Synthetic Methods

Metal Carbene Dimerization: Versatile Approach to Polyalkynylethenes**

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In memory of Lorenzo Pueyo

The last years have witnessed an increasing interest in conjugated organic molecules and polymers due primarily to their potential applications as advanced materials, molecular wires, and switches, chemo- and biosensors, nonlinear optics (NLO), organic conductors, etc.[1] The main focus has been on molecules containing an ethene unit, which is surrounded by alkynyl or mixed alkynyl/alkenyl branches, because of their planarity, two-dimensional conjugation, and potential for acetylenic scaffolding.[2] Whereas the area of polyethynylethenes has been a motif of special emphasis, the access to hybrid ethynyl/ethenyl ethenes has been explored to a lesser extent.[3] Despite the fact that some dimerization reactions involving carbenoid species[4] or palladium catalysis[3] have been disclosed, most work has focused on protocols for dimer preparation by multiple $C_{(sp2)}$–$C_{(sp)}$ and $C_{(sp)}$–$C_{(sp)}$ coupling processes,[5] which generally require protection/deprotection steps.

Recently, we advanced that in situ generated, non-heteroatom stabilized alkynyl carbene complexes of group six metals dimerize below room temperature.[6] This finding indicates that transition-metal carbene complexes might actually be synthetically useful precursors of complex polyunsaturated molecules.[7,8] Described herein is a rapid, one-pot process to access a diverse array of enyne-based frameworks by a simple nucleophile-induced dimerization reaction of non-heteroatom–metal carbenes **2–5**, which are formed in situ from readily available Fischer methoxycarbene complexes **1** [Eq. (1)].[9]

The working model is outlined in Equation (1). This single process involves the low-temperature generation of alkynyl
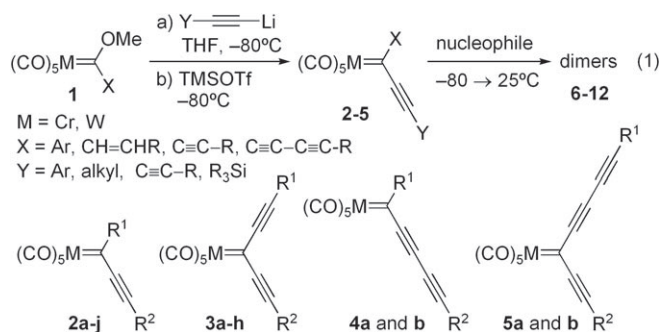
carbene complexes **2–5** (the R groups are defined in Schemes 1–4)[10] in THF by sequential treatment of alkoxycarbene complexes **1** with various lithium acetylides and trimethylsilyl triflate at −80°C. The solution was then warmed to room temperature in the presence of a substoichiometric amount of a nucleophile to provide an arsenal of different types of dimers (**6–12**; see below; Scheme 1–6). The types of metal carbene structures studied were based on the number of ethyne units in the dimer precursors: 1) alkynyl carbenes **2**, 2) cross-conjugated diynyl carbenes **3**, 3) linear-conjugated diynyl carbenes **4**, and 4) cross-conjugated triynyl carbenes **5**. As both chromium and tungsten complexes work similarly in terms of efficiency, only the organic framework of reagents **2–5** is outlined throughout the text, schemes, and tables (for the specific metal used in each case see the Supplementary Information). All the yields reported for dimers **6–12** refer to the one-pot process and represent the overall yield from metal carbenes **1**.

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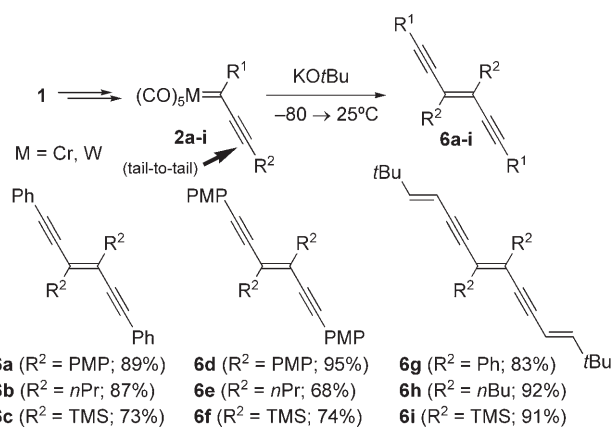
Scheme 1. Diethynylethene (DEE) scaffolds **6** from tail-to-tail dimerization of metal carbene complex **2**. PMP = 4-MeOC$_6$H$_4$; TMS = Me$_3$Si.

