[3 + 2] Cycloaddition

DOI: 10.1002/anie.201403014

[3+2] Cycloaddition of Propargylic Alcohols and α-Oxo Ketene Dithioacetals: Synthesis of Functionalized Cyclopentadienes and Further Application in a Diels–Alder Reaction**

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Abstract: *Cyclopentadienes are valuable intermediates in organic synthesis and also ubiquitous as the Cp ligands in organometallic chemistry. As part of ongoing efforts to develop novel organic reactions that employ functionalized alkynes, a [3+2] cycloaddition of propargylic alcohols and ketene dithioacetals has been developed, which leads to fully substituted 2,5-dialkylthio cyclopentadienes in good to excellent yields. In an unusual dethiolating Diels–Alder reaction, the cyclopentadienes were further reacted with maleimides to afford a family of novel fluorescent polycyclic compounds.*

Since the first report by Kelber in 1910,[1] α-oxo ketene dithioacetals have been shown to be versatile intermediates in organic synthesis because of the characteristic bis(alkylthio) groups, which are strongly electron-donating moieties and easily cleaved.[2] α-Oxo ketene dithioacetals and their extended conjugated derivatives are important 1,3-,[3] 1,5-,[4] and 1,7-electrophilic synthons[5] and have been extensively investigated in cyclization reactions. As α-oxo ketene dithioacetals are polar functionalized alkenes, they can be used as a two-carbon fragment in cyclization reactions. However, such synthetic applications are rare, and all of the reports are limited to the synthesis of heterocycles by classic alkylthio displacement reactions (Figure 1).[6] Applications to the synthesis of carbocycles have remained elusive. As part of our ongoing efforts to develop novel organic reactions that employ functionalized alkynes,[2,7] we herein report a novel [3+2] cycloaddition of propargylic alcohols and α-oxo ketene dithioacetals, which affords a new class of fully substituted 2,5-dialkylthio cyclopentadienes (Figure 1).[8] To the best of our knowledge, this is the first example in which α-oxo ketene dithioacetals were used as the polarized alkene component for the synthesis of carbocycles. Cyclopentadienes are valuable intermediates in organic synthesis and also ubiquitous as the Cp ligands in organometallic chemistry.[9] Despite a number of available synthetic strategies, the development of new efficient methods,[10–14] particularly those starting from easily available starting materials to afford densely functionalized cyclopentadienes, is still of great value.

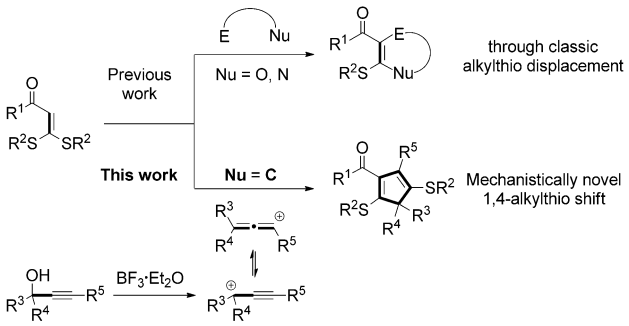
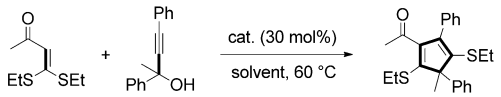


Figure 1. α-Oxo ketene dithioacetals as polarized alkenes in [2+*x*] cyclization reactions.

Initially, the reaction conditions were optimized using α-oxo ketene dithioacetal **1a** and propargylic alcohol **2a**. As shown in Table 1, different catalysts and solvents were screened. First, metal-based Lewis acids were investigated; $FeCl_3$, $TiCl_4$, and $SnCl_4$ afforded a trace amount of the desired cyclopentadiene **3a** in 1,4-dioxane, whereas $CuCl_2{\cdot}H_2O$ was ineffective (entries 1–4). To our delight, the nonmetal Lewis acid $BF_3{\cdot}Et_2O$ efficiently catalyzed the cycloaddition of **1a** and **2a**, affording **3a** in very good yield (86%; entry 5). The strong protonic acid CF_3SO_3H was also an effective catalyst of this reaction, but provided the desired product in a slightly

Table 1: Optimization of the reaction conditions.



