

# Investigations of stable molybdenum carbene complexes for the metathesis synthesis of dialkylsubstituted poly(*p*-phenylenevinylene)s (PPVs)

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## Abstract

Different Schrock-type molybdenum carbene complexes with hexafluoroalkoxy-ligands were examined for their suitability for the acyclic diene metathesis (ADMET) polycondensation of 2,5-dialkyl-1,4-divinylbenzenes (DRDVB). Kinetic studies on cross-metathesis showed that catalysts with (2,6-dimethylphenyl)imido ligands are the most active. <sup>1</sup>H-NMR investigations of the reaction of 2,5-diheptyl-1,4-divinylbenzene using Mo(NAr<sup>Me2</sup>)(CHC(Me)<sub>2</sub>Ph)(OCMe)(CF<sub>3</sub>)<sub>2</sub> as catalyst show the in situ formation of a new carbene species as well as molybdenacyclobutane intermediate.

*Keywords:* Carbene; ADMET; Molybdenacyclobutane; Poly(*p*-phenylenevinylene); Metathesis

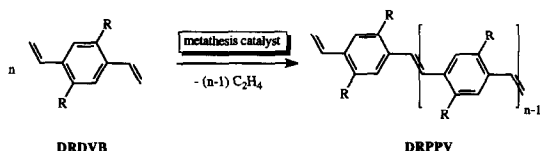
## 1. Introduction

Olefin metathesis [1] is a versatile reaction both for the preparation of polymers [2,3] and valuable low-molecular compounds [4,5]. Metal carbenes are the catalytically active species [6]. They can be generated in situ (classical systems) or added as well defined single components. The latter stable metal carbene complexes offer a range of advantages, e.g. enhanced tolerance against functional groups and conjugated systems. Now that metal carbene complexes can be obtained in multigram scale [7–10] they provide potential for enlarged application of metathesis in various fields.

A few years ago we introduced metathesis as

a method for the preparation of *p*-phenylenevinylene oligomers, homopolymers (PPV) and copolymers [11]. PPV, a conjugated polymer, has gained special attention in recent years chiefly as the active element in light-emitting diodes but also due to other valuable properties such as photoluminescence and its nonlinear optical response. PPV can be prepared metathetically either via ring-opening metathesis polymerization (ROMP) [12] or via acyclic diene metathesis (ADMET) polycondensation [13,14]. Very recently we succeeded for the first time in the metathesis preparation of soluble PPV-derivates [15]. This contribution reports our studies concerning the suitability of different Schrock-type catalysts for the metathesis condensation reaction of 2,5-dialkyl-1,4-divinylbenzenes (DRDVB) (Scheme 1). In order to investigate the behaviour of the catalytic species

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Scheme 1.

during chain growth in situ proton NMR was performed using the most active catalyst.

## 2. Results and discussion

### 2.1. Suitability of carbene complexes for polycondensation of DRDVB

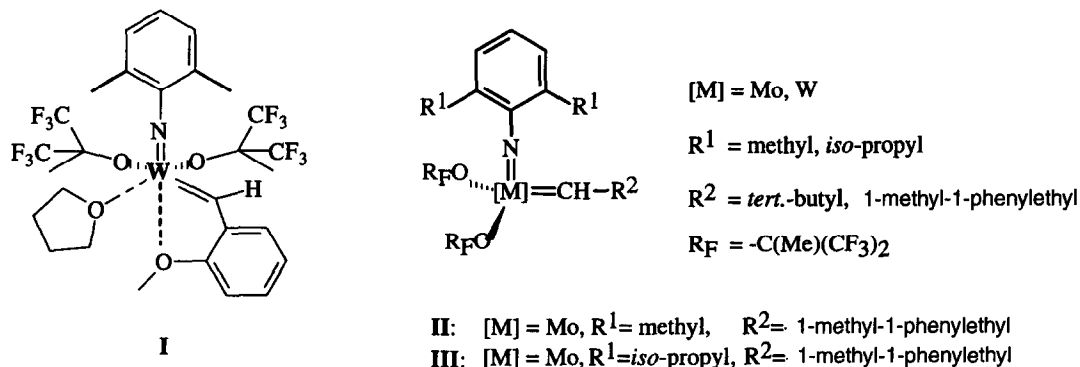
In our earlier works on the metathesis preparation of PPV we used a stable tungsten carbene complex first described by Grubbs and coworkers [16] (Scheme 2, I). However, in the meantime we focused our interest on the tungsten and molybdenum based catalysts developed by Schrock et al. [7,8] (Scheme 2, right) in order to investigate their structure–property relations in detail [17].