6a (R^2 = PMP; 89%)   **6d** (R^2 = PMP; 95%)   **6g** (R^2 = Ph; 83%)
6b (R^2 = nPr; 87%)   **6e** (R^2 = nPr; 68%)   **6h** (R^2 = nBu; 92%)
6c (R^2 = TMS; 73%)   **6f** (R^2 = TMS; 74%)   **6i** (R^2 = TMS; 91%)

Communications

The access to the diethynylethene scaffold (DEE) was first accomplished by starting from metal the alkynyl carbene (**2**). Thus, addition of KOtBu (0.5 equiv) to a solution of complex **2** (THF, −80°C), generated in situ from **1**, with subsequent warming to room temperature, the removal of volatiles, and then column chromatography afforded the dimeric products (**6**) in overall yields ranging from 68 to 95% from **1** (Scheme 1).[10] In all cases, the homocoupling takes place exclusively in a tail-to-tail fashion, with the *trans* stereoisomer being solely formed. Other than the participation of alkyl and aryl groups, valuable TMS (compounds **6c, f**, and **i**) and alkenyl (compounds **6g–i**) functional groups were efficiently incorporated.
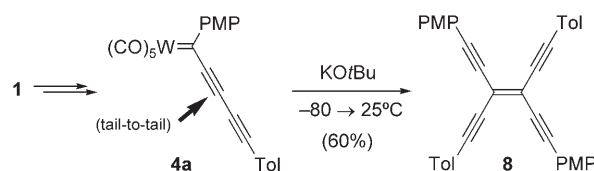
According to the regiochemistry observed, the synthesis of the more complex dibutadynylethene (DBDE) structure would be feasible by using cross-conjugated dialkynylcarbenes **3** (Scheme 2). Thus, symmetrical carbenes **3a** and **b**

Scheme 3. Tetraethynylethene (TEE) scaffold **8** from tail-to-tail dimerization of metal carbene complex **4**. Tol = 4-Me-C$_6$H$_4$.

with complete selectivity wherein the C$_\beta$ atom, rather than the C$_\delta$ atom, is solely involved.

The alkynyl homologated cross-conjugated triynyl carbene complexes (**5**) are very attractive because they may produce adducts of greater complexity. Moreover, the chemoselectivity is another interesting goal to be addressed as linear- or cross-conjugated structures might result (Scheme 4). Our first observation made it clear that the

Scheme 2. Dibutadynylethene (DBDE) scaffolds **7** from tail-to-tail dimerization of metal carbene complex **3**. TIPS = (Me$_2$CH)$_3$Si.
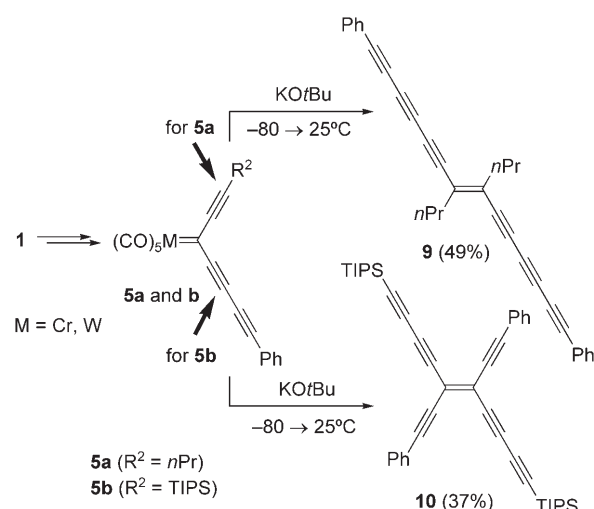
Scheme 4. Hexaethynylethene (HEE) scaffolds **9–10** from tail-to-tail dimerization of metal carbene complex **5**. TIPS = (Me$_2$CH)$_3$Si.

