

## Lewis-acidic organometallic compounds of the lanthanides and the alkaline earth metals as catalysts for the activation of carbonyl groups\*

Herbert Schumann<sup>†</sup>, Mario Glanz, Jochen Gottfriedsen,  
Sebastian Dechert, and Dietmar Wolff

Technische Universität Berlin, Institut für Anorganische und Analytische Chemie,  
Sekt. C2, Straße des 17. Juni 135, D-10623 Berlin, Germany

**Abstract:** 1,3-dialkyl-4,5-dimethylimidazol-2-ylidenes form adducts with various bis(alkylcyclopentadienyl) complexes of magnesium, calcium, strontium, barium, samarium, and ytterbium. The X-ray structures of selected metallocenes and carbene adducts are discussed. Liquid-crystalline homo- and block copolymers with a narrow molecular mass distribution index were obtained in high yields by living polymerization of mesogenic methacrylates with organosamarium complexes. Depending on the structure of the catalyst and the polarity of the solvent used, different, partially competitive reaction mechanisms are observed.

### SYNTHESIS OF CARBENE ADDUCTS OF GROUP II METALLOCENES AND LANTHANIDOCENES

1,3,4,5-tetramethylimidazol-2-ylidene (Me-carb) and 1,3-di(iso-propyl)-4,5-dimethylimidazol-2-ylidene (Pr-carb) react with  $(C_5Me_4H)_2Mg$  (**1a**),  $(C_5Me_4H)_2Ca(NH_3)_2$  (**1b**),  $(C_5Me_4iPr)_2Ca(THF)$  (**2b**),  $(C_5Me_4H)_2Sr(THF)_2$  (**1c**),  $(C_5Me_5)_2Sr(THF)_2$  (**2c**),  $(C_5Me_4tBu)_2Ba(py)_2$  (**1d**),  $(C_5Me_5)_2Sm(THF)_2$  (**1e**),  $(C_5Me_4Et)_2Sm(THF)_2$  (**2e**),  $(C_5Me_4H)_2Yb(THF)$  (**1f**),  $(C_5Me_5)_2Yb(THF)$  (**2f**),  $(C_5Me_4Et)_2Yb(THF)$  (**3f**), and  $(C_5H_3tBu)_2Yb(THF)$  (**4f**) in toluene or THF at room temperature to give the air- and moisture-sensitive adducts  $(C_5Me_4H)_2Mg(Pr-carb)$  (**2a**),  $(C_5Me_4H)_2Ca(Pr-carb)$  (**3b**),  $(C_5Me_4iPr)_2Ca(Pr-carb)$  (**4b**),  $(C_5Me_4H)_2Sr(Pr-carb)$  (**3c**),  $(C_5Me_5)_2Sr(Pr-carb)$  (**4c**),  $(C_5Me_4tBu)_2Ba(Pr-carb)$  (**2d**),  $(C_5Me_5)_2Sm(Pr-carb)$  (**3e**),  $(C_5Me_4Et)_2Sm(Pr-carb)$  (**4e**),  $(C_5Me_4H)_2Yb(Pr-carb)$  (**5f**),  $(C_5Me_5)_2Yb(Me-carb)$  (**6f**),  $(C_5Me_5)_2Yb(Pr-carb)$  (**7f**),  $(C_5Me_4Et)_2Yb(Me-carb)$  (**8f**), and  $(C_5H_3tBu)_2Yb(Me-carb)$  (**9f**) [1].

All compounds are thermally very stable (decomposition  $>150$  °C/0.1 mbar) and can be isolated as colorless (alkaline earth metallocene adducts) or almost black crystals (lanthanidocene adducts). They are soluble in polar and aromatic solvents such as tetrahydrofuran (THF), diethyl ether, toluene, or benzene, but are only sparingly soluble in hexane or pentane (Fig. 1).

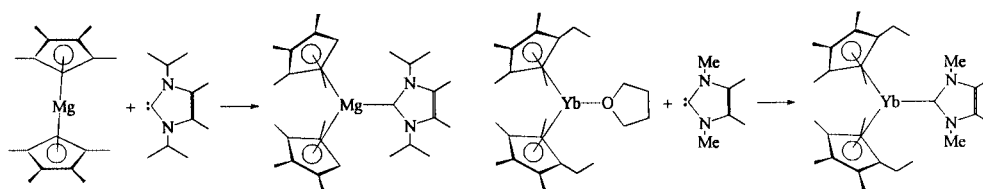


Fig. 1 Selected examples for the preparation of carbene complexes (**2a**, **8f**).

