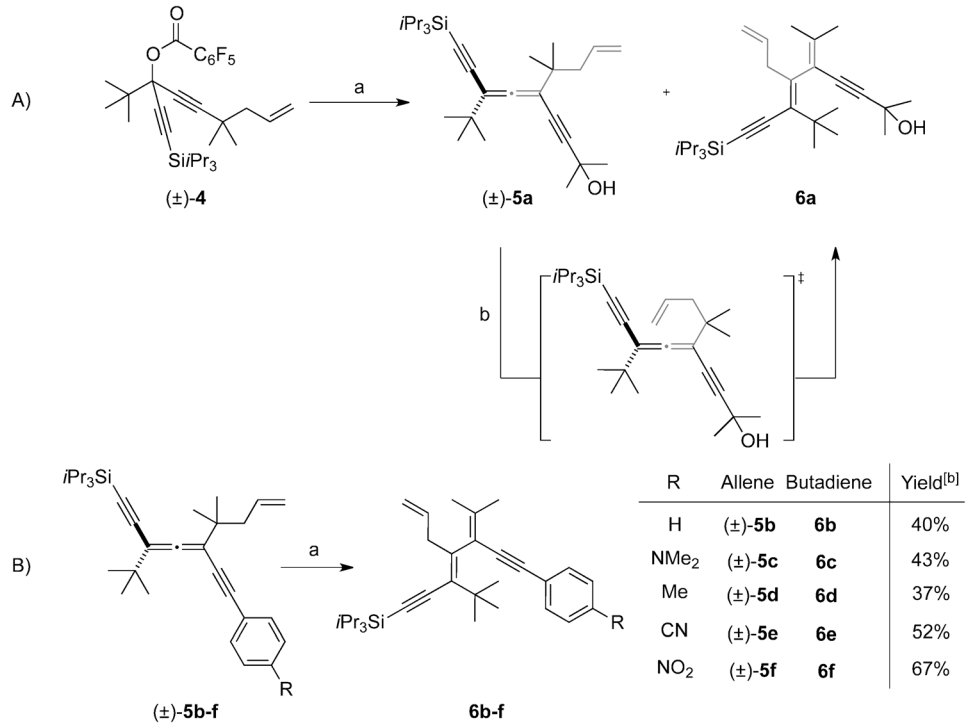
[a] Dr. C. M. Reisinger, P. Rivera-Fuentes, S. Lampart, Dr. W. B. Schweizer, Prof. F. Diederich
Laboratorium für Organische Chemie, ETH Zürich
Hönggerberg, HCI, CH-8093 Zurich (Switzerland)
Fax: (+41) 44-632-1109
E-mail: diederich@org.chem.ethz.ch

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201102852.



Scheme 1. CA/CR/4π EC cascade reaction: Formation of butadienes (±)-**2** and cyclobutenes **3**, and X-ray crystal structures of **3a** and **3b**. Hydrogen atoms and minor occupied positions of disordered atoms (**3b**) omitted for clarity; atomic displacement parameters obtained at 100 K are drawn at 50% probability level (for details see the Supporting Information).[10] Reaction conditions: a) TCNQ (1 equiv), CH_2Cl_2, 25°C, 4 h, 98%; b) TFA (10 equiv), $(CH_2Cl)_2$, 60°C, 1 h, 55%; c) TCNE (1 equiv), CH_2Cl_2, 25°C, 1 h, 91%; d) TFA (10 equiv), $(CH_2Cl)_2$, 60°C, 4 h, 60%.

