

Zirconocene(II)-catalyzed Linear Dimerization of Terminal Alkynes

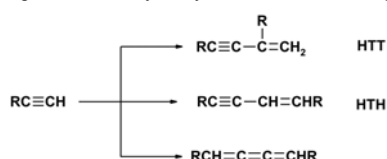
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Introduction

Linear dimerization of terminal acetylenes affording 2,4-disubstituted but-1-en-3-yne, head-to-tail dimers (HTT), (*E*)- and (*Z*)-1,4-disubstituted but-1-en-3-yne, head-to-head dimers (HTH), or rather rarely (*E*)- and (*Z*)-1,4-disubstituted buta-1,2,3-trienes is thermodynamically less favorable than their cyclotrimerization to benzene derivatives [1] and requires the catalysis by transition metal complexes.



The phenomenon of catalyzed dimerization of 1-alkynes was first described in 1961 for Cr and in 1962 for Cu catalysts; however, it has never been extensively studied, like e.g. polymerization or cycloaddition reactions. The reasons can be sought in low activity and/or selectivity of the catalysts which, on the other hand, did not stimulate eventual

research of applications of the dimers in organic synthesis. The dimers have the potential to be used as cross-linking reagents or building elements in constructions of supramolecular structures; so far, however, no such application has been reported. Accordingly, results of linear dimerization of 1-alkynes were only occasionally mentioned in reviews covering oligomerizations of alkynes and alkenes by particular metals [2].

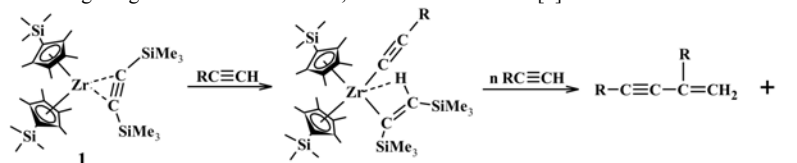
From transition metals of group IV, titanium-catalyzed dimerization of 1-alkynes has several unique features: an enzymatic-like selectivity for exclusive formation of head-to-tail dimers (for 1-alkynes not bearing electron donor atoms), apparently different catalytic cycles initiated by either Ti(III) [3a] or Ti(II) [3b] precursors, and an activity sharply controlled by unprecedented relationship between titanocene auxiliary ligands and the alkyne substituent. The latter phenomenon is complementary — the $[Ti(\eta^5-C_5Me_5)_2]$ -based catalysts dimerize all alkynes except *t*-butylethyne and the $[Ti(\eta^5-C_5HMe_4)_2]$ -based catalysts dimerize only this 1-alkyne [3]. In this contribution we report on results of zirconium based catalysts. The present state of art in investigations of the formation of catalytic species and of the dimerization mechanisms comprising substitution of zirconocene complexes will be given.

Materials and Methods

All manipulations, including spectroscopic measurements, were performed under vacuum, using all-sealed glass devices equipped with breakable seals. Low-valent zirconocene complexes were prepared by conventional methods from the tetravalent compounds via reduction by magnesium in the presence some stabilize ligands [4]. New compounds were characterized using standard spectroscopic methods (UV-near-IR, NMR, EI-MS, X-ray analysis and IR spectroscopy).

Results and Discussion

The reactivity of zirconocenes (Zr^{II}) can be very conveniently studied using them in a form of their η^2 -bis(trimethylsilyl)ethyne (BTMSE) complexes. BTMSE is an excellent replaceable ligand which can be substituted by a number of electron donor reagents, including other alkynes. The reactions of highly-substituted zirconocene-BTMSE complexes with terminal alkynes result in the formation of agostic alkenyl-alkynyl complexes. The zirconium atom binds one terminal alkynyl group whereas the hydrogen is transferred to btmsa to generate the alkenyl group. The methyl substituted complexes do not react further with excess terminal alkynes, however when one methyl group is replaced by different substituent such as $SiMe_3$ the electronic and steric properties are changed being suitable for the catalytic reactions. The $SiMe_3$ substituted alkenyl-alkynyl complexes formed in situ from the zirconocene - btmsa complexes and *tert*-butylethyne dimerized this alkyne exclusively to head-to-tail isomer, achieving a high total turnover number, albeit with a low rate [5].



The present state of art in investigations of new zirconocene complexes with *t*-Bu or Ph groups will be presented and discussed.

Significance

This contribution discussed the effect of substituents on the cyclopentadienyl ligand in new zirconocene complexes which have an important influence on the electronic properties of the metal centre that is active in catalytic reactions. The understanding of the effect has been beneficial for fundamental research as well as for industrial relevance.

References

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