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Tantalum pentachloride-catalyzed reactions of alkynes with Et_3Al

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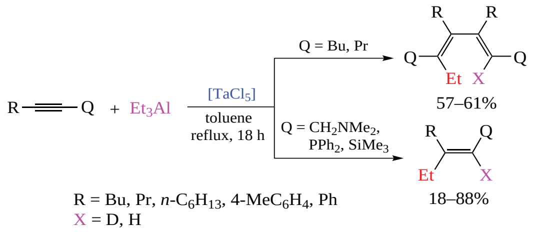
Tantalum pentachloride-catalyzed reaction of 1,2-dialkylacetylenes with Et_3Al affords regio- and stereoselectively tetraalkyl-substituted (*Z*,*E*)-hexa-1,3-dienes and (*Z*)-trisubstituted olefins in a ratio of 2 : 1. In cases of 1-alkynylphosphines, 1-alkynylsilanes and 2-alkynylamines, the corresponding functionalized monoolefins are formed.



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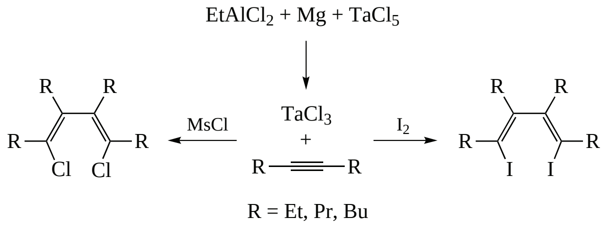
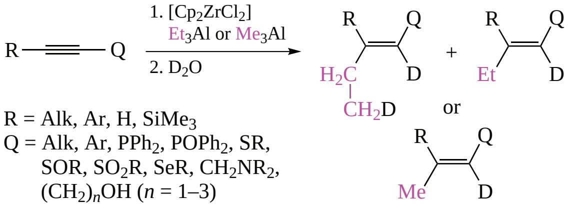
Organic and inorganic derivatives of tantalum are widely used in the synthesis of amides[1–5] and olefins.[6–9] Low-valent tantalum complexes also initiate alkyne trimerization reactions.[10–12] An unusual cleavage of the carbon–heteroatom bond (C–S) occurs as a result of the interaction of tantalum pentakis(dimethylpyrazolate) with CS_2 to form compound $[Ta(=S)(dmpz)_2\{(dmpz)_3CS\}]$.[13] Although $TaCl_5$-catalyzed carbomagnesation of α-olefins is known,[14–16] there are no examples of Ta-initiated carbometallation of alkynes in the literature. Carbometallation of acetylenic compounds under the action of transition metal catalysts is one of the effective tools for the selective synthesis of various tri- and tetrasubstituted olefins.[17–26] At present, we have discovered $TaCl_5$-promoted homocoupling of alkynes under the action of the $EtAlCl_2$–Mg reagent system with selective formation of buta-1,3-dienes (Scheme 1).[27] However, this approach is limited to carboalumination of 1,2-dialkylacetylenes and does not allow carbometallation of functionally substituted alkynes.



Scheme 1

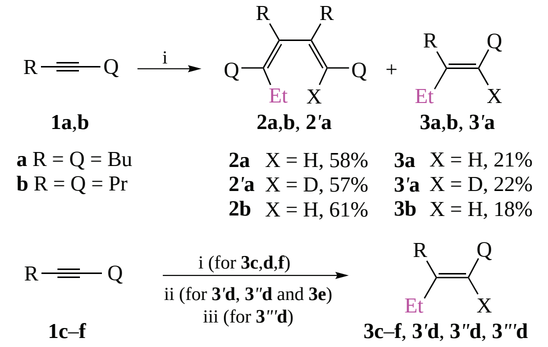
The found transformation is the only example of the selective production of buta-1,3-dienes under the conditions of the carboalumination reaction. Despite detailed studies of alkyne carboalumination reactions using the Et_3Al–Cp_2ZrCl_2 reagent system, there are no effective methods of intermolecular coupling of acetylenic compounds under the action of zirconocene. Thus, Negishi was the first to demonstrate that the reaction of diphenylacetylene with Et_3Al in the presence of 10 mol% Cp_2ZrCl_2 in benzene at 55 °C was accompanied by the formation of a 1 : 1 mixture of ethyl-substituted olefin and diene with a total yield of 90%.[28] However, the Cp_2ZrCl_2-catalyzed carboalumination of dec-5-yne under the Negishi[28] conditions was accompanied only by the formation of an ethyl-substituted olefin, (*Z*)-5-ethyldec-5-ene. Zirconium-catalyzed carboalumination of both non-functionalized[20,21,28] and functionally substituted alkynes was accompanied by the selective formation of olefins[17,29–36] (Scheme 2).