to buta-1,3-diene (*E*)-**6a** amounts to an allenyl-Cope [3,3]-sigmatropic rearrangement. Intrigued by the remarkable ease of the allenyl-Cope rearrangement of DEA (±)-**5a**, compared to prior known examples,[11] we eagerly probed modified substrates (±)-**5b–f** bearing different *para*-substituted phenyl rings (Scheme 2B) and their propensity to give buta-1,3-dienes **6b–f**. The allenyl-Cope rearrangement was found to be substantially accelerated in the case of electron-withdrawing substituents (*p*-CN and in particular *p*-NO_2, see Table in Scheme 2), and conversions after a reaction time of 1 h were considerably higher than those of the parent phenyl-substituted derivative (**6b** (*p*-H): 40%; **6f** (*p*-NO_2): 67%). This allenyl-Cope rearrangement of DEAs allows facile access to highly substituted, sterically congested buta-1,3-diene systems in a stereoselective manner.[12] Theoretical calculations predict rotational barriers about their central C–C single bond in the range of 20 kcal mol^{-1} (see the Supporting Information). With the aid of the calculations, we further rationalized that the observed (*E*)-stereoselectivity most likely results from steric control by the *tert*-butyl substituent in the transition state of the [3,3]-sigmatropic rearrangement (cf. Scheme 2A; for details, see the Supporting Information). The observation that electron-withdrawing substituents considerably facilitate the allenyl-Cope rearrangement led us to introduce the more potent electron-accepting 1,1,4,4-tetracyanobuta-1,3-diene (TCBD) moiety by the CA/CR reaction. Exposure of *N*,*N*-dimethylanilino (DMA)-substituted DEA (±)-**5c** to TCNE led to the formation of the TCBD derivative (±)-**7**, which was readily converted to the rearranged product, [4]dendralene **8**, within one hour upon heating to reflux in 1,2-dichloroethane. Remarkably, cyclobutene formation via competing 4π EC (cf. Scheme 1) of the TCBD-substituted allene intermediate (±)-**7** could not be detected over the course of the reaction, underlining its excellent selectivity. Gratifyingly, the CA/CR/allenyl-Cope reaction one-pot cascade also took place smoothly at room temperature over a period of 40 h. Monitoring the reaction by NMR spectroscopy revealed the very rapid formation of the TCBD-substituted allene (±)-**7** and its subsequent, slower skeletal reorganization by the [3,3]-al-