(R^1 = R^2 = Ph or PMP) dimerized as expected to afford **7a** and **b**, respectively (56–88% yield), as the only products. In the case of unsymmetrical carbenes **3c–h**, tail-to-tail dimerization products **7c–h** were obtained in overall yields ranging from 48 to 87% with complete chemo-, regio-, and stereoselectivity under the standard reaction conditions.[10] Significantly, these results also make clear that the resulting isomer can be predicted on the basis of the nature of R^1 and R^2, and on the proposed mechanism (initial nucleophilic attack at C$_\beta$–R^1 versus C$_\beta$–R^2; see Scheme 6). The directing effect of R^2 over R^1 can be explained by invoking either steric effects (compounds **7c** and **d**: preference of Ph over *t*Bu and TIPS, respectively; compounds **7e** and **f**: preference of TMS over *t*Bu and TIPS, respectively) or electron-based effects (compounds **7g–h**; preference of *n*Pr over Ph and PMP).
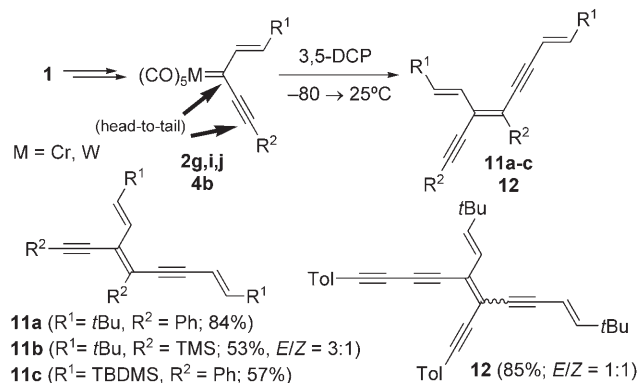
Moreover, the suitability of butadiynylcarbene metal complex **4** towards dimerization is exemplified in Scheme 3. In this case, the reaction allowed the preparation of the tetraethynylethene (TEE) scaffold (**8**) in good yield (60%).[10] The tail-to-tail dimerization reaction was found to take place

selectivity, and consequently the structure of the adduct not only depends on the substituent of the monoalkyne moiety, but also on the ability to control the reaction at either C$_\beta$ center (for comparison see the above discussion on the dimerization of the structurally analogous diynylcarbene complexes **3**, Scheme 3). Thus, the dimerization of complex **5a** (R^2 = *n*Pr) led exclusively to dihexatriynylethene (DHTE) scaffold **9** (49% yield), wherein the dimerization occurred through the C$_\beta$ carbon atom appended to the *n*Pr group. On the contrary, hexatriynylcarbene **5b** (R^2 = TIPS) cleanly dimerized by coupling of the C$_\beta$ center of the diyne branch (C$_\beta$–C≡C-Ph), rather than through the C$_\beta$ carbon atom appended to the TIPS group, to provide the mixed 1,2-diethynyl-1,2-dibutadiynylethene (DEDBDE) structure (**10**; 37% yield).[10]

Finally, additional efforts were made to expand this method by undertaking the head-to-tail and head-to-head dimerization. After screening several protocols (e. g. nature and amount of nucleophile, dimerization conditions, metal-

exchange/dimerization sequence) the head-to-tail dimerization was accomplished with excellent selectivity in the case of alkenyl-substituted carbene complexes of the types **2** and **4** (Scheme 5). Thus, addition of 3,5-dichloropyridine (3,5-DCP;

11a (R^1 = *t*Bu, R^2 = Ph; 84%)
11b (R^1 = *t*Bu, R^2 = TMS; 53%, *E/Z* = 3:1)
11c (R^1 = TBDMS, R^2 = Ph; 57%)

12 (85%; *E/Z* = 1:1)

Scheme 5. Mixed diethenyl/polyethynylethenes **11–12** from head-to-tail dimerization of metal carbene complexes **2** and **4**. 3,5-DCP = 3,5-dichloropyridine; TBDMS = (Me$_3$C)Me$_2$Si.