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<sup>†</sup>Corresponding author

The molecular structures of the carbene adducts show planar five-membered ylidene ring units with all the atoms directly bonded to the heterocycle also lying in this plane. Whereas the almost trigonal-planar configuration of the carbene atoms indicating their  $sp^2$ -hybridization and the  $p_\pi$ - $p_\pi$  interactions within the C–N bonds of the cycle are characteristic features of classical carbene complexes, the distance of the respective metal to the carbene carbon atom is not in the range expected for a double bond. These distances rather correspond to elongated single bonds demonstrating the lack of back-bonding. As a consequence, all carbene compounds described here must be considered as adducts. In the structures of **3b**, **3c**, **4c**, and **2d** slight contacts between the ylidene iso-propyl groups and the metal center are observed (Fig. 2).

## PREPARATION OF LIQUID-CRYSTALLINE POLYMETHACRYLATES USING SAMAROCENES AS CATALYSTS

During the last decade, side-group liquid-crystalline polymers attracted great attention with regard to their high application potential in e.g., optical data storage, nonlinear optics, or solid polymer electrolytes [2]. The polymerization of the monomers I to V (Fig. 3) promises the formation of liquid-crystalline polymers containing three different structural units, mesogenic groups, flexible alkyl chain spacers, and a polymethacrylate backbone [3].

In fact, the living polymerization of these mesogenic methacrylates in the presence of the organosamarium complexes **1e**, **2e**, **3e**,  $(C_5Me_5)_2Sm(C_3H_5)$  (**5e**) [4],  $(C_5Me_5)_2SmMe(THF)$  (**6e**) [5],

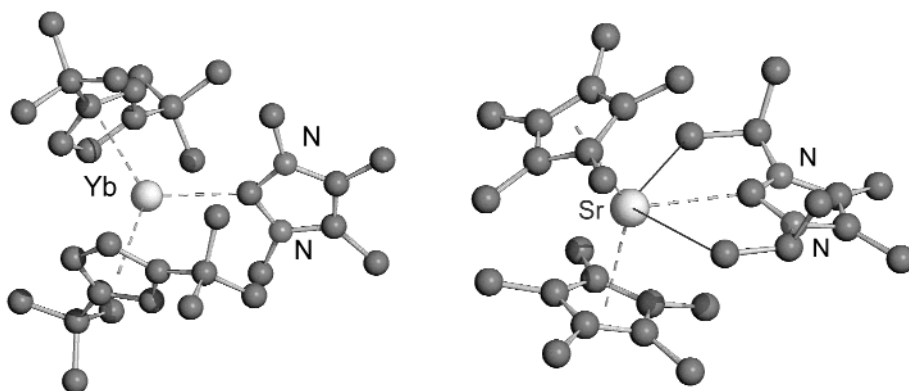


Fig. 2 Crystal structures of selected carbene adducts (**9f**, **4c**).

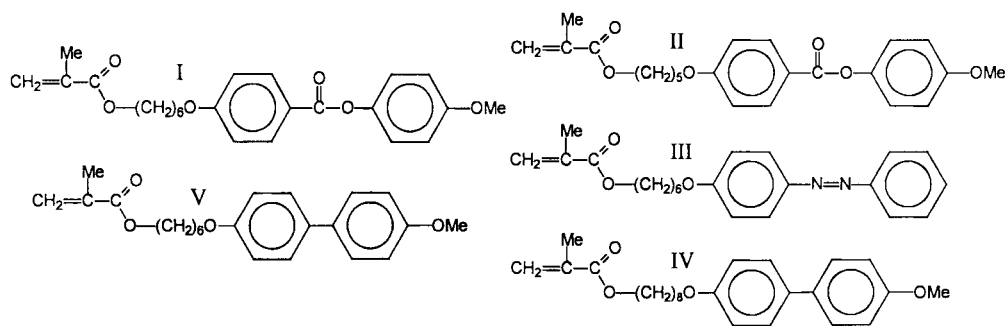


Fig. 3 Selected mesogenic functionalized methacrylate monomers.

$[(C_5Me_4Et)_2SmMe(AlMe_3)_2]$  (**7e**), and  $(C_5Me_4Et)_2SmCH(SiMe_3)_2$  (**8e**) [6] allows the isolation of liquid-crystalline homo- and block copolymers in high yields (Fig. 4). In contrast to radical or anionic polymerization reactions which either produce polymers showing a broad molar mass distribution or require expensive reaction conditions, the homogeneously catalyzed polymerization runs at ambient temperatures within a few minutes leading to polymers of very narrow mass distribution. These homogeneously catalyzed polymerization reactions are characterized by the following remarkable features: a) the polydispersities of the resulting liquid-crystalline polymers show  $M_w/M_n$  ratios up to 1,05 at room temperature; b) dependent on the concentration of the catalyst, oligomers (2000 g/mol) or high-molecular-weight polymers (2.5 Mio g/mol) can be prepared; and c) the polymerization reactions can be conducted in a great number of different solvents such as e.g., THF, dme, dioxan, toluene, benzene.