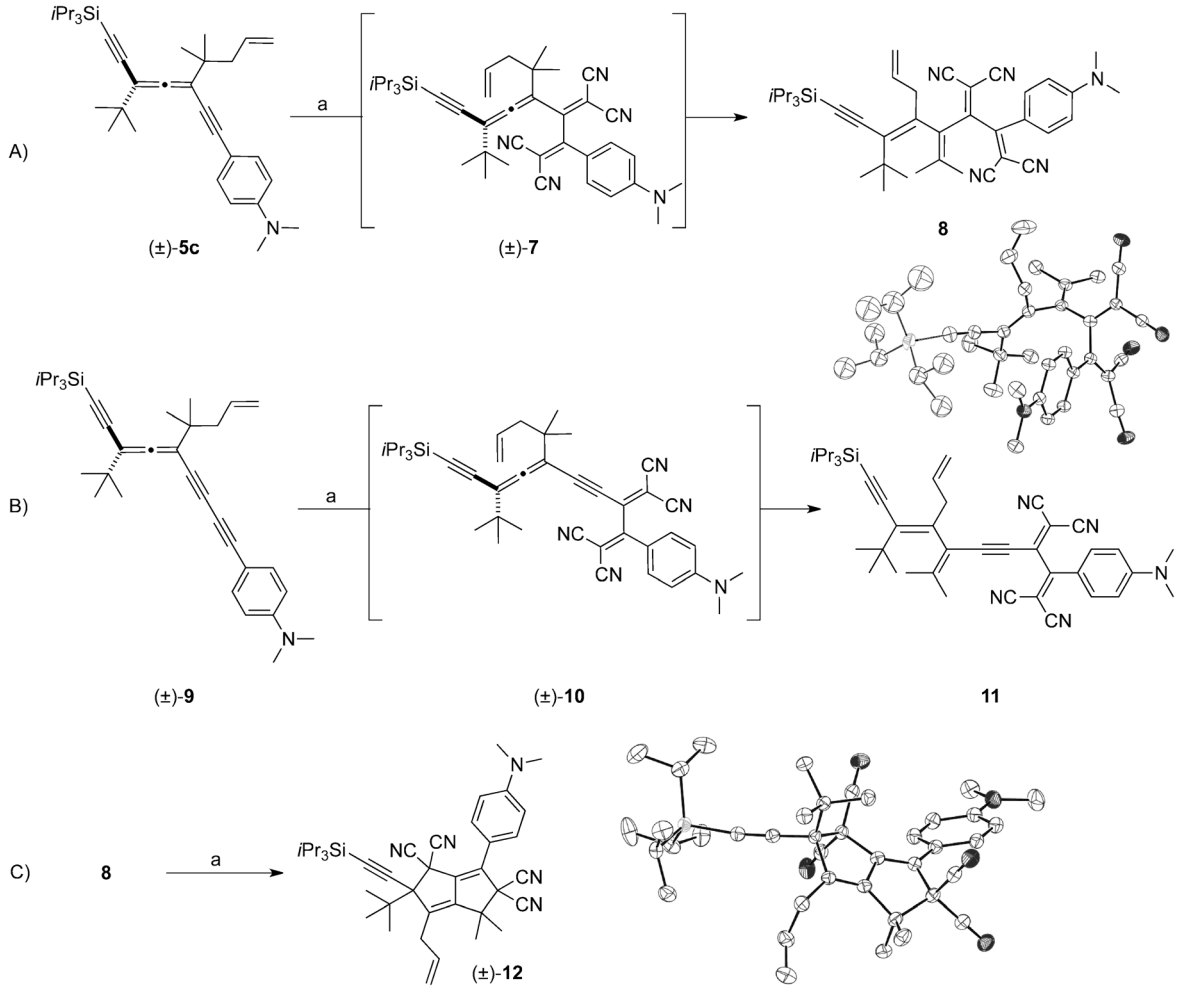
R	Allene	Butadiene	Yield[b]
H	(±)-**5b**	**6b**	40%
NMe_2	(±)-**5c**	**6c**	43%
Me	(±)-**5d**	**6d**	37%
CN	(±)-**5e**	**6e**	52%
NO_2	(±)-**5f**	**6f**	67%

Scheme 2. A) First attempts towards the synthesis of 1,1-dimethylhomoallyl-substituted allene (±)-**5a** and its thermal rearrangement. Reaction conditions: a) 2-methylbut-3-yn-2-ol (2-5 equiv), [$PdCl_2(PPh_3)_2$] or [$Pd(PPh_3)_4$] (10 mol%), CuI (10 mol%), various amine bases (*i*PrNH$_2$, *i*Pr$_2$NH, *i*Pr$_2$NEt, among others; 2–5 equiv), solvent ($(CH_2Cl)_2$ or toluene (0.02–0.2 M)), 25–60 °C, 24–72 h; varying yields of allene and buta-1,3-diene products were isolated; b) $(CH_2Cl)_2$ (0.02 M), reflux, 10 h; **6a**: 86%. B) Thermal allenyl-Cope rearrangement of aryl-substituted allenes (±)-**5b–f**. Reaction conditions: a) $(CH_2Cl)_2$ (0.02 M), reflux, 1 h; yields of buta-1,3-diene products **6b–f** were determined by ^{1}H NMR spectroscopy with triphenylmethane as internal standard; b) average of two runs.

lenyl-Cope pathway (for details, see the Supporting Information). The molecular structure of [4]dendralene **8** was established by X-ray crystallography (Scheme 3A and the Supporting Information).[10] NMR spectroscopy revealed the co-existence of different conformers at room temperature, which converged to a single species upon heating to 100 °C. In accordance to previous studies,[13] slow interconversion of similar dendralenes at room temperature is a consequence of steric crowding.

