# Alkynyl Fischer carbene complex as a traceless directing group for the regioselective cycloaddition of dithiolethiones to arylacetylene: synthesis of *E*-dithiafulvene thione and dithioesters†‡

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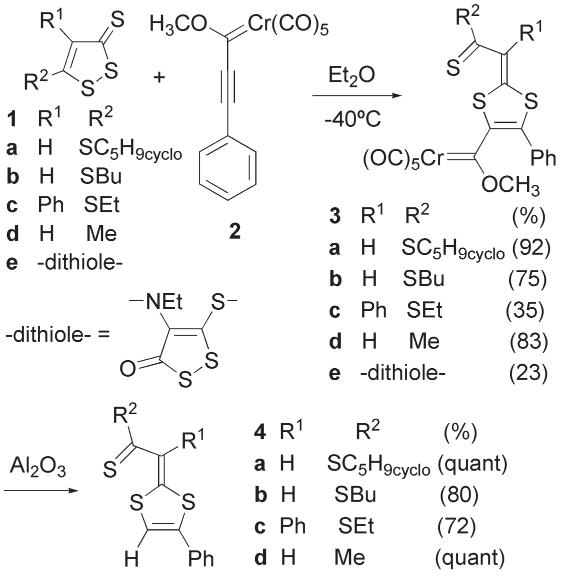
**A phenylethynyl Fischer carbene complex was used as a traceless directing group for the regioselective cycloaddition of dithiolethiones to arylacetylene, which constitutes the first synthesis of *E*-dithiafulvene thione or dithioesters.**

The dithiafulvene unit (1,3-dithiole-2-ylidene group) is a good electron donor currently used in the design and synthesis of new organic materials, especially in the search for extended tetrathiafulvalene derivatives.[1] The design of hybrid extended tetrathiafulvalene oligomers, in which a conjugated *p*-quinodimethane[2] or vinylogous[3] spacer separates two or more dithiafulvene units or incorporates some metal–dithiolate fused units,[4] is an emerging and important area of investigation with exciting prospects which has already afforded materials with a large variety of electronic properties and structural flexibility for specific applications.[1,4b] The dithiafulvene unit is also found as part of push–pull donor–acceptor dyads and cruciforms with unprecedented non-linear optical and redox-controlled characteristics.[5] A common method for the synthesis of dithiafulvene functionalized units is the cycloaddition of 3*H*-1,2-dithiole-3-thiones to electrophilic alkynes such as acetylenedicarboxylate or acetylenedicarbaldehyde.[6] Aryl acetylenes and alkyl phenylpropiolates are less reactive and mixtures of regioisomers are obtained.[6c] Notwithstanding, the preparation of non-symmetrically substituted dithiafulvene intermediates may be a significant first step in the way to the preparation of geometrically pure extended bis-substituted tetrathiafulvalene derivatives. Currently, mixtures of isomers are used in rotaxanes,[7a] nanovalves,[7b] sensors and nanodevices.[7c] We recalled that the Fischer carbene moiety acts as an electron withdrawing group that enhances the electrophilic character of the alkyne group, acting as a Michael acceptor and dipolarophile in thermal cycloadditions between alkynyl Fischer carbenes and 1,3-dipoles.[8] Nitrones and diazoalkanes are particularly well studied cases.[9] A few other heterocycloaddition reactions involving alkynyl Fischer carbene complexes and nitrogen-containing reagents are known[10] as well as addition of sulfur nucleophiles to alkynyl Fischer carbene complexes,[11] but cycloadditions involving sulfur-containing reagents are not reported. We have previously reported that 3*H*-1,2-dithiole-3-thione derivatives reacted with aryl Fischer carbene complexes, giving 1,3-dithiin dithioortho esters through insertion of the carbonic carbon into the S–S bond next to the thiocarbonyl function of the substrate.[12] In this communication we report the fully regioselective cycloaddition of dithiolethiones to alkynyl Fischer carbene complexes followed by stepwise elimination of methanol and chromium hexacarbonyl, which constitutes the first regioselective synthesis of *E*-dithiafulvene thiones and dithioesters.

