Alkynyldichlorogalliums are Unstable in Hydrocarbon Solvents Dimerization of Alkynyldichlorogalliums *via* Carbogallation

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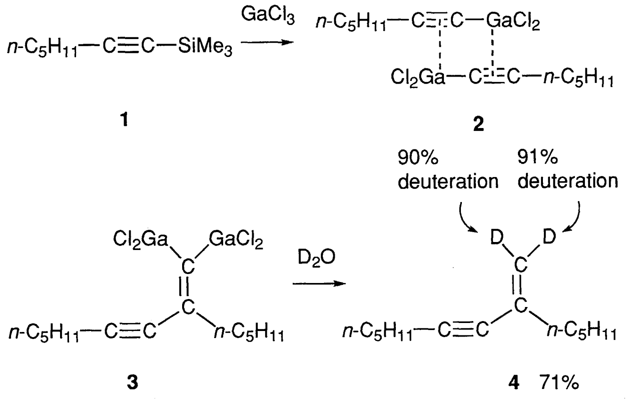
(Received August 31, 1995)

Alkynyldichlorogalliums dimerize in hydrocarbon solvents *via* carbogallation giving 1,1-dimetallo-1-buten-3-yne derivatives.

Main element alkynyl metals are versatile intermediates in organic synthesis. They are usually stable at ambient temperature in the absence of water and oxygen. During our synthetic studies using alkynylmetals,[1] we found that alkynyldichlorogalliums spontaneously dimerized in hydrocarbon solvents giving 1,1-dimetallo-1-buten-3-yne derivatives.

Treatment of alkynyltrimethylsilanes with $GaCl_3$ (1.0 mol eq) in methylcyclohexane at room temperature for 30 min gave dimeric products after aqueous workup (Table 1). They possess enyne structure and not butadiyne structure. The reaction also proceeded in hexane and benzene, but not in methylene chloride and acetonitrile. Since treatment of an alkynyllithium and an alkynyltributyltin with $GaCl_3$ also gave the enyne at -20 °C, alkynylgallium intermediates are involved in these reactions. Presence of 2,6-di(*t*-butyl)-4-methylpyridine (0.1 mol eq) inhibited the oligomerization of 1-alkyne, and improved the yield of the coupling product. 1-Alkynes with primary and secondary alkyl groups dimerized readily, while *t*-butylacetylene did not. The moderate yield of phenylacetylene dimerization is partly due to instability of the product.

It is reasonable to assume that the dimerization proceeds *via* alkynyldichlorogalliums, since alkynyldimethylgalliums are stable in hydrocarbon solvents.[2] Formation of 1,1-dimetallo-1-buten-3-yne **3** was indicated by deuteration experiments (Scheme 1). When reaction of 1-(trimethylsilyl)-1-heptyne (**1**) and $GaCl_3$ was quenched with D_2O, deuterium was incorporated at both methylene protons of enyne **4**. NMR spectra of the reaction mixture did not show any sign of olefinic proton. While carboalumination reaction of alkynes is well documented,[3] the carbogallation reaction is not known. The alkynylgallium, however, dimerize more readily than the alkynylaluminum, since treatment of $AlCl_3$ with an alkynyllithium gave low yield of the dimer. Other group 13 metal salts, $GaBr_3$, $Ga(OTf)_3$, $EtAlCl_2$, Et_2AlCl, $InCl_3$, and TlCl were not effective. Although certain transition metal complexes promote such alkyne dimerization,[4] their mechanisms are different from the present reaction.

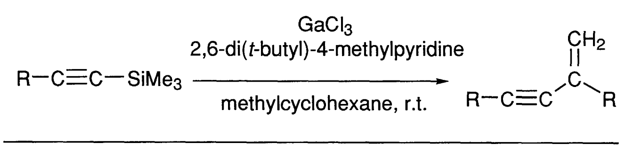


Scheme 1.

Since 1-alkyne with tertiary substituent was inert to the dimerization, cross-coupling was conducted (Scheme 2). Addition of $GaCl_3$ (4 mol eq) to a mixture of lithiated 1-alkyne (1 mol eq) and *t*-butylacetylene (3 mol eq) gave the expected cross-coupling product, the structure of which was determined by NOE studies. The bulky 1-alkyne serves as the donor of the carbogallation reaction.

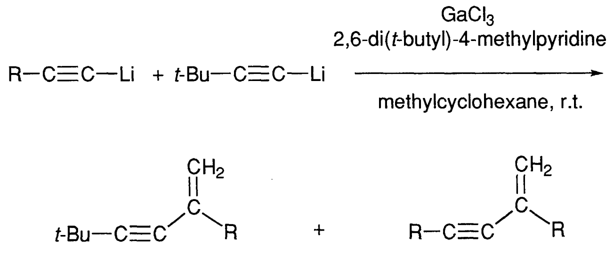
The above studies revealed the unusual instability of alkynyldichlorogalliums. Alkynyldimethylgalliums are dimeric in benzene,[5] and are assumed to possess π-coordinated structure

Table 1. Dimerization of alkynylsilanes promoted by $GaCl_3$[a]



R	yield / %
n-C_5H_{11}	85
n-$C_{11}H_{23}$	73 (8)[b]
	58 (23)[b,c]
cyclo-C_6H_{11}	81, 69[d]
(*S*)-$(CH_3)_2C{=}CH(CH_2)_2CH(CH_3)CH_2$	74
$CH_3(CH_2)_9CH(CH_3)$	74
Ph	38

[a] Reactions were conducted in 1.0 mmol scale. [b] Shown in parenthesis is the yield of alkyne oligomers. [c] Yields in the absence of 2,6-di-(*t*-butyl)-4-methylpyridine. [d] The reaction was conducted in 10 mmol scale.



R = *cyclo*-C_6H_{11}: 60 % (4.5 : 1)
R = *n*-C_5H_{11}: 69% (6 : 1)

Scheme 2.

such as **2** by analogy with the solid state structure of alkynyldimethylindium (Scheme 1).[2] In view of this knowledge and our recent works on alkynyltrichlorotins,[1] we are tempted to think that the strong perturbations on the π-electrons exerted by the π-coordinated $GaCl_2$ and/or by the covalently bonded $GaCl_2$ destabilize **2**, which then collapses to **3** *via* carbogallation. Solvent complexation with alkynyldichlorogallium may be the reason of the inertness in polar solvents. Although organogalliums have scarcely been used in organic synthesis, they appear to possess interesting properties.

Typical experimental procedure is as follow. Under an argon atmosphere, 1.0 M solution of $GaCl_3$ in methylcyclohexane (10 mL, 10 mmol) was added to a mixture of 1-trimethylsilyl-2-cyclohexylacetylene (1.8 g, 10 mmol) and 2,6-di(*t*-butyl)-4-methylpyridine (0.21g, 1.0 mmol) in methylcyclohexane (50 ml) at room temperature. After stirring for 30 min at the temperature, water was added. Organic materials were extracted twice with ethyl acetate, washed with water and brine, dried over Na_2SO_4, and concentrated. Flash column chromatography on silica gel (hexane) gave 2,4-dicyclohexyl-1-buten-3-yne (0.75 g, 69%). Identical spectral data were obtained with the reported values.[6] When the reaction was conducted in 1.0 mmol scale, the product was obtained in 81% yield.

This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, and Culture, Japan (No. 07554065). Generous gifts of silicon reagents from Shin-Etsu Chemical Co., LTD. are also gratefully acknowledged.

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