

Preliminary communication

CONTROLLED CARBOMETALLATION

II*. THE ADDITION REACTION OF TRIMETHYLALANE-TITANOCENE DICHLORIDE WITH ACETYLENES**

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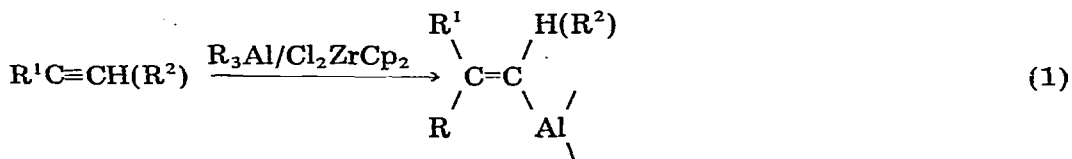
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Summary

An organometallic complex obtained by mixing Me_3Al and Cl_2TiCp_2 reacts with acetylenes to form monocarbometallated products in favorable cases, while dehydrometallation and polymerization compete in the cases of dialkylacetylenes having propargylic hydrogens and terminal acetylenes, respectively.

We have recently reported a highly stereoselective carbometallation reaction of $\text{R}_3\text{Al}/\text{Cl}_2\text{ZrCp}_2$ with acetylenes shown in eq.1 [1].



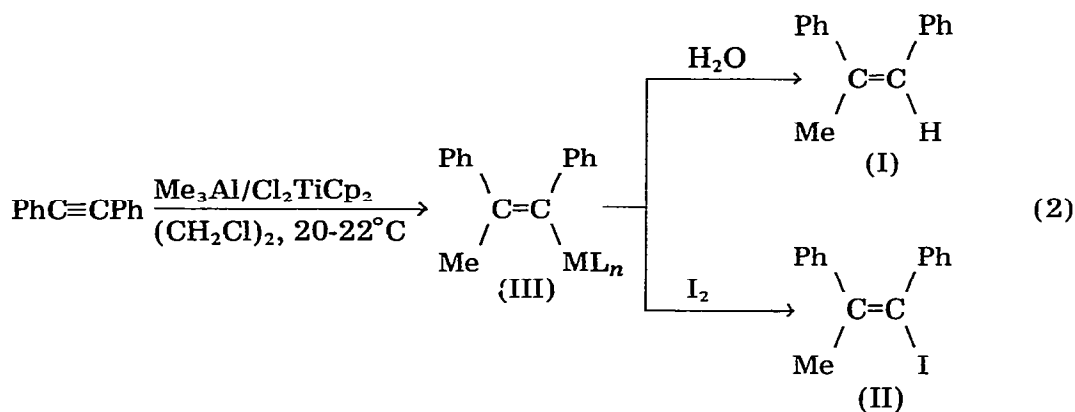
We now wish to report some preliminary results on the reaction of a complex obtained by mixing trimethylalane and titanocene dichloride, Cl_2TiCp_2 , with acetylenes.

Diphenylacetylene was initially chosen as a test system and its reaction with a 1/1 mixture of Me_3Al and Cl_2TiCp_2 , which is known to produce via $\text{Me}-\text{Cl}$ exchange $\text{Cl}(\text{Me})\text{TiCp}_2$ and Me_2AlCl in high yield [2], was carried out as follows. To a dark orange-red solution of Me_3Al (1.44 g, 1.92 ml, 20 mmol) and Cl_2TiCp_2 (4.98 g, 20 mmol) in 40 ml of 1,2-dichloroethane kept under an atmosphere of nitrogen was added diphenylacetylene (1.78 g, 10 mmol) at

*For part I see ref. 1.