These results indicate that the polymerization reactions proceed in a living fashion. Independent from the concentration of the catalyst, the  $M_n$  value of the polymer increases linearly related to the amount of the appropriate monomer added while the  $M_w/M_n$  ratio remains unaffected during the course of the polymerization. As a consequence, we were able to synthesize the first narrow distributed di- and triblock copolymers with liquid-crystalline side chains. Various types of block copolymers can be prepared in a strategic manner using the monomers I–V in different relative proportions and sequences (Fig. 5).

Samarocenes activate the methylen double bond of the monomer by coordination of its carbonyl group to the metal center and start the polymerization with transfer of the samarocenic alkyl group to the

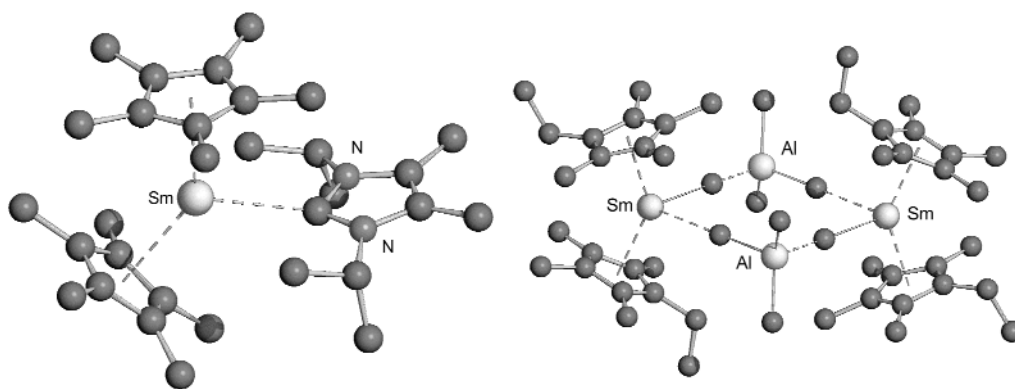


Fig. 4 Crystal structures of selected polymerization catalysts (**3e**, **7e**).

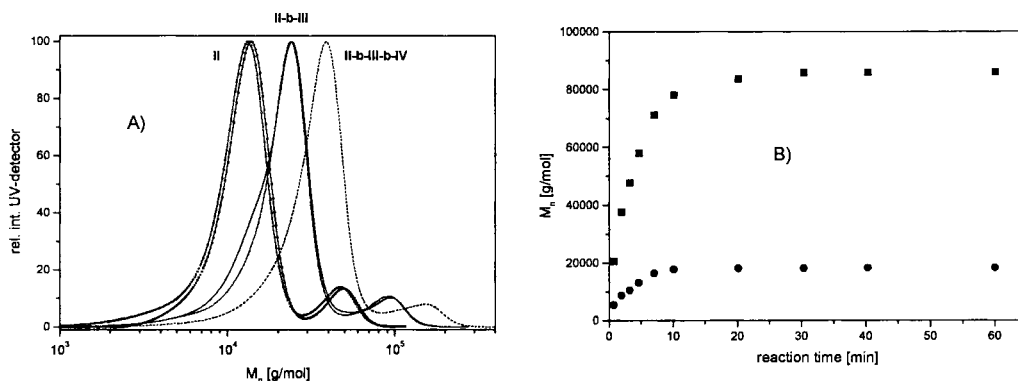


Fig. 5 A) Preparation of a II-b-III di- and a II-b-III-b-IV triblockcopolymer with 2.25 mol % **5e** in THF; B) Duration of the polymerization of **V** with 1.50 mol % **5e** in THF at room temperature.

the methylene group of the methacrylate unit, thus regaining an empty coordination site suitable for the activation of a second monomer. After bonding of the first methylated monomer to the second one, the third can be activated and the polymerization continues [7]. The formation of the polymers by this mechanism was investigated by means of MALDI-ToF-MS [8]. To take advantage of the high resolution of the MALDI-ToF MS in the lower mass region, the average molar mass ( $M_w$ ) of the polymers was adjusted between 2000 and 24 000 g/mol.

Dependent on the kind of catalyst and solvent used, polymers with different chain lengths are formed. Carbene complexes such as **3e** prevent the formation of polymer species with half of the molar mass, whereas the use of the lanthanide(III) complexes in polar solvents, especially in the case of allyl compounds such as **5e**, cause the additional formation of polymers with a 5 to 7 times longer polymer chain. The variation of the substituents at the Cp-ligands of the catalyst has only a slight influence on the product distribution.

Organolanthanid(II) complexes also catalyze such polymerization processes, but in this case a modified mechanism is to discuss [9]. Comparative investigations with corresponding complexes of the alkaline earth metals calcium (b), strontium (c), and barium (d) demonstrate that they are also able to activate carbonyl functions and will be potential catalysts for the polymerization and derivatization of organic substrates.

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