Scheme 2

In this article, we report on studies of the $TaCl_5$-catalyzed carboalumination of acetylenic compounds using Et_3Al. We found that the reaction of 1,2-dialkylacetylenes **1a**,**b** with 4 equiv. of Et_3Al in the presence of 20 mol% $TaCl_5$ in toluene at reflux for 18 h and subsequent hydrolysis leads to regio- and stereoselective formation of tetraalkyl-substituted (*Z*,*E*)-hexa-1,3-dienes **2a**,**b** and minor (*Z*)-trisubstituted olefins **3a**,**b** (see Scheme 1). When the reaction was quenched with D_2O, the corresponding deuterium-containing products **2′a** and **3′a** were obtained. However, in cases of functionalized alkynes **1c–f** only monoolefins of type **3**, ethylalumination products, were exclusively formed (Scheme 3). The structure of the resulting compounds was established using 1D- and 2D-NMR spectroscopy.

In the literature, we found only two examples of the formation of substituted hexa-1,3-dienes from alkynes under the action of organometallic compounds. It is known that the Zr-catalyzed reaction of ethylene with tetraalkyl-substituted magnesacyclopentadienes results in structurally identical hexa-1,3-dienes.[37] The previously discovered Ti–Mg-catalyzed reaction of dialkyl-substituted alkynes with Et_2Zn also affords substituted hexa-1,3-dienes.[38] The exclusive formation ethylalumination products



a R = Q = Bu
b R = Q = Pr

2a X = H, 58% **3a** X = H, 21%
2′a X = D, 57% **3′a** X = D, 22%
2b X = H, 61% **3b** X = H, 18%

1c R = *n*-C_6H_{13}, Q = CH_2NMe_2
1d R = Bu, Q = PPh_2
1e R = 4-MeC_6H_4, Q = PPh_2
1f R = Ph, Q = $SiMe_3$

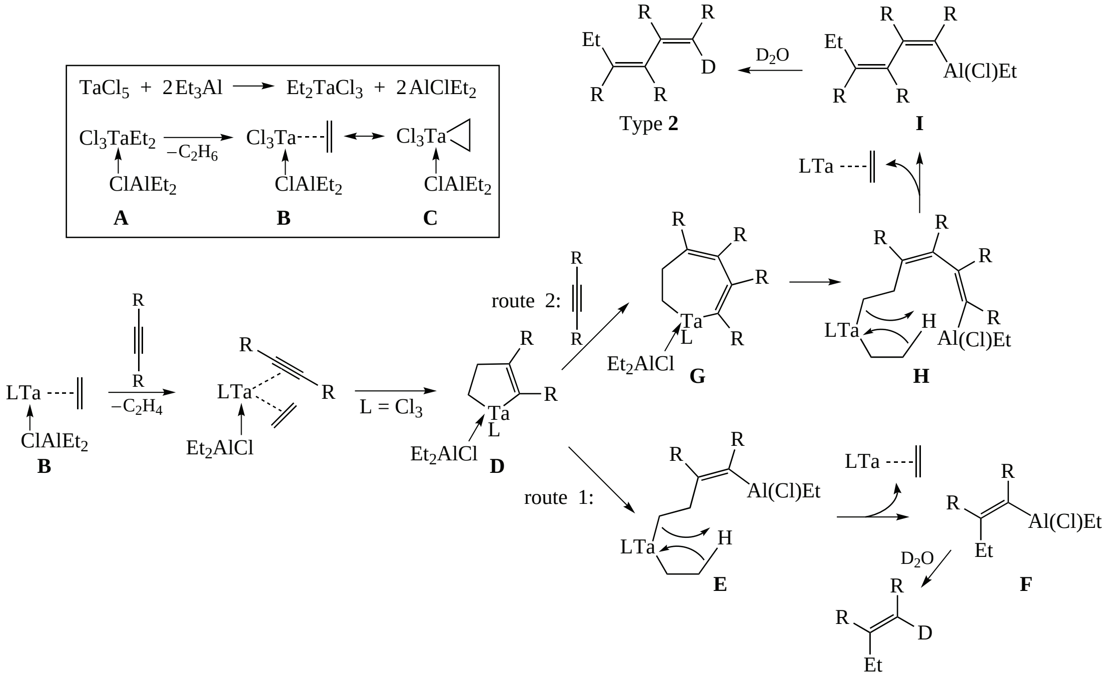
3c R = *n*-C_6H_{13}, Q = CH_2NMe_2, X = H, 88%
3d R = Bu, Q = PPh_2, X = H, >95%
3′d R = Bu, Q = $P(O)Ph_2$, X = H, 83%
3″d R = Bu, Q = $P(O)Ph_2$, X = D, 79%
3‴d R = Ph, Q = $P(S)Ph_2$, X = H, 74%
3e R = 4-MeC_6H_4, Q = $P(O)Ph_2$, X = H, 70%
3f R = Ph, Q = $SiMe_3$, X = H, 81%