Thus, we added 5-cyclopentylthio-3*H*-1,2-dithiole-3-thione **1a** (1 equiv) to a solution of [pentacarbonyl(phenylethynylmethoxy)]-chromium(0) **2** in dry ether at −40 °C and the mixture was stirred under nitrogen for 30 min, until complete disappearance of **1a** as evidenced by thin layer chromatography. Work-up and flash column chromatography (silica, hexane–dichloromethane 80 : 20 v/v) afforded product **3a** as black crystals characterized by the usual spectroscopic and analytical techniques (Scheme 1). Single crystal X-ray diffraction analysis confirmed the structure of **3a**§ as the *Z*-isomer (Fig. 1).



**Scheme 1** Reaction of 1,2-dithiole-3-thiones **1a–c** and alkynyl Fischer carbene complex **2**.

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† The HTML version of this article has been enhanced with colour images.

‡ Electronic supplementary information (ESI) available: Crystallographic details for **3a**, **4a**, and **4d** and the complex between **1d** and chromium pentacarbonyl. Complete description of the experimental procedures. Physical and spectral data of all new products. $^1$H and $^{13}$C NMR spectra of **3a–e** and **4a–d**. See DOI: 10.1039/b715857b

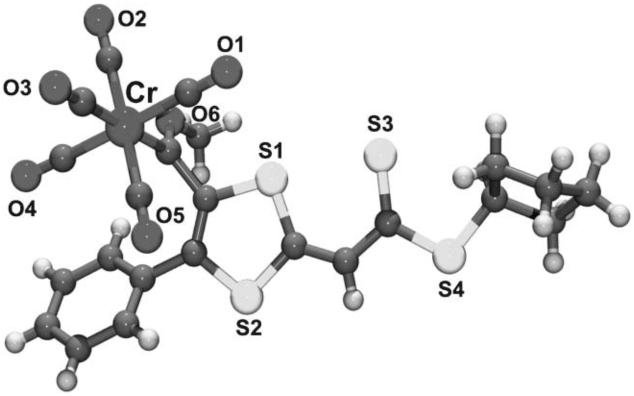


**Fig. 1** Single crystal X-ray diffraction structure of **3a**.

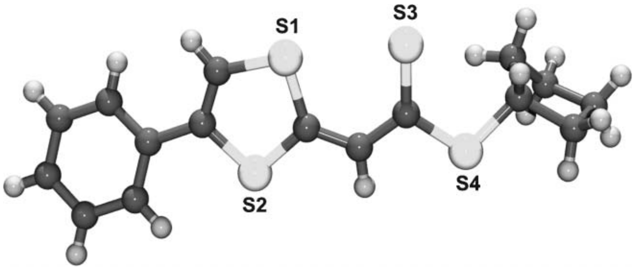


**Fig. 2** Single crystal X-ray diffraction structure of **4a**.

Treatment of **3a** in dichloromethane with neutral aluminium oxide followed by flash chromatography (neutral aluminium oxide, hexane–dichloromethane 80 : 20 v/v) gave quantitatively product **4a** (Scheme 1) as orange crystals characterized by the usual spectroscopic and analytical techniques. Single crystal diffraction analysis confirmed the structure of **4a**§ as the *E*-isomer (Fig. 2).

Similarly, reactions of **1b–e** and **2** afforded, respectively, products **3b–e** and **4b–e** in variable yields (**4e** was not obtained). It is remarkable that we never obtained even traces of the product from the insertion of the carbene moiety into the S–S bond and some attempts of reacting **1a–b** and **2** under the insertion conditions[12] (dioxane, 40 °C, 3 h) gave only traces of **3a–b** in addition to a complex mixture of unstable products from which the insertion product could not be found. The reaction of the simple 5-methyl-1,2-dithiole-3-thione **1d** and Fischer carbene **2** afforded, after aluminium oxide treatment, *E*-dithiafulvene thione **4d** as orange crystals suitable for single crystal X-ray diffraction, which again confirmed the structure of **4d**§ as the *E*-isomer (Fig. 3).