0.5 equiv) as the nucleophile to a THF solution containing the carbene complex (**2**) at −80°C, with subsequent warming to room temperature resulted in the stereoselective formation of the head-to-tail dimerization products (**11a–c**; ethenyldiethynylethene scaffold (EDEE)) along with small amounts of the head-to-head regioisomer (head-to-tail/head-to-head ratio: > 20:1 for **11a** and **b**; 10:1 for **11c**). The major components was readily isolated in pure form after flash column chromatography in 53–84% yields. Under the same reaction conditions, diynylcarbene **4** afforded the ethenyltriethynylethene scaffold (ETEE) (**12**) in 85% yield as a 1:1 *E/Z* diastereisomeric mixture.

Although a mechanistic explanation is not obvious at this stage, a tentative proposal is given in Scheme 6 for the formation of the different dimeric structures (**6–12**). Thus, conjugate addition of *t*BuO$^-$ or 3,5-DCP at the electrophilic C$_\beta$ of non-heteroatom-stabilized carbenes **2–5** would lead to the allenyl metallate species **I** and **III**. The nature of this intermediate, anionic **I** versus zwitterionic **III**, seems to direct the process. Thus, conjugate addition of intermediate **I** by its propargylic metallate structure to carbene complexes **2–5**
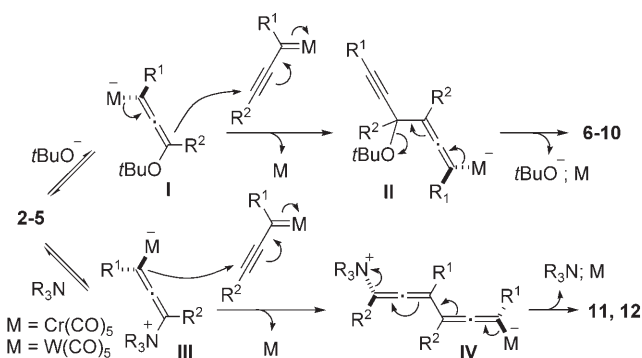
Scheme 6. Mechanistic proposals for the dimerization reactions.

would lead to intermediate **II**, which would afford adducts **6–10** upon the elimination of *tert*-butoxide and the metal.[11] On the contrary, zwitterionic species **III** undergoes conjugate addition by the allenyl metallate structure to carbenes **2** and **4** to generate intermediate **IV**, which evolves into dimers **11** and **12**, respectively upon the elimination of 3,5-DCP and the metal.

In conclusion, we have described a new family of polyalkynylcarbene complexes (**2–5**) and a preliminary study on their potential synthetic utility. The simple dimerization reaction not only provides an array of structurally-diverse and highly-conjugated molecules (**6–12**) with complete chemo-, regio- and stereoselectivity, but it also makes feasible the tailored access to other polyunsaturated systems, particularly the relevant ethane-based push-pull derivatives. Moreover, this finding makes these metal carbenes excellent and synthetically useful surrogates for very elusive nonmetal propargylic carbenes: 1) propynylidene **a** (metal carbenes **2**),

a (*n*=1); **b** (*n*=2); **c** (*n*=3)   **d** (*n*=1); **e** (*n*=2)
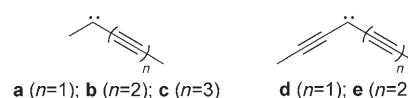
2) pentadiyn-1-ylidene **b** (metal carbenes **4**), 3) pentadiyn-3-ylidene **d** (metal carbenes **3**), 4) heptatriyn-1-ylidene **c** and heptatriyn-3-ylidene **e** (metal carbenes **5**).[12] The nature of the molecules produced, as well as the presence of the removable substituents for synthetic modification, provides a way to investigate these structures, particularly in the solid state (applications in materials science, nature of packing, etc).

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