Entry	Catalyst	Solvent	*t* [h]	Yield[a] [%]
1	$FeCl_3$	1,4-dioxane	3.0	trace
2	$TiCl_4$	1,4-dioxane	3.0	trace
3	$SnCl_4$	1,4-dioxane	3.0	trace
4	$CuCl_2{\cdot}H_2O$	1,4-dioxane	1.0	0
5	$BF_3{\cdot}Et_2O$	1,4-dioxane	1.5	86
6	CF_3SO_3H	1,4-dioxane	1.0	65
7	$BF_3{\cdot}Et_2O$	toluene	1.0	70
8	$BF_3{\cdot}Et_2O$	CH_3CN	1.0	75
9	$BF_3{\cdot}Et_2O$	MeOH	1.0	43

[a] Yields of isolated products.

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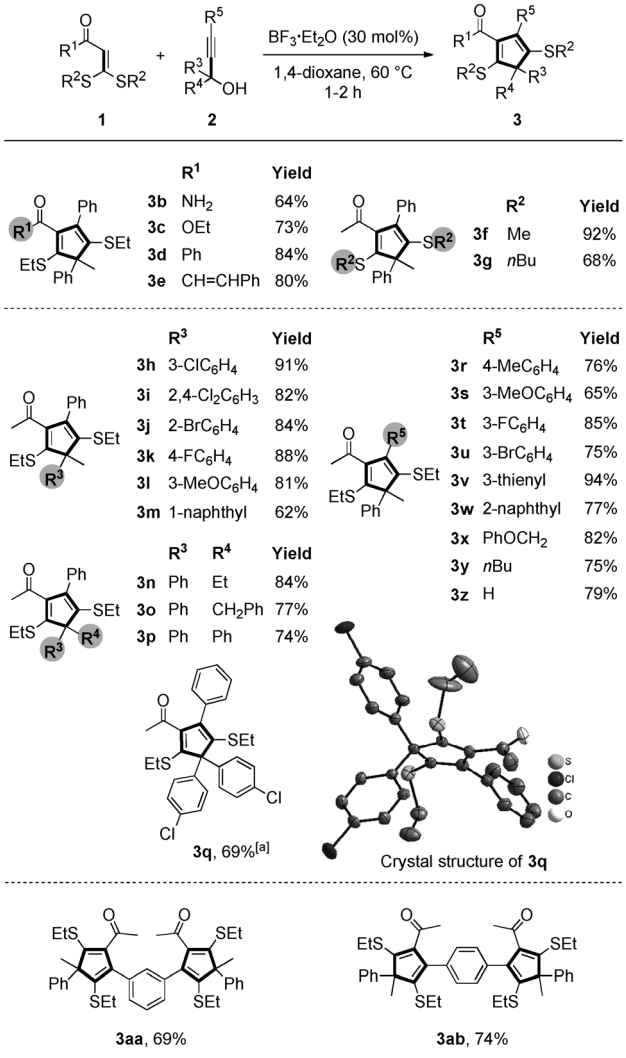
[**] This work was supported by the NNSFC (21172029, 21202016, 21372038, 31101010), the Ministry of Education of the People's Republic of China (NCET-13-0714), and the Jilin Provincial Research Foundation for Basic Research (20140519008JH).

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201403014.

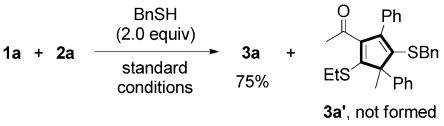
lower yield (65%; entry 6). Next, the influence of the solvent was studied using $BF_3{\cdot}Et_2O$ as the catalyst; non-polar (toluene), polar (CH_3CN), and protic (MeOH) solvents could be used, but the products were obtained in lower yields (entries 7–9). Therefore, the reaction conditions that are described in Table 1, entry 5 were found to be the most suitable for this transformation and selected for further investigations.