These steric constraints may already be present in the transient intermediate (±)-**7** and impede favorable orbital overlap in the transition state of the allenyl-Cope rearrangement. Thus, we reasoned that alleviating the steric constraints should lead to an even more facile rearrangement cascade. Indeed, diyne substrate (±)-**9** reacted with TCNE at room temperature to form intermediate (±)-**10**, which subsequently produces buta-1,3-diene **11** in a significantly shorter reaction time (Scheme 3B, formation of **8** at 28 °C: 40 h; of **11**: 2.5 h). NMR studies revealed a very rapid Cope rearrangement event rather than accumulation of the TCBD-substituted allene intermediate (±)-**10** in the reaction mixture, as opposed to what was observed in the reaction of alleno-acetylene (±)-**5c** (see the Supporting Information).[14] Rearranged product **11** displays a single set of signals in NMR spectroscopy, suggesting that it exists as a mixture of rapidly interconverting conformers at room temperature in contrast to [4]dendralene **8**. The release of steric constraints by the introduction of an alkyne spacer in diyne substrate (±)-**9** also allowed the use of the more sterically demanding TCNQ instead of TCNE, with the cascade sequence still operating under mild reaction conditions (for details, see the Supporting Information). Intriguingly and depending on the precise reaction conditions, the cascade reaction depicted in Scheme 3A does not necessarily stop with the formation of [4]dendralene **8**. Indeed, heating product **8** to 100 °C over 12 h causes a further highly selective rearrangement sequence which ultimately furnishes 1,2,4,5-tetrahydropentalene (±)-**12** in nearly quantitative amounts (94% yield; Scheme 3C). The sequence of events may be regarded as a Nazarov-type cyclization followed by ring closure of the resulting intermediate (for details, see the Supporting Information). The molecular structure of compound (±)-**12** was confirmed by X-ray crystallography (Scheme 3C and the Supporting Information).[10] It is a homo-conjugated CT chromophore, and its UV/Vis spectrum reveals the bathochromically shifted but low-intensity intramolecular CT band characteristic for homo-conjugated push–pull chromophores (see the Supporting Information).[15]