**We wish to dedicate this paper to Professor Herbert C. Brown on the occasion of his 66th birthday.

room temperature (20–22°C). After stirring the reaction mixture for 12 h at this temperature, an aliquot was quenched with water (several hours at 20–22°C). GLC examination indicated the formation of (*Z*)- α -methylstilbene (I), 84% GLC yield; m.p. 46.5–47°C (lit. [3] m.p. 48°C), along with a very minor amount (<3%) of an unidentified by-product with a somewhat longer retention time (SE-30). No other product was detected by GLC. The ¹H NMR [4], ¹³C NMR and IR [5] spectra of I indicated the essential absence ($\leq 2\%$) of the (*E*)-isomer. Another aliquot of the diphenylacetylene/Me₃Al/Cl₂TiCp₂ reaction mixture was quenched with iodine (3 mol of I₂/1 mol of Me₃Al). GLC examination indicated the formation of (*E*)-1-iodo-1,2-diphenylpropene (II): yield by GLC 75%; ¹H NMR (CCl₄, Me₄Si) δ 2.63 (s, 3H) and 7.10 (m, 10H) ppm. Its stereochemistry was established by converting it to $\geq 97\%$ pure I by treatment with *n*-butyllithium followed by protonation.

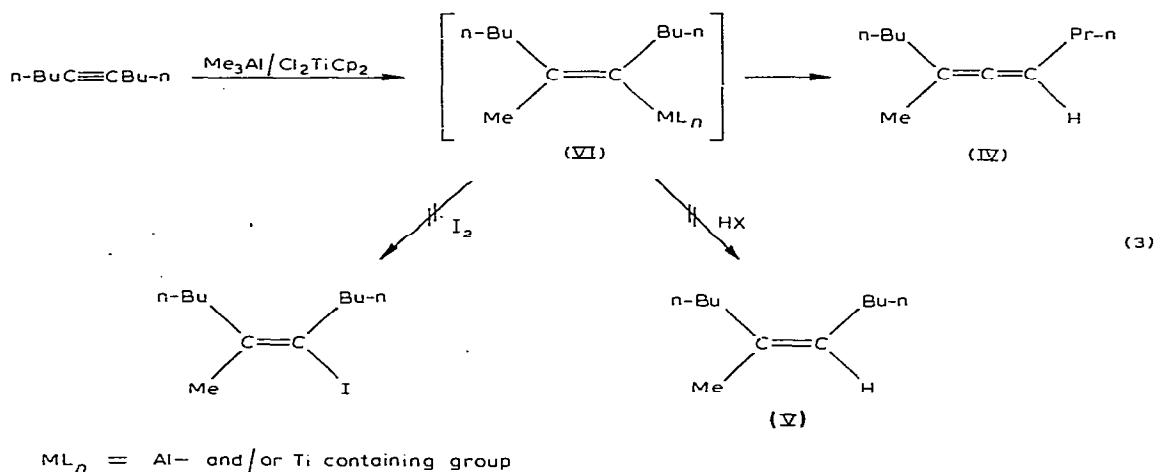


ML_{*n*} = Al- and/or Ti-containing group

The results presented above clearly indicate that the reaction produced in high yield an (*E*)-1,2-diphenyl-1-propenylmetal derivative represented by III as a discrete intermediate in a highly stereoselective manner. Unfortunately, our attempts to clarify the nature of the carbon–metal bond in III by NMR have been severely hampered by the formation of paramagnetic species under the reaction conditions. Coleman and his co-workers [6] have previously reported a few related reactions of alkynols with Al–Ti complexes which are reported to require the presence of an appropriately located hydroxy group. It has also been reported recently that photolysis of a solution of Me₂TiCp₂ and diphenylacetylene produced the *cis*-methyltitanated addition compound in 18% yield [7]. However, the results presented here appear to represent the first reported mono-carbometallation in high yield of a simple acetylene which does not contain any hetero-functional group with an Al–Ti complex reagent. It should also be pointed out that the corresponding reaction of diphenylacetylene with Me₃Al/Cl₂ZrCp₂ is not only much slower than the above-described Ti reaction, producing I in only a low yield (<30%), but also complicated by the formation of an unidentified by-product, presumably a chlorinated α -methylstilbene. Thus, at least in some such cases, the Ti reaction appears superior to the Zr reaction.