With the optimized reaction conditions in hand (Table 1, entry 5), the substrate scope of the cyclopentadiene synthesis was investigated (Scheme 1). First, the use of various α-oxo ketene dithioacetals with different R^1 and R^2 substituents was investigated in the reaction with **2a**. Diverse functional groups, such as amino, alkoxy, aryl, and styryl groups, as the R^1 group were tolerated under these reaction conditions, and the corresponding cyclopentadienes were obtained in good to high yields (**3b**–**3e**, 64–84%). The length of the alkylthio moiety of the α-oxo ketene dithioacetal significantly affected the outcome of the reaction. For example, the methylthio-substituted substrate afforded cyclopentadiene **3f** in 92% yield, whereas the bulky *n*-butylthio-substituted substrate was converted into product **3g** in only 68% yield. Next, we systematically varied the R^3, R^4, and R^5 substituents of the propargylic alcohol derivative and subjected these derivatives to the reaction with **1a**. To our delight, diverse tertiary propargylic alcohols could be used in this cycloaddition reaction, affording the corresponding cyclopentadienes in good to excellent yields (**3h**-**3z**; 62–94%). Various functional groups, such as electron-donating and -withdrawing (hetero)-aryl, fused aryl, alkyl, and ether groups, could be installed at the 1- and/or 3-position of the cyclopentadiene skeleton. Notably, a substrate possessing a terminal alkyne unit (R^5 = H) also participated in the reaction with **1a**, the corresponding cyclopentadiene **3z** with an unoccupied 3-position was isolated in 79% yield. Although cyclopentadienes **3** were thoroughly characterized by NMR spectroscopy and high-resolution mass spectrometry (HRMS), their structures were confirmed by X-ray diffraction (XRD) of compound **3q**. Moreover, biscyclopentadienes, such as **3aa** and **3ab**, could be prepared in one step from the corresponding bispropargylic alcohols.



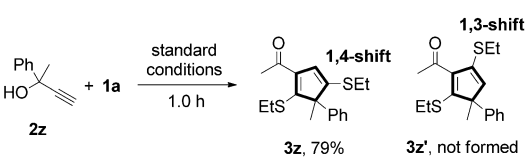
Scheme 1. Substrate scope of the cyclopentadiene formation. [a] CF_3SO_3H (30 mol%).

Sulfur migration has emerged as a valuable process for organic chemists; 1,2-sulfur migration has been widely investigated and applied in organic synthesis.[15] However, other types of sulfur migration, such as a 1,4-sulfur shift, are rarely described. Recently, Wang and co-workers reported an unprecedented 1,4-shift of the sulfanyl group in the transition-metal-catalyzed reaction of allenyl sulfides.[16] We envisioned that a 1,4-alkylthio shift may be involved in the formation of cyclopentadienes **3**. To confirm this hypothesis, control experiments were carried out. First, a competition experiment was performed by adding two equivalents of benzyl mercaptan (BnSH) to the reaction of **1a** with **2a** under the standard reaction conditions [$BF_3{\cdot}Et_2O$ (30 mol%), 1,4-dioxane, 60 °C; Eq. (1)]. Cyclopentadiene **3a** was obtained in



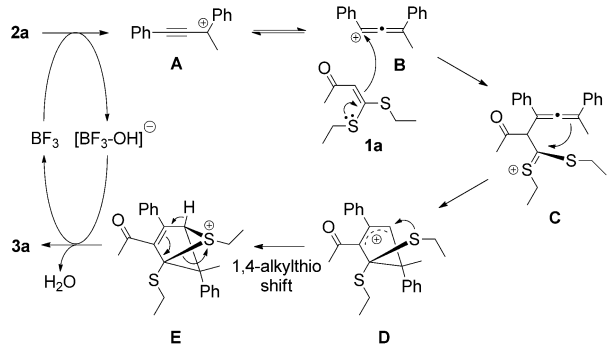
(1)

75% yield, whereas the benzylthio-substituted cyclopentadiene **3a′** was not observed by HRMS analysis of the reaction mixture, indicating that the alkylthio shift is an intramolecular process. Moreover, to test the specificity of the alkylthio shift, propargylic alcohol **2z**, which contains a terminal alkyne group, was subjected to the reaction with **1a**, because **2z** would facilitate both 1,4- and 1,3-alkylthio shifts. However, only the 1,4-alkylthio shift occurred, affording **3z** as the sole product, without forming **3z′** through a 1,3-alkylthio shift [Eq. (2)]. This result confirmed that the 1,4-alkylthio shift occurred as a specific process.