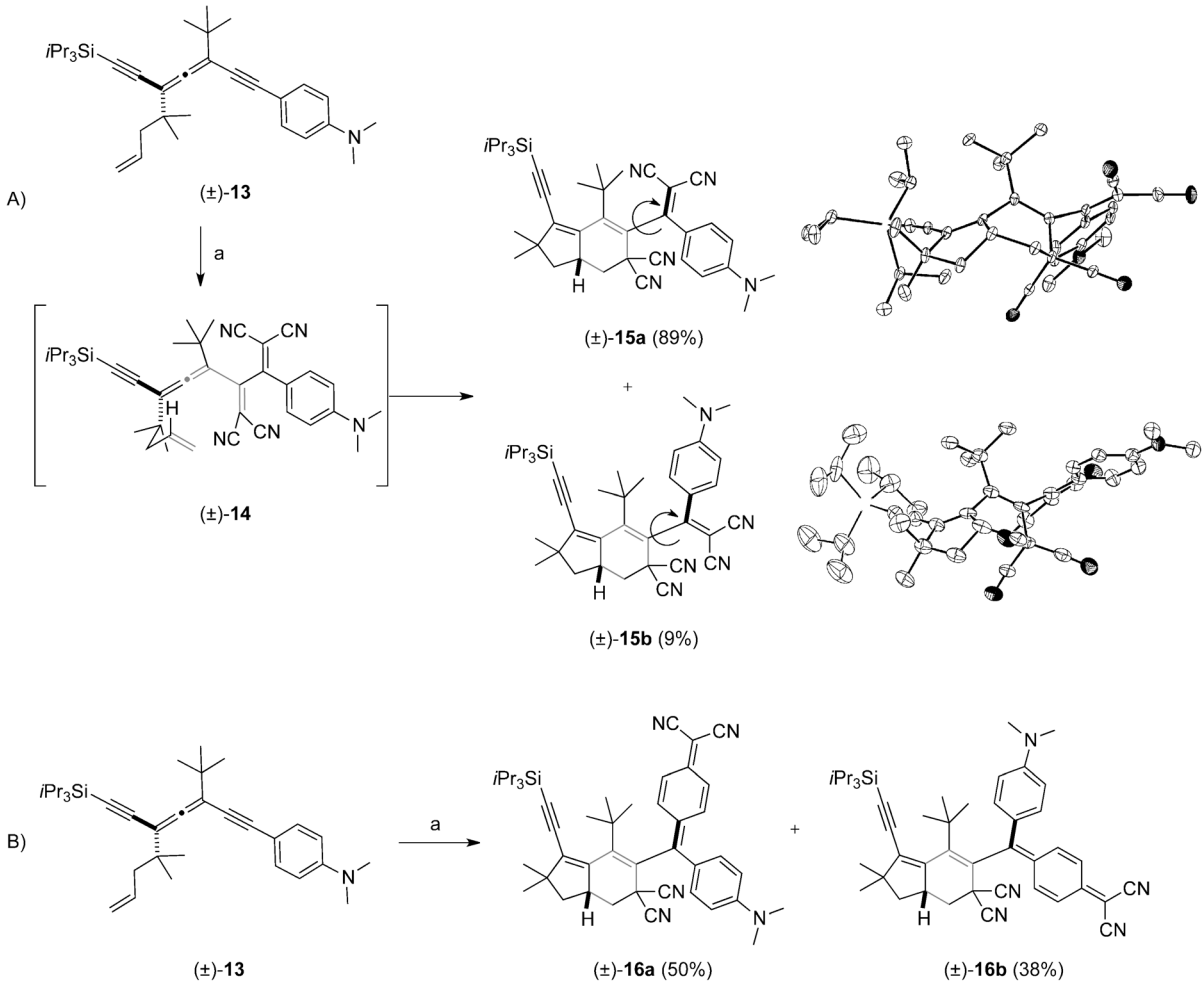
The manner in which the rate of the allenyl-Cope rearrangement can be manipulated by judicious introduction of electronic- and steric-biasing elements (cf. Scheme 3) manifests itself dramatically in the transformations of isomeric allene (±)-**13**, in which the 1,1-dimethylhomoallyl lateral chain has exchanged positions with the *tert*-butyl substituent (Scheme 4A). The fact that the [3,3]-allenyl Cope rearrangement of compound (±)-**13** remains extremely slow at room temperature (<5% after 48 h) opens up an entirely new reaction pathway for DEA (±)-**13**. Exposure to TCNE at room temperature now generates intermediate (±)-**14**, which reacts further to produce the 2,6,7,7a-tetrahydro-1*H*-indene skeleton (±)-**15** in very high yield and short reaction time (Scheme 4A). Presumably, an intramolecular Diels–Alder reaction of diene-allene (±)-**14** accounts for the observed result, thereby shutting down both the [3,3]-sigmatropic (and subsequent Nazarov-type cyclization) and the 4π electrocyclization pathways in favor of a [4+2] reaction



Scheme 3. CA/CR/allenyl-Cope cascade reaction: A) Formation of [4]dendralene **8** from (±)-**5c** and X-ray crystal structure of **8**. Hydrogen atoms and minor occupied positions of disordered atoms are omitted for clarity; atomic displacement parameters obtained at 100 K are drawn at 50% probability level (for details see the Supporting Information).[10] Reaction conditions: a) TCNE (1.05 equiv), $(CH_2Cl)_2$ (0.02 M), 90 °C, 1 h, 90%; b) TCNE (1.05 equiv), CH_2Cl_2 (0.02 M), 28 °C, 40 h, 96%. B) Formation of buta-1,3-diene **11** from diyne (±)-**9**. Reaction conditions: a) TCNE (1.05 equiv), CH_2Cl_2 (0.02 M), 28 °C, 2.5 h, 93%. C) Thermal rearrangement of **8** to (±)-**12** and X-ray crystal structure of (±)-**12**. Hydrogen atoms are omitted for clarity; atomic displacement parameters obtained at 100 K are drawn at 50% probability level (for details see the Supporting Information).[10] Reaction conditions: a) $(CDCl_2)_2$ (0.028 M), 100 °C, 12 h, 94%.