DRDVBs are terminal olefins hence investigation using 1-hexene as substrate [17] can be used to establish any general influence of catalyst. Fig. 1 displays dependence on time of the formation of *t/c*-5-decene. A value of 1 corresponds to maximum yield obtained at equilibrium. Various molybdenum and tungsten cata-

lysts with different imido and alkylidene ligands were examined. Results showed that molybdenum carbene complexes are better catalysts for terminal olefins than those based on tungsten, see Fig. 1. Fig. 1 illustrates that for conventional  $\alpha$ -olefins there is no big difference in activity with variation of substituents either at the imido ligand or at the alkylidene ligand. Nevertheless, additional investigations were carried out as the DRDVBs are sterically much more demanding substrates than an  $\alpha$ -olefin. For practical reasons we chose only the two molybdenum catalysts with neophylidene ligands (Scheme 3), since they cost 1/50th of the price of the neopentylidene analogues and are easier to make [7].

They differ from each other in the imido ligand, one containing a 2,6-dimethylphenyl (**II** in Scheme 3) and the other one an 2,6-diisopropyl group (**III** in Scheme 3). **III** is one of the most common Schrock-type catalysts to be used in academic research, whereas catalyst **II** is more demanding and is difficult to crystallize and tends to decompose via bimolecular reactions. To determine the activity of both catalysts regarding the conversion of dialkylsubstituted divinylbenzenes cross-metathesis of 2,5-dibutyl-1,4-divinylbenzene (DButDVB) and *t*-5-decene (molar ratio: 1:5) was performed in toluene, see Scheme 4.

As this reaction can be followed quantitatively by gas chromatography it can be analyzed



Scheme 2.