Quite unexpectedly, the reaction of 5-decyne with Me₃Al/Cl₂TiCp₂ under

essentially the same reaction conditions as in the reaction of diphenylacetylene produced 6-methyl-4,5-decadiene (IV) in 92% yield: n_D^{18} 1.4516; ^1H NMR (CCl_4 , Me_4Si) δ 0.7–1.1 (m, 6H), 1.1–1.6 (m, 6H), 1.63 (d, J 3 Hz, 3H), 1.7–2.2 (m, 4H), and 4.7–5.1 (m, 1H) ppm; ^{13}C NMR (CDCl_3 , Me_4Si) δ 13.75, 14.05, 19.36, 22.60, 22.79, 30.10, 31.82, 34.07, 90.08, 99.12 and 209.00 ppm; IR (neat) 1970w cm^{-1} . The expected product, 5-methyl-5-decene (V), was not detected by either GLC or NMR. The ^1H NMR spectrum of the reaction mixture was not informative due to broadening of the signals caused presumably by the presence of paramagnetic Ti species. Attempted iodination and deuteration of the presumed carbometallated product (VI) did not produce any iodinated and deuterated C_{11} -products, respectively. We therefore conclude tentatively that the carbometallation of 5-decyne took place as expected but that the carbometallated product (VI) underwent dehydro-metallation under the carbometallation conditions (eq. 3).

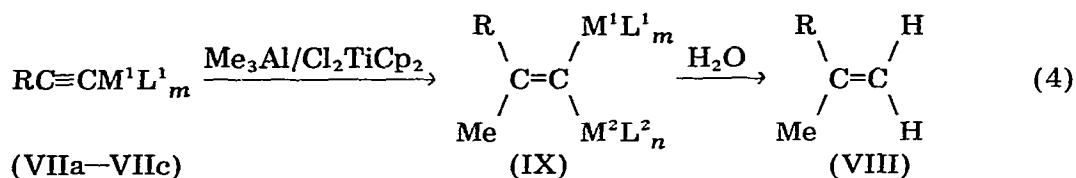


Terminal acetylenes, such as 1-octyne, react readily with $\text{Me}_3\text{Al}/\text{Cl}_2\text{TiCp}_2$. However, the yields of the monocarbometallated products have been generally low, the maximum yield of 2-methyl-1-octene obtained from 1-octyne being 25%. GLC examination (SE-30) of this reaction mixture indicated the presence of at least three closely bunched peaks of significant sizes in the region where dimeric products are expected to appear. The ^1H NMR spectrum of the crude isolated mixture shows singlets at δ 1.70 and 1.73 ppm and multiplets at δ 4.7–7.0 ppm with a relatively sharp dominant singlet at δ 5.96 ppm. These data together with its IR and ^{13}C NMR spectra indicate the presence of methyl-substituted olefins, although no further attempts have yet been made to fully identify these compounds.

In order to overcome the two major limitations associated with alkyl-substituted acetylenes and terminal acetylenes, we turned our attention to the carbometallation of metal-substituted alkynes represented by VII. 1-Octyne was chosen as a test system and was converted to 1-octynylzinc chloride (VIIa) by lithiation with *n*-butyllithium followed by treatment with ZnCl_2 , 1-octynyldicyclohexylborane (VIIb) by a reported procedure [8], 1-

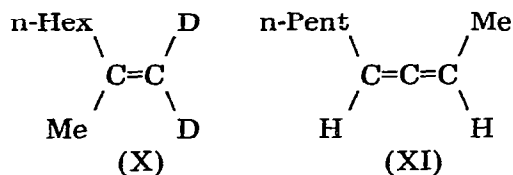
octynyldimethylalane (VIIc) by the reaction of 1-octyne with Me_3Al at 85°C [9], and 1-octynyltrimethylsilane (VIId) by treating 1-octynyllithium with trimethylchlorosilane.