mode.[16] X-ray diffraction studies (Scheme 4A and the Supporting Information) allowed the unambiguous structural assignment of tetrahydroindene (±)-**15**,[10] which was obtained as a mixture of diastereoisomers ((±)-**15a** and (±)-**15b**). Putatively, the co-existence of the two diastereoisomeric forms (±)-**15a** and (±)-**15b** at room temperature is a result of hindered rotation about the butadiene axis (cf. Scheme 4A). However, the convergence of the diastereoisomeric mixture to a single product (±)-**15a** was accomplished by heating (±)-**15b** at 120 °C for 5.5 h, thus suggesting that tetrahydroindene (±)-**15a** is thermodynamically favored over its isomer (±)-**15b**. Whilst the diastereoselectivity of the Diels–Alder reaction triggered by the addition of TCNE to allene (±)-**13** is high (91:9), the corresponding stereoisomeric tetrahydroindenes stemming from the reaction of alleno-acetylene (±)-**13** with TCNQ are formed in almost equimolar amounts (Scheme 4B). It is particularly remarkable that even heating the individual pairs of diastereoisomers (±)-**16a** and (±)-**16b** to 120 °C over extended time periods did not cause any interconversion.

In conclusion, we have developed multiple cascade transformations of 1,3-diethynylallenes, which constitute kinetically stable and easy to handle "reactivity reservoirs". The cascades are triggered by the reaction of TCNE or TCNQ with donor-substituted alkynes by a [2+2] cycloaddition/cycloreversion (CA/CR) sequence and terminated by a) 4π electrocyclization, b) allenyl-Cope (followed by a Nazarov-type-cyclization/cyclization sequence), or c) [4+2] cycloaddition reaction. These novel cascade reactions provide rapid access, in one-pot processes, to highly substituted cyclobutenes, dendralenes, tetrahydropentalenes, and tetrahydroindenes, chromophoric advanced materials with great molecular complexity. Most remarkably, the reaction pathway can be steered at will by the judicious introduction of tailored



Scheme 4. CA/CR/Diels–Alder reaction cascade: A) Formation of diastereoisomeric tetrahydroindenes (±)-**15a** and (±)-**15b** from DMA-substituted alleno-acetylene (±)-**13** and X-ray crystal structures of (±)-**15a** and (±)-**15b**. Hydrogen atoms and minor occupied positions of disordered atoms ((±)-**15b**) are omitted for clarity; atomic displacement parameters obtained at 100 K are drawn at 50% probability level (for details see the Supporting Information).[10] Reaction conditions: a) TCNE (1.05 equiv), CH_2Cl_2 (0.02 M), 30 min, (±)-**15a**: 89% and (±)-**15b**: 9%. B) Formation of diastereoisomeric tetrahydroindenes (±)-**16a** and (±)-**16b** from (±)-**13**. Reaction conditions: a) TCNQ (1.05 equiv), CH_2Cl_2 (0.02 M), 72 h, (±)-**16a**: 50% and (±)-**16b**: 38%.

substituents to the alleno-acetylenic core. Current efforts are aimed at expanding the scope and complexity of these cascade processes and exploring enantioselective variants when working with optically pure starting materials.

Acknowledgements

C.M.R. acknowledges the Alexander von Humboldt Foundation for a Feodor-Lynen postdoctoral fellowship and P. R.-F. the Stipendienfonds der Schweizerischen Chemischen Industrie (SSCI) for a doctoral fellowship. This research was supported by the European Research Council (ERC Advanced Grant No. 246637 "OPTELOMAC").