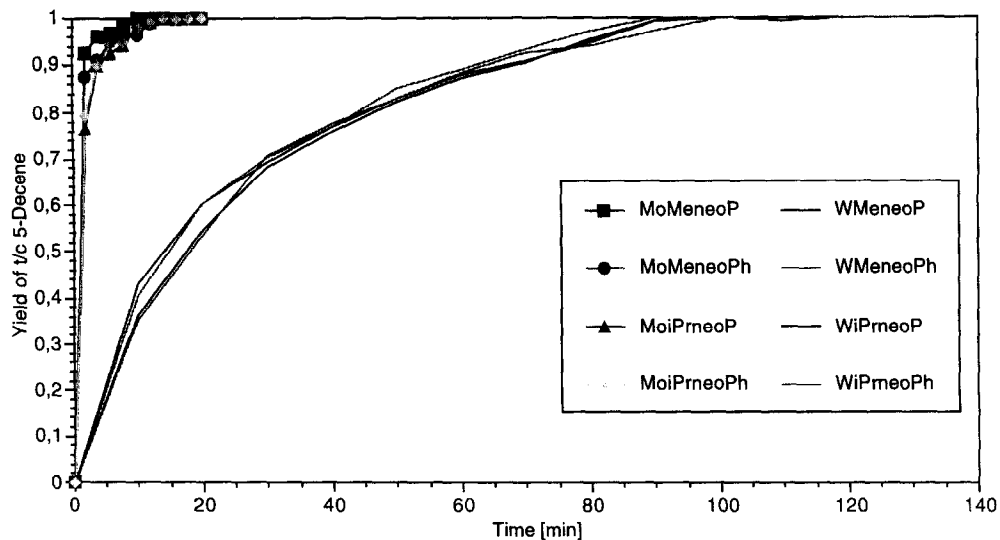
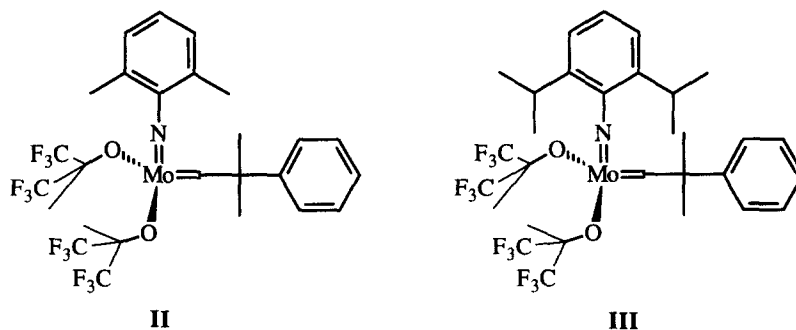
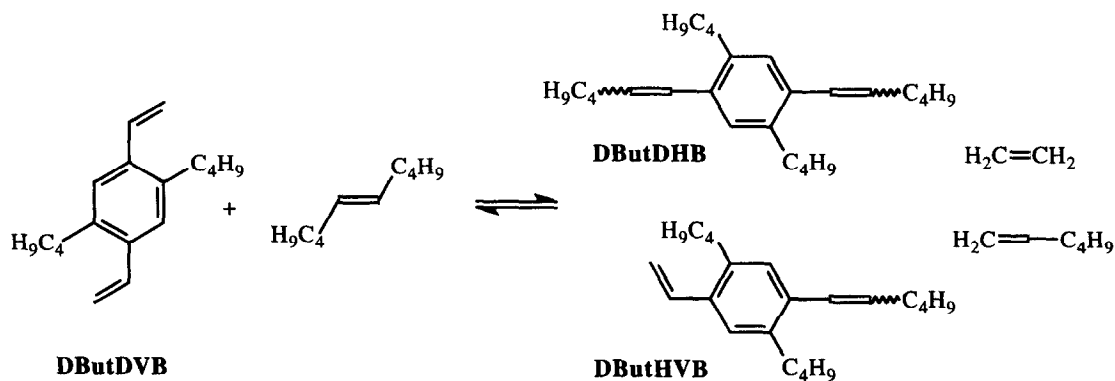


Fig. 1. Activity of different molybdenum and tungsten carbene complexes with hexafluoro *tert*-butoxy ligands in the metathesis of 1-hexene (hexene:  $M = 500:1$ ;  $[M] = 2 \text{ mmol l}^{-1}$ ; solvent: methyl cyclohexane at RT). Abbreviations as follows: Me: (2,6-dimethylphenyl)imido; iPr: (2,6-diisopropylphenyl)imido; neoP: neopentylidene; neoPh: neophylidene).



Scheme 3.



Scheme 4.

more conveniently than the polycondensation, reaction products were identified by GC/MS. Fig. 2 shows the consumption of the starting material DButDVB and the formation of reaction products (only those containing 1 DBut-DVB unit) plotted versus time.

Differences in activity compared to terminal olefins can be observed very clearly. Catalyst **II** converts the substrate DButDVB completely into products within 30 min. The equilibrium state product distribution is established nearly in the same time. *Cis* / *trans*-ratios of the products are in thermodynamic equilibrium from the very

beginning of reaction (e.g. DBut-*tt*-DHB: DBut-*tc*-DHB = 10:1). In the case of catalyst **III** the reaction occurs more gentle (its activity is  $\sim 1/10$  that of **II**). A short induction period both for the consumption of starting material DButDVB as well as for the formation of the first transalkylation product (DButHVB) can be observed. As expected for consecutive reactions the amount of the DButHVB reaches a maximum before being converted to DButDHB, the final product. The higher activity of the molybdenum carbene complex **II** compared to **III** can be explained as follows: during the