(2)

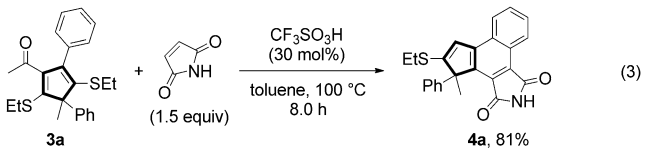
Based on these results and related precedents,[2,17] a plausible mechanism for the cyclopentadiene synthesis was proposed (Scheme 2). The polarity of the hydroxy group in



Scheme 2. Proposed reaction mechanism.

2a was enhanced by the interaction between $BF_3{\cdot}Et_2O$ and the hydroxy group, which leads to the formation of propargylic carbocation **A** by the loss of the OH species. Because of the resonance stabilization between propargylic carbocation **A** and allenic carbocation **B**, less sterically hindered **B** is preferably attacked by the electron-rich α-carbon atom of **1a**, affording intermediate **C**. The allenic carbon atom attacks the thiolanium ion species to afford a five-membered carbocycle, along with allylic carbocation **D**. Next, attack of a lone pair of electrons of the sulfur atom to the allylic carbocation affords intermediate **E** with the formation of a new C–S bond, thus enabling the 1,4-alkylthio shift.[18] Finally, elimination of a proton and cleavage of the C–S bond produce cyclopentadiene **3a**. Meanwhile, the catalyst is regenerated by the elimination of one molecule of H_2O, which completes the catalytic cycle.

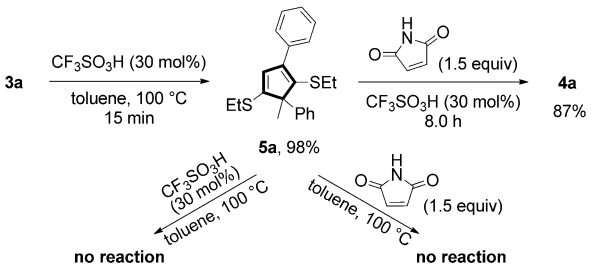
Interestingly, when **3a** and maleimide were reacted in the presence of CF_3SO_3H (30 mol%), the desired Diels–Alder cycloaddition reaction with the cyclopentadiene ring acting as the diene was not observed [Eq. (3)].[19] Instead, an unprece-



(3)

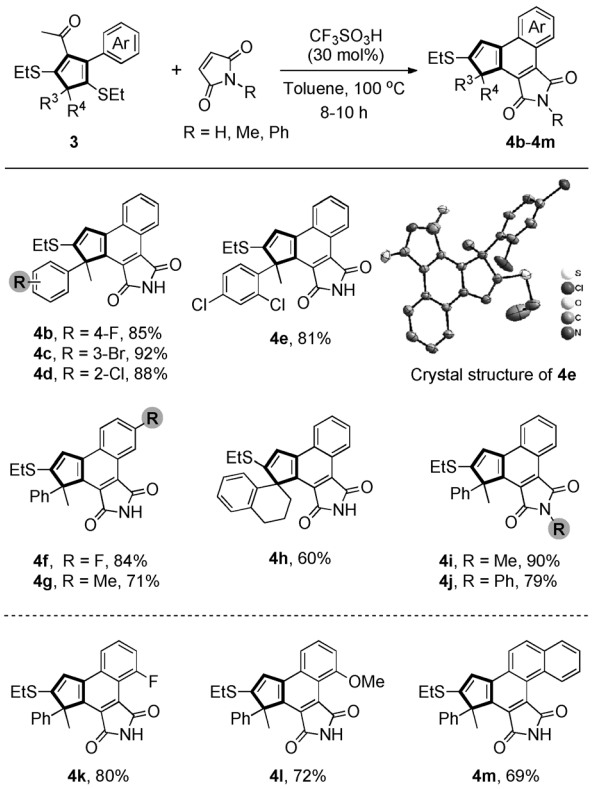
dented dethiolating Diels–Alder reaction with participation of the phenyl ring in the 3-position occurred; polycyclic compound **4a** was isolated in high yield (81%).[20] Notably, **4a** represents a new family of polycyclic structures. This unusual reactivity of **3a** can be attributed to the unique substitution pattern. Moreover, the type of dienophile also played a critical role in this cascade reaction because the use of maleic anhydride resulted in a mixture of unidentified products. Naturally, we were interested in studying this unusual Diels–Alder reaction.

