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*Published in:*  
Recueil des Travaux Chimiques des Pays-Bas

*DOI:*  
[10.1002/recl.19800990608](https://doi.org/10.1002/recl.19800990608)

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*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
1980

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Blenkers, J., Liefde Meijer, H. J. D., & Teuben, J. H. (1980). Formation of ( $\eta^3$ -methallyl) and ( $\eta^4$ -butadiene) ligands from ( $\eta^1$ -2-buten-1-yl) coordinated to group IVB metals. *Recueil des Travaux Chimiques des Pays-Bas*, 99(6). DOI: 10.1002/recl.19800990608

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# Preliminary Communication

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Formation of ( $\eta^3$ -methallyl) and ( $\eta^4$ -butadiene) ligands from ( $\eta^1$ -2-buten-1-yl) coordinated to group IVB metals

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*(Received April 10th, 1980)*

**Abstract.** The synthesis and some properties of the novel triallyl compounds  $\text{Cp}^*\text{M}(\text{CH}_2\text{CH}=\text{CHCH}_3)_3$  ( $\text{Cp}^*=\eta^5\text{-C}_5(\text{CH}_3)_5$ ;  $\text{M}=\text{Ti}$ ,  $\text{Zr}$  or  $\text{Hf}$ ) and the butadiene-methallyl compounds  $\text{Cp}^*\text{M}(\eta^4\text{-butadiene})(\eta^3\text{-methallyl})$  therefrom are reported. The compounds are very reactive towards carbon monoxide and other small molecules.

Metal butadiene compounds are often involved in a variety of interesting reactions, e.g. insertion and oligomerisation reactions, or formation of  $\pi$ -allyl complexes if intramolecular hydride groups are present.<sup>1</sup> Until recently little was known about early transition metal-butadiene compounds. Some years ago our group reported the isolation of ( $\eta^5\text{-C}_5\text{H}_5$ )Ti( $\eta^3$ -methallyl)( $\eta^4$ -butadiene) from reaction between ( $\text{C}_5\text{H}_5$ )TiCl<sub>3</sub> and ( $\text{C}_5\text{H}_5$ )TiCl<sub>2</sub> and 1-methylallylmagnesium bromide in ether.<sup>2</sup> Recently a more detailed investigation of the formation of cyclopentadienyl butadiene-methallyl compounds of the group IV metals Ti, Zr and Hf was started. Their properties, like the interconversion of the butadiene and allyl ligands, and their reactivity towards molecules like CO, CO<sub>2</sub>, H<sub>2</sub>, olefins and acetylenes are also studied. Recent publications on group IV butadiene compounds<sup>3,4</sup> prompt us to report some of our preliminary results.

Reaction of  $\text{CpMCl}_3$  ( $\text{Cp}=\eta^5\text{-C}_5\text{H}_5$  or  $\eta^5\text{-C}_5(\text{CH}_3)_5$ ;  $\text{M}=\text{Ti}$ ,  $\text{Zr}$  or  $\text{Hf}$ ) with 3 equiv of 2-butenylmagnesium bromide in ether at low temperature gives the triallyl complex  $\text{CpMR}_3$  ( $\text{R}=\text{2-butenyl}$ ). At higher temperatures this compound reacts according to eq. [1]



The triallyl species with  $\text{Cp}=\eta^5\text{-C}_5(\text{CH}_3)_5$  ( $=\text{Cp}^*$ ) and  $\text{M}=\text{Hf}$  could be isolated as a yellow-orange oil and characterized by <sup>1</sup>H NMR (benzene-d<sub>6</sub>):  $\delta$ 1.75 (s, 15H,  $\eta^5\text{-C}_5(\text{CH}_3)_5$ );  $\delta$ 1.25 (d, 6H, Hf-CH<sub>2</sub>);  $\delta$ 1.79 (d, 9H, CH<sub>3</sub>);  $\delta$ 4.70 and 5.49 (m, 2 x 3H, CH=CH). The compound is stable at room temperature, but at higher temperatures it slowly converts into a butadiene-methallyl species; eq. [1]. We followed this conversion by <sup>1</sup>H NMR spectroscopy (benzene-d<sub>6</sub>, 60°C). The original  $\text{Cp}^*\text{HfR}_3$  spectrum transforms into a new complicated one, which is compatible with the presence of  $\eta^5\text{-Cp}^*$ ,  $\eta^4\text{-C}_4\text{H}_6$  and  $\eta^3\text{-C}_4\text{H}_7$  ligands. However, there are two  $\text{Cp}^*$  singlets ( $\delta$ 1.80 and 1.90 ppm) and a complex resonance from the CH-CH<sub>3</sub> part of the  $\eta^3$ -allylic ligand, indicating that two isomers (*syn* and *anti*) are present.

On prolonged heating the  $\text{Cp}^*$  singlet at  $\delta$ 1.90 ppm increases at the expense of the singlet at  $\delta$ 1.80 ppm. Simultaneously the CH-CH<sub>3</sub> resonance also becomes simpler ( $\eta^4$ -butadiene:  $\delta$ 0.9 and 1.5 (m, 4H, CH=CH<sub>2</sub>);  $\delta$ 5.5 (m, 2H, CH=CH<sub>2</sub>);  $\eta^3$ -methallyl:  $\delta$ 1.0 (m, 2H, CH<sub>2</sub>...CH);  $\delta$ 1.6 (m, 4H, CH-CH<sub>3</sub>);  $\delta$ 6.0 (m, 1H, CH<sub>2</sub>...CH)). This observation indicates that at higher temperatures isomerization proceeds to the thermodynamically more favourable *syn*-isomer. This was confirmed by IR spectroscopy:  $\nu(\text{C}=\text{C})$  1533 cm<sup>-1</sup>, while methylsubstituents in *anti*-position give rise to an absorption at lower frequencies.<sup>5</sup>

The triallyl compounds of Ti and Zr are thermally much less stable and could not be isolated in a pure form. They decompose smoothly, giving good yields (50-75%) of the butadiene-methallyl compound. These compounds were identified by usual methods (satisfactory elemental analyses, NMR and IR spectroscopy).

The compounds appeared active towards organic substrates. For instance with CO a smooth reaction takes place and an absorption of two equiv of CO per mole of butadiene-methallyl compound was observed. These reactions are under investigation.

## Acknowledgement

This investigation was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for the Advancement of Pure Research (ZWO).

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