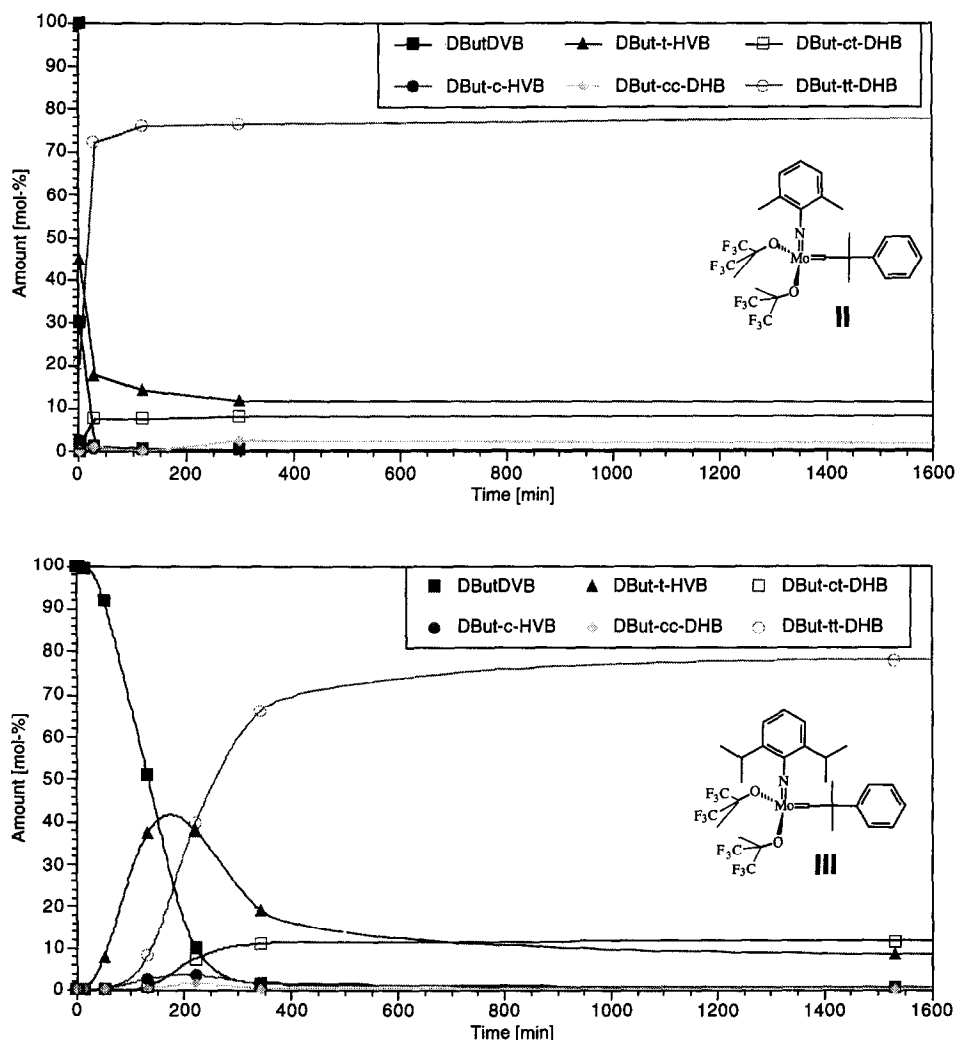
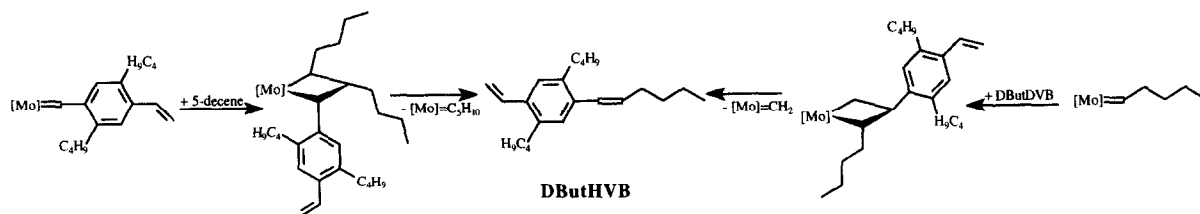