We were pleased to find that all four acetylenes VIIa–VIId reacted smoothly with $\text{Me}_3\text{Al}/\text{Cl}_2\text{TiCp}_2$ under essentially the same conditions as in the previous cases. Hydrolysis of the carbometallated mixtures derived from VIIa, VIIb and VIIc produced 2-methyl-1-octene (VIII) in 75, 81, and 84% yields, respectively, indicating that these reactions took place according to eq. 4.



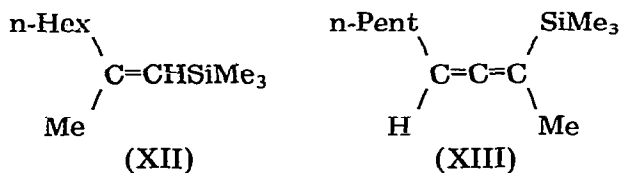
$\text{R} = n\text{-C}_6\text{H}_{13}$; $\text{M}^1\text{L}^1_m = \text{ZnCl}, \text{BR}_2$, or AlR_2 ; $\text{M}^2\text{L}^2_n = \text{Al}$ - and/or Ti -containing group

The intermediacy of the geminally dimetal-substituted alkenes (IX) has been further supported by the formation of >95% pure 1,1-dideuterio-2-methyl-1-octene (X) from VIIa and VIIc. No attempt has been made to convert VIIb into X.



In no case was there any indication for the formation of 2,3-nonadiene (XI), which was expected to be formed via dehydrometallation of the regioisomer of IX, in any greater than 2–3% yield. These reactions must therefore be highly regioselective. The facile hydrolysis of the carbometallated intermediate derived from VIIb producing VIII was somewhat unexpected. The exact course of the reaction is currently under investigation.

1-Octynyltrimethylsilane (VIId) also underwent a facile reaction with $\text{Me}_3\text{Al}/\text{Cl}_2\text{TiCp}_2$ at room temperature. Somewhat disappointingly, however, the product obtained in 80% combined yield, after hydrolysis, proved to be a 70/30 mixture of XII and XIII identified spectroscopically as the mixture.



Although the scope, synthetic utility and mechanistic details of the new carbometallation reaction of acetylenes remain to be further investigated, the results presented in this paper suggest that the present Al–Ti reaction and the recently reported Al–Zr reaction [1] would often be complementary

to each other. Specifically, we note that the considerably faster rate of the Al—Ti reaction as compared with that of the Al—Zr reaction would prove advantageous in dealing with relatively unreactive acetylenes. The reaction also promises as a potentially attractive route to geminally dimetal-substituted olefins.

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References

- 1 D.E. Van Horn and E. Negishi, *J. Amer. Chem. Soc.*, **100** (1978) 2252.
- 2 K. Clauss and H. Bestian, *Liebigs Ann. Chem.*, **654** (1962) 8.
- 3 D.J. Cram and F.A. Abd Elhafez, *J. Amer. Chem. Soc.*, **74** (1952) 5828.
- 4 A.F. Casy, A. Parulkar and P. Pocha, *Tetrahedron*, **24** (1968) 3031.
- 5 The Sadtler Standard Infrared Spectra No. 1932 and 2081.
- 6 (a) T.V. Harris, R.A. Coleman, R.B. Dickson and D.W. Thompson, *J. Organometal. Chem.*, **69** (1974) C27; (b) H.E. Tweedy, R.A. Coleman and D.W. Thompson, *ibid.*, **129** (1977) 69; (c) L.C. Smedley, H.E. Tweedy, R.A. Coleman and D.W. Thompson, *J. Org. Chem.*, **42** (1977) 4147.
- 7 W.H. Boon and M.D. Rausch, *J. Chem. Soc. Chem. Commun.*, (1977) 397.
- 8 H.C. Brown and J.A. Sinclair, *J. Organometal. Chem.*, **131** (1977) 163.
- 9 (a) T. Mole and J.R. Surtees, *Austral. J. Chem.*, **17** (1964) 1229; (b) J.J. Eisch and W.C. Kaska, *J. Organometal. Chem.*, **2** (1964) 184; (c) R. Rienäcker and D. Schwengers, *Liebigs Ann. Chem.*, **737** (1970) 182.