To elucidate the reaction mechanism for the formation of **4a**, the overall transformation was conducted in a stepwise fashion (Scheme 3). In the absence of maleimide, deacetylated product **5a** was obtained in nearly quantitative yield under the acid-catalyzed conditions. Further treatment of **5a** with CF_3SO_3H at 100 °C for two hours did not result in any reaction. Similarly, no reaction was observed when a mixture of **5a** and maleimide was heated at 100 °C in the absence of CF_3SO_3H for two hours. However, when the CF_3SO_3H catalyst was added to the reaction mixture of **5a** and maleimide, the Diels–Alder reaction smoothly proceeded and afforded **4a** in 87% yield. Apparently, CF_3SO_3H played a dual role in the cycloaddition of cyclopentadiene with maleimide: 1) It promotes the deacetylation of the cyclopentadiene and 2) enhances the ability of maleimide to act as the dienophile, probably through protonation of the nitrogen and/or oxygen atom.[21] Therefore, the mechanism for the Diels–Alder reaction of cyclopentadienes with maleimides may involve sequential deacetylation, Diels–Alder cycloaddition with participation of the aryl ring at the 3-position, and final dethiolation, which leads to aromatization.



Scheme 3. Investigation of the reaction mechanism.

Next, we investigated the substrate scope of this unusual Diels–Alder reaction (Scheme 4). Diverse cyclopentadienes **3** underwent this cascade reaction with maleimides to afford the corresponding polycyclic products in good to excellent yields (**4b**–**4m**, 60–92%; Scheme 4). Variations in the substituents and their position on the aryl ring at the 1-position of cyclopentadienes **3** did not affect the efficiency of this reaction (**4b**–**4e**). Although the structures of products **4** were evident from the NMR and HRMS data, additional confirmation was obtained by single-crystal XRD analysis of product **4e**. The efficiency of this transformation was not significantly affected by the nature of the aryl group at the 3-position of cyclopentadienes **3**. Thus, substrates with electron-rich or electron-deficient substituents afforded the corresponding polycyclic products in comparable yields (**4f** and **4g**; Scheme 4). Moreover, a cyclopentadiene with a spiro center underwent facile cycloaddition with maleimide to give the desired product in a good yield (**4h**, 60%). Furthermore, the reactions of *N*-protected maleimides, such as *N*-methyl or *N*-phenyl derivatives, with **3a** smoothly produced the corresponding products, **4i** and **4j**, in 90 and 79% yield, respectively. Remarkably, cyclopentadienes **3** with an unsymmetric aryl group at the 3-position reacted with excellent regioselectivity, and the reactive site was the sterically hindered *ortho* position (**4k**, **4l**, and **4m**; Scheme 4).



Scheme 4. Substrate scope of the Diels–Alder reaction.

Polycyclic compounds **4** exhibited a strong yellowish green fluorescence in organic solutions; therefore, a first study on their photophysical properties was conducted using compounds **4a**, **4g**, and **4k** (Figure 2). Certain notable features were: 1) large Stokes shifts of approximately 80 nm; 2) narrow emission bandwidth, resulting in high peak intensity; and 3) variable fluorescence intensity depending on the substituents of the aryl moiety. Moreover, compounds **4** are electrically neutral and relatively nonpolar, thus minimizing the dye-induced perturbation of conjugate functional properties. Moreover, the all-carbon quaternary center in the cyclopentadiene unit is capable of preventing intermolecular stacking interactions, a major reason for fluorescence quenching.[22] From a synthetic perspective, they are amenable to functionalization or modification. Thus, these properties indicate that polycyclic compounds **4** have great potential as a family of small-molecule fluorophores.

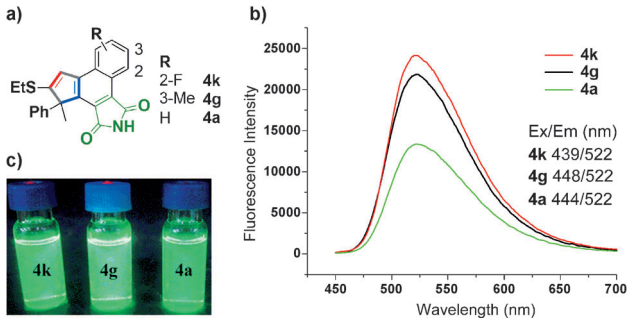


Figure 2. Photophysical properties.