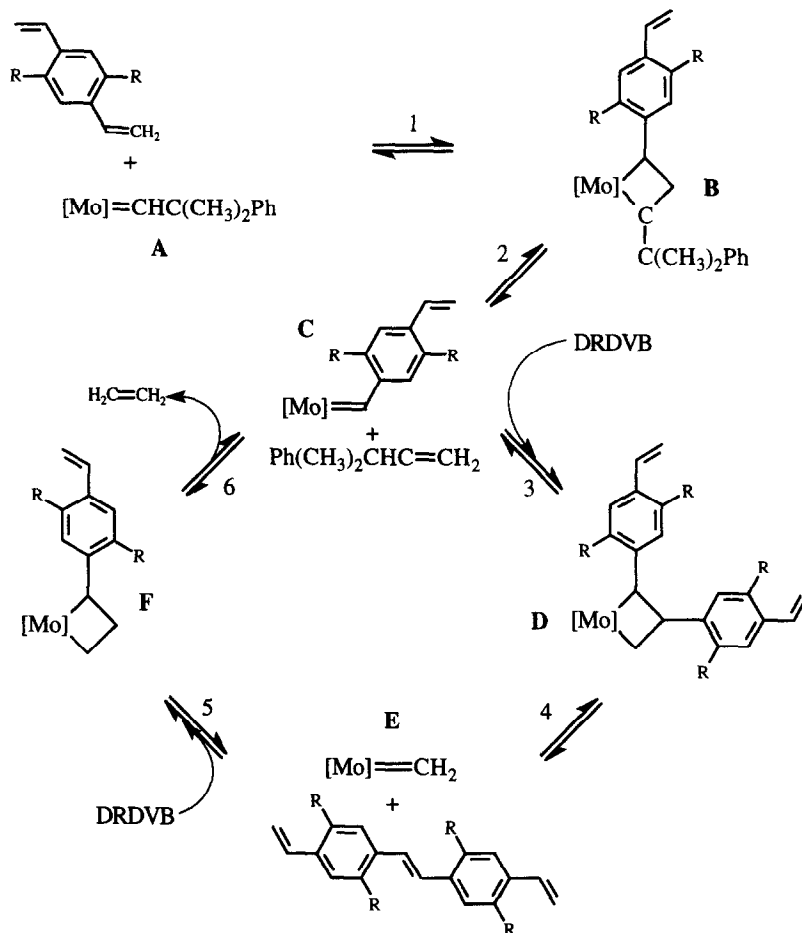
Fig. 2. Kinetic investigations on cross-metathesis using molybdenum based catalysts **II** and **III** (5-decene:DButDVB: $M = 250:50:1$ ;  $[M] = 10 \text{ mmol l}^{-1}$ , solvent: toluene at RT).



Scheme 5.

catalytic procedure steric constraints develop. Scheme 5 displays two possible ways that lead to the formation of DButHVB. Starting from left side the intermediate molybdenacyclobutane is trisubstituted, whereas the route from the right side proceeds via a disubstituted metallacyclobutane. Nevertheless in both cases the substrates have to approach the active center ([Mo]

= CHR) which is capped by the imido ligand to prevent bimolecular decomposition of the catalyst. The enhanced steric demand of the isopropyl groups compared to methyl groups decreases the probability that a substrate enters the coordination sphere in the necessary position, hence reaction proceeds slower. Compared to the above described cross-metathesis polycon-



Scheme 6.