A plausible mechanism should consist of a very asynchronous[9] cycloaddition oriented from the thiono group of **1a–e** to the β-position of the Fischer carbene **2** as in **5** to give **3a–e** (Scheme 2).

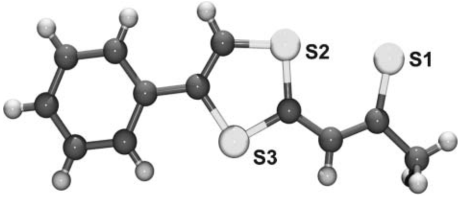
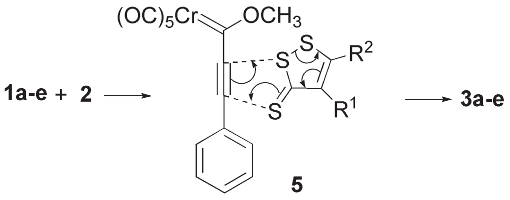


**Fig. 3** Single crystal X-ray diffraction structure of **4d**.



**Scheme 2** Mechanism of reaction of dithiolethiones **1a–e** and **2**.

As expected,[13] compound **1e** reacted only by the dithiolethiono moiety, and 5-cyclopentylthio-1,2-dithiole-3-one did not react with **2** under the same conditions.

In our case, also the complex between **1d** and chromium pentacarbonyl§ did not react with **2**, showing that the free thione group was necessary for the reaction. The demetalation–decarboxylation step has no direct precedent but a lateral elimination of methanol from a (2-oxacyclopentylidene)pentacarbonylchromium(0) complex by treatment with basic aluminium oxide in ether[14] as well as the formal substitution of an (allyloxy)carbene metal unit for hydrogen in a l-(allyloxy)-3-(4-methylphenyl)prop-2-yn-l-ylidenepentacarbonylchromium(0) derivative under treatment with silica, that promoted retro-Fischer reactions, are known,[15] therefore a elimination of methanol by hydrolysis on alumina, followed by elimination of chromium hexacarbonyl by a retro-Fischer reaction similar to Dötz's example, should appropriately give rise to **4a–d**.

Compounds **3a–e** and **4a–d** were stable in the solid state but they slowly isomerized in deuterated chloroform solution during the NMR spectra acquisition. The $^1H$ NMR spectra showed a small signal of the *E* or *Z* isomer respectively, that increased with time until reaching an equilibrium concentration. The $^{13}C$ NMR spectra showed an important amount of the corresponding geometric isomer due to the longer acquisition time required (see ESI‡). This fact was intriguing and the reason could be that these types of products have never before been described as pure regioisomers. To be sure that interconversion did not occur in the reaction mixture, we acquired $^1H$ NMR data ($\delta$ 4.8–8.2) of a crude ethereal reaction mixture of **3d** (0.5 mL) dissolved in $CDCl_3$ (0.5 mL) and compared the corresponding peaks to pure authentic samples of **1d** and **3d** dissolved in 1 : 1 $Et_2O$–$CDCl_3$ mixtures. 20 min after the preparation of the crude reaction mixture less than 4% of the minor isomer **3d** could be detected by NMR, somewhat less than the amount of minor isomer observed by NMR in a solution of pure **3d** 18 min after the preparation of the sample. Taking into account the uncertainty of the method, the regioselectivity of the reaction can be considered higher than 98% (see ESI‡).

In summary, we have shown the use of an alkynyl Fischer carbene complex as a traceless directing group for the regioselective cycloaddition of dithiolethiones to arylacetylene, which constituted a safe synthesis of *E*-dithiafulvene thione or dithioesters that are stable in the solid state but slowly interconvert in $CDCl_3$ solution to *Z*–*E*-mixtures.

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## Notes and references

§ CCDC 664202 (the complex between **1d** and chromium pentacarbonyl), 664203 (**3a**), 664204 (**4a**), 664205 (**4d**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b715857b

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