



## Unusual pathway of the tantalum-catalyzed carboalumination reaction of alkenes with triethylaluminum



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### ABSTRACT

Carboalumination of 1-alkenes (1-hexene, 1-octene, 1-decene) with  $\text{Et}_3\text{Al}$  in the presence of catalytic amounts of  $\text{TaCl}_5$  results in a mixture of 2-(*R*-substituted)- and 3-(*R*-substituted)-*n*-butylaluminums (1:1 ratio) in total yields of 75–85%. The  $\text{TaCl}_5$ -catalyzed reaction of bicyclo[2.2.1]hept-2-ene, *endo*-tricyclo[5.2.1.0<sup>2,6</sup>]deca-3,8-diene, and (*exo/endo*)-5-methylbicyclo[2.1.1]hept-2-ene with  $\text{Et}_3\text{Al}$  leads to the formation of diethyl[2-*exo*-(2'-norbornylethyl)]aluminums in high yields. DFT calculations confirm the thermodynamic preference of the final *exo* product. The multistep reaction mechanisms for the formation of the resultant organoaluminums through tantalacyclopentanes as key intermediates are also discussed.

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The carboalumination reaction is widely used as an efficient procedure for the construction of the metal–carbon and carbon–carbon bonds giving rise to new types of higher organoaluminum compounds (OACs). The catalytic systems for this reaction based upon titanium and zirconium compounds or complexes are recognized to be the most active and well studied (Scheme 1).<sup>1</sup>

However, there is practically no data in the literature regarding the catalytic behavior of Ta complexes and compounds in the reaction between OACs and unsaturated hydrocarbons, though Ta and Nb complexes are reported to catalyze dimerization, codimerization, and oligomerization of 1-alkenes,<sup>2</sup> as well as metathesis<sup>3</sup> and polymerization of ethylene.<sup>4</sup>

In this Letter, we report the first use of  $\text{TaCl}_5$  as a catalyst for the carboalumination of linear alkenes and norbornenes with  $\text{Et}_3\text{Al}$ .

Our preliminary experiments showed that  $\text{TaCl}_5$  catalyzed the reaction between 1-alkenes and  $\text{Et}_3\text{Al}$ . But, in this case, the major products differed from those obtained with Ti and Zr complexes as shown in Scheme 1. We continued our investigations by studying the Ta-catalyzed carboalumination reaction of 1-alkenes with  $\text{Et}_3\text{Al}$  (see Supplementary data). 1-Hexene, 1-octene and 1-decene were selected as the starting reactants.

The model reaction of 1-octene with  $\text{Et}_3\text{Al}$  (1:1 ratio) in the presence of 5 mol % of the  $\text{TaCl}_5$  catalyst (1-octene:[Ta] = 100:5) in hexane at rt for 7 h resulted mainly in a mixture of two OACs, **1b** and **2b**, in 75% yield relative to the starting 1-octene. Together

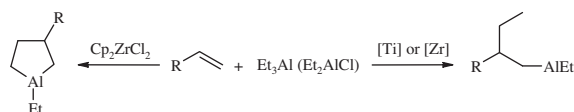
with the carboalumination products, **1b** (classic) and **2b** (with an unusual structure), small amounts of the hydroalumination products **3b** (10–15%) derived initial 1-octene, were also detected in the reaction mixture (Scheme 2) (see Supplementary data).

The structures of the synthesized compounds **4**, **5**, **6a**, **6c**, **8**, and **11** were confirmed by recording IR, <sup>1</sup>H and <sup>13</sup>C NMR spectra, mass measurements and elemental analysis of their derivatives generated upon deuteration and oxidation with molecular oxygen.<sup>5</sup>

The only hydrolysis product, **4b** (3-methylnonane)<sup>5b</sup> was obtained upon treatment of **1b** and **2b** with dilute hydrochloric acid (8%), while their deuteration led to two monodeuterated hydrocarbons, **6b** and **7b** (1:1 ratio). The yield and molar ratio of the resulting regioisomers were determined by calculating their GLC peak area ratios (see Supplementary data).

Oxidation of these reaction products with anhydrous oxygen afforded regioisomeric alcohols **9b** and **10b**, in which the hydroxyl groups were attached to different carbon atoms (see Supplementary data).

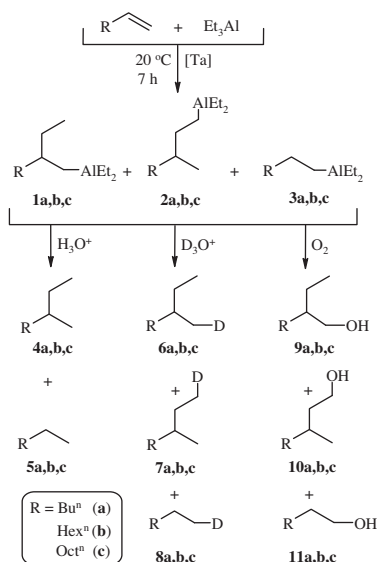
The observations described above confirmed unambiguously the structures of the reaction products **1b** and **2b** as 2-(*R*-substituted)- and 3-(*R*-substituted)-*n*-butylaluminums, respectively.



Scheme 1. Carboalumination of 1-alkenes in the presence of Ti and Zr catalysts.

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**Scheme 2.** The Ta-catalyzed carboalumination of 1-alkenes.

To gain a more detailed insight into this unusual tantalum-catalyzed alkene carboalumination with  $\text{Et}_3\text{Al}$ , we have studied the influence of the solvent, the temperature, the molar ratio of reactants, the ligand environment of tantalum, the concentration of the catalyst as well as the duration of the reaction on the yield and composition of the OACs **1b** and **2b** in the model reaction with 1-octene (Table 1).