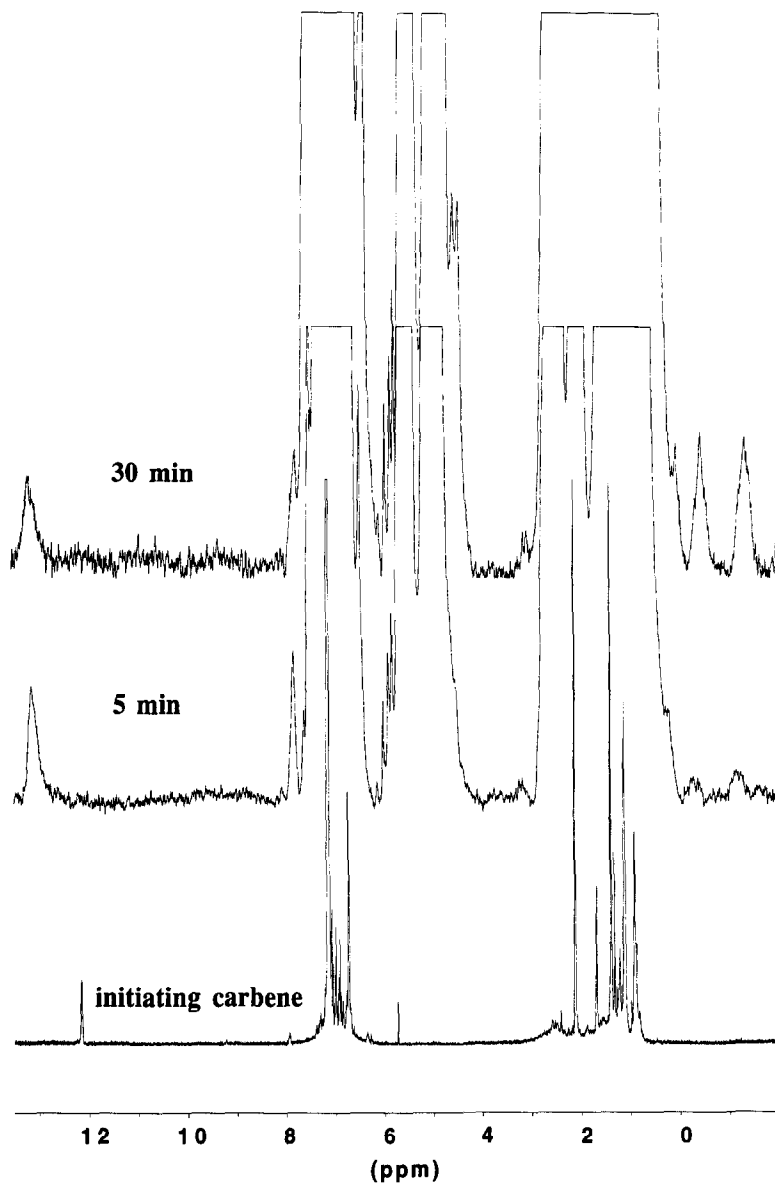


Fig. 3.  $^1\text{H-NMR}$  of DHepDVB and catalyst II (DHepDVB: II = 5:1; [II] =  $10 \text{ mmol l}^{-1}$  in toluene- $d_8$  at RT).

densation of DRDVB is an even more demanding task for the catalyst as two molecules of DRDVB have to form a metallacyclobutane, see Scheme 6.

The intermediates containing the metal species [Mo] are identified by capital letters (A–F) and the reaction steps by numbers (1–6). The initiating catalyst ‘A’ reacts with a molecule DRDVB to form a metallacyclobutane ‘B’ (step

1)<sup>1</sup>. By decomposition of ‘B’ formation of a new metal carbene species ‘C’ occurs. In order to achieve a productive condensation reaction of ‘C’ with another molecule of DRDVB to give

<sup>1</sup> Investigation whether the formation of a methyldene carbene species as starting step has to be taken into account are in progress.

the metallacyclobutane 'D' must occur, otherwise there is non-productive metathesis. The coupling product, a substituted distyrylstilbene, forms by elimination of the methylenecarbene complex 'E'. This metal species can react either with a new molecule DRDVB or the condensed product, respectively, to close the ADMET circle.

If polycondensation of DRDVB is to proceed in convenient reaction times (max. 1 day) only molybdenum based catalysts with (2,6-dimethylphenyl)imido ligand (e.g. **II**, which is the cheapest of all catalysts containing hexafluoro-*tert*-butoxy ligands) are suitable. Catalyst **II** can be used for the metathesis conversion of a range of DRDVBs (R = butyl, heptyl, decyl, cyclohexyl) [15,18]. For terminal olefins with less steric demand other molybdenum carbene complexes can also serve as effective catalysts, these observations are in accordance with the literature [19].