Scheme 3 *Reagents and conditions*: i, $TaCl_5$ (0.2 equiv.), Et_3Al (4 equiv.), toluene, reflux, 18 h, then H_2O or D_2O; ii, the same, with final treatment with 30% H_2O_2 (1.5 equiv.) and $CHCl_3$ (5 ml), room temperature, 8 h; iii the same, with preliminary treatment with elemental sulfur (5.3 equiv., room temperature, 8 h) prior to final hydrolysis.

from functional alkynes **1c–f** has some reported analogies. Previously, we have shown that Ti–Mg-catalyzed 2-zincoethylzincation[39] and Zr-catalyzed 2-aluminamethylalumination of 1-alkynylphosphines[32] and 2-alkynylamines[31] lead selectively to the corresponding (*Z*)-alkenylphosphines and amines.

We hypothesized the following reaction mechanism. According to Scheme 4, the ligand exchange between $TaCl_5$ and Et_3Al gives an unstable diethyltantalum intermediate **A**, which is further converted into tantalacyclopropane intermediate **C** (or into a complex of low-valent tantalum **B** stabilized with an ethylene ligand). A similar reduction of $TaCl_5$ to ‘$TaCl_3$’ was proposed in the reaction of Ta-catalyzed olefin carbomagnesation at a step of $TaCl_5$ alkylation with *n*-alkylmagnesium Grignard reagents.[13] Further insertion of the triple bond of an alkyne at the Ta–C bond of tantalacyclopropane **C** leads to tantalacyclopentene intermediate **D** (see Scheme 4, route 1). The ligand exchange between tantalacyclopentene **D** and Et_2AlCl molecule results in the formation of a bimetallic intermediate **E**. The formation of a similar bimetallic complex is postulated in the Zr-catalyzed ethylmagnesation of non-activated olefins.[40] The subsequent transfer of the β-hydrogen atom of the ethyl group at the tantalum atom of the bimetallic complex **E** leads to the regeneration of tantalacyclopropane **C** and the formation of the ethylalumination product **F**. We believe that the metal–carbon bond of tantalacyclopentene **D**, where the tantalum atom is bonded to a more nucleophilic sp^2-hybridized carbon atom, is more reactive with respect to the second alkyne molecule, which can promote the incorporation of the second molecule of the acetylene substrate with the formation of a seven-membered complex **G** (route 2). Further ligand exchange between the **G** complex and the Et_2AlCl molecule leads to a bimetallic complex **H**. The subsequent transfer of the β-hydrogen atom of the ethyl group at the tantalum atom of the **H** complex provides the regeneration of tantalacyclopropane **C** and the formation of aluminahexadiene **I**. One of the experimental evidences of the proposed scheme is that the deuterolysis affords the corresponding monodeuterated olefins **3′a**, **3″d** and diene **2′a**. According to Scheme 3, carboalumination of functionally substituted alkynes does not give substituted hexadienes. Apparently, in the case of carboalumination of alkynylsilane **1f**, the bulky trimethylsilane group located in the α-position to the tantalum atom in the **D**-type complex exerts steric shielding of the reaction center, which prevents the formation of a seven-membered complex responsible for the formation of substituted hexadienes. It is possible that the interaction between the nitrogen atom or phosphorus atom in the **D**-type complex (substrates **1c–e**) and the Et_3Al (or Et_2AlCl) molecule reduces the nucleophilicity of the sp^2-hybridized carbon atom at the tantalum atom that reduces the polarity of the $C(sp^2)$–Ta bond and suppresses the insertion of the second alkyne molecule into the metal–carbon bond of tantalacyclopentene **D**. Thus, the chemoselectivity of the $TaCl_5$-catalyzed reaction of alkynes with Et_3Al strongly depends on steric and electronic factors.

In conclusion, we have established that the $TaCl_5$-catalyzed reaction of 1,2-dialkylacetylenes with Et_3Al gives regio- and stereoselectively tetraalkyl-substituted (*Z*,*E*)-hexa-1,3-dienes and trisubstituted (*Z*)-olefins in ratios of 2 : 1. Similar ethylalumination of 1-alkynylphosphines, 1-alkynylsilanes and 2-alkynylamines affords only the corresponding functional



Scheme 4

monoolefins. A plausible scheme was proposed for the $TaCl_5$-catalyzed transformations of dialkyl-substituted acetylenes, alkynylphosphines and amines under the action of Et_3Al. Taking into account the efficiency of the reaction for the conversion of alkynylphosphines and amines into phosphorus- and nitrogen-containing olefins, we plan to develop selective methods for the preparation of alkenyl sulfides and alcohols, as well as linear and cyclic amines, based on the current findings.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2023.09.032.

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