In conclusion, we have developed a conceptually new strategy for the synthesis of cyclopentadienes by the $BF_3{\cdot}Et_2O$ catalyzed regiospecific [3+2] cycloaddition of propargylic alcohols and α-oxo ketene dithioacetals. A new class of fully substituted 2,5-dialkylthio cyclopentadienes were obtained in good to excellent yields. A mechanistically novel 1,4-alkylthio shift was observed during the ring-closure process. The unique substitution pattern of these cyclopentadienes facilitated an unusual dethiolating Diels–Alder reaction with maleimides, and therefore afforded a family of novel fluorescent polycyclic compounds.

Received: March 5, 2014
Revised: April 14, 2014
Published online: May 30, 2014

Keywords: [3+2] cycloaddition · cyclopentadienes · Diels–Alder reaction · ketene dithioacetals · propargylic alcohols

[1] C. Kelber, *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1252–1259.
[2] For a recent review, see: L. Pan, X. Bi, Q. Liu, *Chem. Soc. Rev.* **2013**, *42*, 1251–1286.
[3] For reviews, see: a) R. K. Dieter, *Tetrahedron* **1986**, *42*, 3029–3096; b) H. Junjappa, H. Ila, C. V. Asokan, *Tetrahedron* **1990**, *46*, 5423–5506.
[4] a) X. Bi, D. Dong, Q. Liu, W. Pan, L. Zhao, B. Li, *J. Am. Chem. Soc.* **2005**, *127*, 4578–4579; b) D. Dong, X. Bi, Q. Liu, F. Cong, *Chem. Commun.* **2005**, 3580–3582; c) X. Bi, D. Dong, Y. Li, Q. Liu, Q. Zhang, *J. Org. Chem.* **2005**, *70*, 10886–10889; d) J. Tan, X. Xu, L. Zhang, Y. Li, Q. Liu, *Angew. Chem.* **2009**, *121*, 2912–2916; *Angew. Chem. Int. Ed.* **2009**, *48*, 2868–2872.
[5] X. Xu, L. Zhang, X. Liu, L. Pan, Q. Liu, *Angew. Chem.* **2013**, *125*, 9441–9444; *Angew. Chem. Int. Ed.* **2013**, *52*, 9271–9274.
[6] a) H. Yuan, M. Wang, Y. Liu, L. Wang, J. Liu, Q. Liu, *Chem. Eur. J.* **2010**, *16*, 13450–13457; b) D. Liang, M. Wang, B. Bekturhun, B. Xiong, Q. Liu, *Adv. Synth. Catal.* **2010**, *352*, 1593–1599; c) Y. Liu, M. Wang, H. Yuan, Q. Liu, *Adv. Synth. Catal.* **2010**, *352*, 884–892; d) H.-J. Yuan, M. Wang, Y.-J. Liu, Q. Liu, *Adv. Synth. Catal.* **2009**, *351*, 112–116; e) H. S. P. Rao, S. Sivakumar, *J. Org. Chem.* **2006**, *71*, 8715–8723.
[7] a) Z. Liu, J. Liu, L. Zhang, P. Liao, J. Song, X. Bi, *Angew. Chem.* **2014**, *126*, 5409–5413; *Angew. Chem. Int. Ed.* **2014**, *53*, 5305–5309; b) J. Liu, Z. Liu, N. Wu, P. Liao, X. Bi, *Chem. Eur. J.* **2014**, *20*, 2154–2158; c) Z. Fang, P. Liao, Z. Yang, Y. Wang, B. Zhou, Y. Yang, X. Bi, *Eur. J. Org. Chem.* **2014**, 924–927; d) G. Fang, J. Li, Y. Wang, M. Gou, Q. Liu, X. Li, X. Bi, *Org. Lett.* **2013**, *15*, 4126–4129; e) J. Liu, Z. Fang, Q. Zhang, Q. Liu, X. Bi, *Angew. Chem.* **2013**, *125*, 7091–7095; *Angew. Chem. Int. Ed.* **2013**, *52*, 6953–6957; f) Y. Liu, B.-D. Barry, H. Yu, J. Liu, P. Liao, X. Bi, *Org. Lett.* **2013**, *15*, 2608–2611; g) Z. Fang, H. Yuan, Y. Liu, Z. Tong, H. Li, J. Yang, B.-D. Barry, J. Liu, P. Liao, J. Zhang, Q. Liu, X. Bi, *Chem. Commun.* **2012**, *48*, 8802–8804.
[8] Alkylthio-substituted cyclopentadienes have rarely been described in the literature; see: a) M. Wang, F. Han, H. Yuan, Q. Liu, *Chem. Commun.* **2010**, *46*, 2247–2249; b) K. Hartke, K.-H. Lee, *Liebigs Ann. Chem.* **1992**, 413–414.
[9] a) R. L. Halterman, *Chem. Rev.* **1992**, *92*, 965–994; b) E. Winterfeldt, *Chem. Rev.* **1993**, *93*, 827–843; c) Z. Xi, *Top. Catal.* **2005**, *35*, 63–71; d) M. Enders, R. W. Baker, *Curr. Org. Chem.* **2006**, *10*, 937–953; e) P. A. Deck, *Coord. Chem. Rev.* **2006**, *250*, 1032–1055.