As seen in Table 1, the carboalumination reaction of 1-octene with  $\text{Et}_3\text{Al}$  in the presence of  $\text{TaCl}_5$  occurred in hydrocarbon solvents such as hexane, benzene, and toluene (entries 1–4, 6 and 7) over 7 h to afford the OACs **1b** and **2b** (1:1 ratio) in good yields. In 1,2-dichloroethane (entry 5), this reaction produced predominantly the classic carboalumination product **1b** (2:1). It should be noted that we could not obtain the desired result when ethereal solvents such as the diethyl ether, tetrahydrofuran or methyl *tert*-butyl ether were employed.

The search for an efficient catalytic system revealed that the binary  $\text{TaCl}_5\text{-P}(\text{OPr}^i)_3$  (1:1) catalytic system produced the highest yield of the unusual carboalumination product **2b** (Table 1, entry 9). Our experiments also showed that ligand-modified Ta catalysts (Table 1, entries 8, 11–13) reduced the total yield of the carboalumination products but, at the same time, favored predominant formation of the OAC **1b**. As can be seen from Table 1, the above

reaction did not produce **1b** and **2b** when a bidentate ligand (entry 10), or a two-fold excess of other ligands ( $L/\text{Ta} = 2$ ) listed in the Table was used in the carboalumination.

The temperature also played an important role in the reaction of 1-alkenes with  $\text{Et}_3\text{Al}$ , significantly influencing the product yield and the **1b:2b** ratio. Thus, at elevated temperature (60 °C), the yield of **2b** decreased (**1b:2b** = 70:30), while over 5 h the total yield of **1b** and **2b** reached 78%. At a lower temperature ( $\sim 0$  °C), the total yield did not exceed 20% at a molar ratio of **1b:2b** = 4:5.

Taking into account our own experimental findings, as well as published data on the synthesis and transformations of substituted tantalacyclopentanes,<sup>3,6</sup> we can suggest possible routes for the simultaneous formation of OACs **1** and **2** via the carboalumination reaction (Scheme 3).

In accordance with Scheme 3, the reaction between  $\text{TaCl}_5$  and  $\text{Et}_3\text{Al}$  afforded unstable diethyl tantalum complex **12**, which eliminates an ethane molecule to produce the alkene complex **13** as a result of  $\beta$ -hydride transfer. The latter transforms into complex **14** containing molecules of ethylene and the initial 1-alkene in the coordination sphere. Intramolecular oxidative cyclization of complex **14** afforded labile  $\beta$ -alkyl-substituted tantalacyclopentane **15**, of which further reaction with excess  $\text{Et}_3\text{Al}$  may proceed along two possible parallel routes.

The first route involves the formation of a bimetallic complex via transmetallation of **15** with  $\text{Et}_3\text{Al}$  at the C1–Ta bond. The subsequent conversion of **16** leads to the OAC **1** as a result of  $\beta$ -hydride transfer. The second route can be realized through the stepwise transmetallation reaction of intermediate **15** with  $\text{Et}_3\text{Al}$  at the C4–Ta bond to give bimetallic complex **17**, followed by its transformation into the unusual carboalumination product **2** after  $\beta$ -hydride transfer.

As shown in all our experiments the hydroalumination products of the original 1-alkene were also detected in the reaction mixture. This can be explained by the fact that the tantalum alkyl derivatives are easily converted into hydrides,<sup>7</sup> which can serve as promoters for the hydrometallation process.

1-Hexene and 1-decene also reacted with  $\text{Et}_3\text{Al}$  giving rise to the OACs **1a** and **2a**, as well as **1c** and **2c**, respectively. We found that these reactions proceeded in a similar way. They retain all the regularities described above for 1-octene, resulting in deuterated **6a**, **6c**, **7a**, and **7c**, as well as the oxidation products **9a**, **9c** and **10a**, **10c**, respectively (see Supplementary data). In all these experiments, the carboalumination reaction was also accompanied by small amounts of hydroalumination products **3** (10–15%).

For more detailed investigations of the carboalumination reaction and its regio- and stereoselectivity in order to synthesize new

**Table 1**  
The effect of the molar ratio of reactants, the solvent, the ligand environment of tantalum, and the concentration of the catalyst on the yield and composition of the carboalumination products of 1-octene

Entry	$\text{Et}_3\text{Al}$ :1-octene molar ratio	1-Octene: $\text{TaCl}_5$ molar ratio	Solvent	Ligand	Total yield <b>1b</b> + <b>2b</b> (%)	<b>1b:2b</b> molar ratio
1	1:1	100:5	Hexane	—	75	1:1
2	1:1	100:3	Hexane	—	53	1:1
3	2:1	100:5	Hexane	—	85	1:1
4	1:1	100:10	Hexane	—	81	1:1
5	1:1	100:5	1,2-Dichloroethane	—	74	2:1
6	1:1	100:5	Benzene	—	70	1:1
7	1:1	100:5	Toluene	—	71	1:1
8	1:1	100:5	Hexane	$\text{Ph}_3\text{P}$	70	5:4
9	1:1	100:5	Hexane	$(\text{Pr}^i\text{O})_3\text{P}$	72	1:6
10	1:1	100:5	Hexane	$\text{Ph}_2\text{P}-\text{CH}_2-\text{CH}_2-\text{PPh}_2$	—	—
11	1:1	100:5	Hexane	$\text{P}(\text{NMe}_2)_3$	59	1:1
12	1:1	100:5	Hexane	$\text{Et}_3\text{N}$	66	3:2
13	1:1	100:5	Hexane		65	5:1

Reaction conditions: concentration of  $\text{Et}_3\text{Al}$  2 mmol/mL,  $[\text{Ta}]:[\text{L}] = 1:1$ , 20 °C, 7 h.

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