Keywords: allenes · cascade reactions · cyclobutenes · dendralenes · indenes · pentalenes

[1] a) L. F. Tietze, G. Brasche, K. Gericke *Domino Reactions in Organic Synthesis*, Wiley-VCH, Weinheim, **2006**; b) K. C. Nicolaou, J. S. Chen, *Chem. Soc., Rev.* **2009**, *38*, 2993–3009; c) I. Vilotijevic, T. F. Jamison, *Angew. Chem.* **2009**, *121*, 5352–5385; *Angew. Chem. Int. Ed.* **2009**, *48*, 5250–5281; d) C. Grondal, M. Jeanty, D. Enders, *Nat. Chem.* **2010**, *2*, 167–178; e) E. A. Anderson, *Org. Biomol. Chem.* **2011**, *9*, 3997–4006.

[2] a) *Modern Allene Chemistry, Vol. 2* (Eds.: N. Krause, A. S. K. Hashmi), Wiley-VCH, Weinheim, **2008**; for recent reviews on cross-coupling and cycloaddition reactions, see: b) B. Alcaide, P. Almendros, R. Carrascosa, T. Martínez del Campo, *Chem. Eur. J.* **2010**, *16*, 5836–5842; c) F. López, J. L. Mascareñas, *Chem. Eur. J.* **2011**, *17*, 418–428.

[3] a) R. C. Livingston, L. R. Cox, V. Gramlich, F. Diederich, *Angew. Chem.* **2001**, *113*, 2396–2399; *Angew. Chem. Int. Ed.* **2001**, *40*, 2334–2337; b) R. Livingston, L. R. Cox, S. Odermatt, F. Diederich, *Helv. Chim. Acta* **2002**, *85*, 3052–3077; c) S. Odermatt, J. L. Alonso-Gómez, P. Seiler, M. M. Cid, F. Diederich, *Angew. Chem.* **2005**, *117*, 5203–5207; *Angew. Chem. Int. Ed.* **2005**, *44*, 5074–5078. For representative examples of allenic structures of other research groups, see: d) S. Thorand, F. Vögtle, N. Krause, *Angew. Chem.* **1999**, *111*, 3929–3931; *Angew. Chem. Int. Ed.* **1999**, *38*, 3721–3723; e) M. D.

Clay, A. G. Fallis, *Angew. Chem.* **2005**, *117*, 4107–4110; *Angew. Chem. Int. Ed.* **2005**, *44*, 4039–4042; f) M. Leclère, A. G. Fallis, *Angew. Chem.* **2008**, *120*, 578–582; *Angew. Chem. Int. Ed.* **2008**, *47*, 568–572.

[4] J. L. Alonso-Gómez, P. Schanen, P. Rivera-Fuentes, P. Seiler, F. Diederich, *Chem. Eur. J.* **2008**, *14*, 10564–10568.

[5] J. L. Alonso-Gómez, A. G. Petrovic, N. Harada, P. Rivera-Fuentes, N. Berova, F. Diederich, *Chem. Eur. J.* **2009**, *15*, 8396–8400.

[6] a) J. L. Alonso-Gómez, P. Rivera-Fuentes, N. Harada, N. Berova, F. Diederich, *Angew. Chem.* **2009**, *121*, 5653–5656; *Angew. Chem. Int. Ed.* **2009**, *48*, 5545–5548; b) P. Rivera-Fuentes, J. L. Alonso-Gómez, A. G. Petrovic, P. Seiler, F. Santoro, N. Harada, N. Berova, H. S. Rzepa, F. Diederich, *Chem. Eur. J.* **2010**, *16*, 9796–9807; c) P. Rivera-Fuentes, B. Nieto-Ortega, W. B. Schweizer, J. T. López Navarrete, J. Casado, F. Diederich, *Chem. Eur. J.* **2011**, *17*, 3876–3885.

[7] P. Rivera-Fuentes, J. L. Alonso-Gómez, A. G. Petrovic, F. Santoro, N. Harada, N. Berova, F. Diederich, *Angew. Chem.* **2010**, *122*, 2296–2300; *Angew. Chem. Int. Ed.* **2010**, *49*, 2247–2250.