[10] For examples of [4+1] cyclizations that involve metallacyclopentadienes or 1,4-dimetallobutadienes, see: a) L. Liu, W.-X. Zhang, C. Wang, C. Wang, Z. Xi, *Angew. Chem.* **2009**, *121*, 8255 – 8258; *Angew. Chem. Int. Ed.* **2009**, *48*, 8111 – 8114; b) Z. Xi, Q. Song, J. Chen, H. Guan, P. Li, *Angew. Chem.* **2001**, *113*, 1967 – 1970; *Angew. Chem. Int. Ed.* **2001**, *40*, 1913 – 1916; c) Z. Xi, P. Li, *Angew. Chem.* **2000**, *112*, 3057 – 3059; *Angew. Chem. Int. Ed.* **2000**, *39*, 2950 – 2952.

[11] For examples of [3+2] cyclizations of α,β-unsaturated metal carbenes with alkynes, see: a) E. Rettenmeier, A. M. Schuster, M. Rudolph, F. Rominger, C. A. Gade, A. S. K. Hashmi, *Angew. Chem.* **2013**, *125*, 5993 – 5997; *Angew. Chem. Int. Ed.* **2013**, *52*, 5880 – 5884; b) S. Kramer, Y. Odabachian, J. Overgaard, M. Rottländer, F. Gagosz, T. Skrydstrup, *Angew. Chem.* **2011**, *123*, 5196 – 5200; *Angew. Chem. Int. Ed.* **2011**, *50*, 5090 – 5094; c) J. F. Briones, J. Hansen, K. I. Hardcastle, J. Autschbach, H. M. L. Davies, *J. Am. Chem. Soc.* **2010**, *132*, 17211 – 17215; d) Y. Shibata, K. Noguchi, K. Tanaka, *J. Am. Chem. Soc.* **2010**, *132*, 7896 – 7898; for other [3+2] cyclizations, see: e) Y. Gao, W. Wu, H. Huang, Y. Huang, H. Jiang, *Chem. Commun.* **2014**, *50*, 846 – 848; f) P. Wang, S. Liao, S. R. Wang, R.-D. Gao, Y. Tang, *Chem. Commun.* **2013**, *49*, 7436 – 7438.

[12] For Nazarov cyclizations of divinyl carbinols or ketones, see: a) C. J. Hastings, M. P. Backlund, R. G. Bergman, K. N. Raymond, *Angew. Chem.* **2011**, *123*, 10758 – 10761; *Angew. Chem. Int. Ed.* **2011**, *50*, 10570 – 10573; b) C. J. Hastings, M. D. Pluth, R. G. Bergman, K. N. Raymond, *J. Am. Chem. Soc.* **2010**, *132*, 6938 – 6940.

[13] For cycloisomerization reactions of unsaturated compounds, see: a) H. Funami, H. Kusama, N. Iwasawa, *Angew. Chem.* **2007**, *119*, 927 – 929; *Angew. Chem. Int. Ed.* **2007**, *46*, 909 – 911; b) J. Lee, F. D. Toste, *Angew. Chem.* **2007**, *119*, 930 – 932; *Angew. Chem. Int. Ed.* **2007**, *46*, 912 – 914; c) C. Bruneau, P. H. Dixneuf, *Angew. Chem.* **2006**, *118*, 2232 – 2260; *Angew. Chem. Int. Ed.* **2006**, *45*, 2176 – 2203; d) S. Datta, A. Odedra, R.-S. Liu, *J. Am. Chem. Soc.* **2005**, *127*, 11606 – 11607.