### 2.2. *In situ* proton NMR investigation of the polycondensation

In order to investigate the behaviour of the transition metal species during the condensation of DRDVB we used *in situ*  $^1\text{H-NMR}$  spectroscopy. The concentration of the catalyst was the same as for conventional polycondensations of DRDVB ( $[\text{M}] = 10 \text{ mmol l}^{-1}$ ), only the ratio of DHepDVB/catalyst **II** was decreased to 6:1. First DHepDVB was transferred into a NMR tube, after adding the fresh catalyst solution (in toluene- $d_6$ ) and freezing the NMR tube was sealed. The reaction was followed kinetically, in the first minutes during thawing, later at room temperature (Fig. 3).

At the bottom of Fig. 3 the proton NMR of the initiating molybdenum carbene  $\text{Mo}(\text{NAr}^{\text{Me}_2})(\text{CHC}(\text{Me})_2\text{Ph})(\text{OC}(\text{Me})(\text{CF}_3)_2)_2$  is displayed. The sharp signal at 12.15 ppm corresponds with the starting carbene hydrogen resonance. Immediately after mixing of reactants (5 min  $\pm$  1 min) the signal of the initiating Mo-carbene complex disappears completely and

a new carbene species (C in Scheme 6) is formed giving a broad signal at 13.1 ppm. As no trace of the initiating carbene complex can be detected first exchange process seems to be very fast. The downshift of approximately 1 ppm corresponds with the results of investigations by Schrock et al. using styrene as substrate [7], the downshift is attributed to the enlarged conjugation system. Simultaneously resonances at  $-0.3$  and  $-1.2$  ppm appear that increase with time. We assign them to the two  $\beta$ -protons in the molybdenacyclobutane structure (B in Scheme 6) that is formed by the reaction of the methylenecarbene (E in Scheme 6) and DHepDVB. The ratio between carbene proton and metallacyclobutane protons decreases with reaction time, hence during ADMET the latter structure is the most stable one. We did not observe the methylenecarbene, probably because its reactivity is too high in presence of DHepDVB or the respective condensation products. It is possible that the signal at  $\sim 0.2$  ppm is due to the  $\beta$ -proton in structure D (see Scheme 6). After 24 h no signals of any active species (neither a carbene nor metallacyclobutane structure) can be detected in the NMR spectrum, presumably because of decomposition processes.

### 3. Summary and conclusion

The suitability of different Schrock-type carbene complexes for the polycondensation of 2,5-dialkyl-1,4-divinylbenzenes was investigated. As the substrates are sterically very demanding only molybdenum based catalysts with (2,6-dimethylphenyl)imido ligands offer enough activity for convenient reaction rates. Regarding convenience of synthesis of DRPPVs and also for economic reasons catalyst **II** ( $\text{Mo}(\text{NAr}^{\text{Me}_2})(\text{CHC}(\text{Me})_2\text{Ph})(\text{OC}(\text{Me})(\text{CF}_3)_2)_2$ ) is the most favoured.

Investigation of the reaction by proton NMR spectroscopy showed that the first exchange of the alkylidene species occurs very fast, whereas

the condensation steps proceeds more slowly. Molybdenacyclobutane intermediates are stable enough on the NMR time scale to be observed during reaction.

#### 4. Experimental

All reactions were carried out under argon using standard Schlenk techniques under rigorous exclusion of water and oxygen (Oxysorb, Fa. Messer Griesheim, Germany). Solvents (toluene, toluene- $d_8$ ) (Fa. Merck, Germany) and *t*-5-decene (Lancaster, GB) were predried over lithium aluminum hydride, distilled and transferred to butyl lithium and degassed. DButDVB and DHepDVB were synthesized as described [15,18]. Purity of compounds was checked by gas chromatography. The catalysts II and III were prepared according to literature [7].

$^1\text{H}$ -NMR spectra were obtained on a Bruker WA 100 spectrometer. GC measurements and GC-MS, respectively, were recorded using a Hewlett Packard 5890A GC with a 50m Permabond SE-52-DF capillary column coupled to VG analytical 70 SE spectrometer and VAX 2000 data system.

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