[8] For an account of allene-multiple bond cycloadditions, see: F. Inagaki, S. Kitagaki, C. Mukai, *Synlett* **2011**, 594–614.

[9] a) T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross, F. Diederich, *Chem. Eur. J.* **2006**, *12*, 1889–1905; b) M. Kivala, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Chem. Commun.* **2007**, 4731–4733.

[10] CCDC-834582 (**3a**), CCDC-834583 (**3b**), CCDC-834584 (**8**), CCDC-834587 ((±)-**12**), CCDC-834585 ((±)-**15a**), and CCDC-834586 ((±)-**15b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

[11] a) A. Doutheau, G. Balme, M. Malacria, J. Gore, *Tetrahedron* **1980**, *36*, 1953–1960; b) J. A. Duncan, D. S. Bohle, C. A. Blanchard, M. L. Bosse, T. W. Noland, C. M. Ford, M. A. Powell, M. C. Sutton, A. C. Eggleston, *J. Am. Chem. Soc.* **1982**, *104*, 2837–2839; c) J. A. Duncan, R. T. Hendricks, K. S. Kwong, *J. Am. Chem. Soc.* **1990**, *112*, 8433–8442; d) E. Vedejs, A. Cammers-Goodwin, *J. Org. Chem.* **1994**, *59*, 7541–7543; for theoretical studies, see: e) J. A. Duncan, J. K. Azar, J. C. Beathe, S. R. Kennedy, C. M. Wulf, *J. Am. Chem. Soc.* **1999**, *121*, 12029–12034; f) J. A. Duncan, M. C. Spong, *J. Org. Chem.* **2000**, *65*, 5720–5727; related sigmatropic processes are reviewed in g) J. J. Gajewski *Hydrocarbon Thermal Isomerizations*, 2nd ed., Elsevier, Amsterdam, **2004**, pp. 171–209.

[12] a) K. W. F. Kohlrausch, H. Wittek, *Ber. Dtsch. Chem. Ges.* **1942**, *75*, 227–232; b) G. Köbrich, A. Mannschreck, R. A. Misra, G. Rissmann, M. Rösner, W. Zündorf, *Chem. Ber.* **1972**, *105*, 3794–3806; c) M. Rösner, G. Köbrich, *Angew. Chem.* **1974**, *86*, 775–776; *Angew. Chem. Int. Ed. Engl.* **1974**, *13*, 741–742; d) M. Yamada, P. Rivera-Fuentes, W. B. Schweizer, F. Diederich, *Angew. Chem.* **2010**, *122*, 3611–3615; *Angew. Chem. Int. Ed.* **2010**, *49*, 3532–3535, and references therein; e) M. Betz, H. Hopf, L. Ernst, P. G. Jones, Y. Okamoto, *Chem. Eur. J.* **2011**, *17*, 231–247.

[13] M. Kivala, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, F. Diederich, *Angew. Chem.* **2007**, *119*, 6473–6477; *Angew. Chem. Int. Ed.* **2007**, *46*, 6357–6360.

[14] Control experiments with blank samples of both monoyne (±)-**5c** and diyne (±)-**9** confirmed the accelerating effect of the TCBD unit on the allenyl-Cope rearrangement.

[15] For a recent study on homoconjugated charge-transfer chromophores, see: S.-I. Kato, M. T. R. Beels, P. La Porta, W. B. Schweizer, C. Boudon, J.-P. Gisselbrecht, I. Biaggio, F. Diederich, *Angew. Chem.* **2010**, *122*, 6343–6347; *Angew. Chem. Int. Ed.* **2010**, *49*, 6207–6211.

[16] For a related intramolecular Diels–Alder reaction of ene-allenes, see: R. A. Gibbs, K. Bartels, R. W. K. Lee, W. H. Okamura, *J. Am. Chem. Soc.* **1989**, *111*, 3717–3725.

Received: September 13, 2011
Published online: October 5, 2011