[14] For isocyanide-based multicomponent reactions, see: V. Nair, R. S. Menon, P. B. Beneesh, V. Sreekumar, S. Bindu, *Org. Lett.* **2004**, *6*, 767 – 769.

[15] For a review on 1,2-sulfur migration, see: a) A. W. Sromek, V. Gevorgyan, *Top. Curr. Chem.* **2007**, *274*, 77 – 124; see also: b) A. S. Dudnik, A. W. Sromek, M. Rubina, J. T. Kim, A. V. Kel'in, V. Gevorgyan, *J. Am. Chem. Soc.* **2008**, *130*, 1440 – 1452; c) L. Peng, X. Zhang, S. Zhang, J. Wang, *J. Org. Chem.* **2007**, *72*, 1192 – 1197; d) L. Peng, X. Zhang, J. Ma, Z. Zhong, J. Wang, *Org. Lett.* **2007**, *9*, 1445 – 1448; e) X. Meng, Z. Fang, B.-D. Barry, P. Liao, X. Bi, *Chin. Sci. Bull.* **2012**, *57*, 2361 – 2363.

[16] L. Peng, X. Zhang, M. Ma, J. Wang, *Angew. Chem.* **2007**, *119*, 1937 – 1940; *Angew. Chem. Int. Ed.* **2007**, *46*, 1905 – 1908.

[17] For examples of the synthetic utilization of propargylic alcohols as three-carbon allenic carbocation precursors in cyclization reactions, see: a) X. Zhang, W. T. Teo, P. W. H. Chan, *Org. Lett.* **2009**, *11*, 4990 – 4993; b) Y. Zhu, G. Yin, D. Hong, P. Lu, Y. Wang, *Org. Lett.* **2011**, *13*, 1024 – 1027; c) W. Zhao, E. M. Carreira, *Org. Lett.* **2003**, *5*, 4153 – 4154.

[18] For reports on sulfonium species, see: a) K. K. Ellis-Holder, B. P. Peppers, A. Y. Kovalevsky, S. T. Diver, *Org. Lett.* **2006**, *8*, 2511 – 2514; b) R. Robiette, G. Y. Fang, J. N. Harvey, V. K. Aggarwal, *Chem. Commun.* **2006**, 741 – 743; c) T. Mori, Y. Sawada, A. Oku, *J. Org. Chem.* **2000**, *65*, 3620 – 3625.

[19] For examples of Diels–Alder reactions of multisubstituted cyclopentadienes, see: a) H. Isobe, S. Sato, T. Tanaka, H. Tokuyama, E. Nakamura, *Org. Lett.* **2004**, *6*, 3569 – 3571; b) M. S. Bultman, J. Ma, D. Y. Gin, *Angew. Chem.* **2008**, *120*, 6927 – 6930; *Angew. Chem. Int. Ed.* **2008**, *47*, 6821 – 6824; c) H. Modrzejewska, K. Wojciechowski, *Synlett* **2008**, 2465 – 2470; d) R. P. Hughes, A. S. Kowalski, J. R. Lomprey, D. R. Neithamer, *J. Org. Chem.* **1996**, *61*, 401 – 404; e) E. L. Allred, C. L. Anderson, *J. Org. Chem.* **1967**, *32*, 1874 – 1877.

[20] For reviews on the Diels–Alder reaction, see: a) G. Brieger, J. N. Bennett, *Chem. Rev.* **1980**, *80*, 63 – 97; b) P. Wessig, G. Müller, *Chem. Rev.* **2008**, *108*, 2051 – 2063; c) X. Jiang, R. Wang, *Chem. Rev.* **2013**, *113*, 5515 – 5546.

[21] a) D. A. Klumpp, R. Rendy, Y. Zhang, A. Gomez, A. McElrea, *Org. Lett.* **2004**, *6*, 1789 – 1792; b) D. A. Klumpp, Y. Zhang, M. J. O'Connor, P. M. Esteves, L. S. deAlmeida, *Org. Lett.* **2007**, *9*, 3085 – 3088.

[22] G. T. Hwang, H. S. Son, J. K. Ku, B. H. Kim, *J. Am. Chem. Soc.* **2003**, *125*, 11241 – 11248.

