Chem. Rev. **2000,** *100,* 1565–1604

Homogeneous Metathesis Polymerization by Well-Defined Group VI and Group VIII Transition-Metal Alkylidenes: Fundamentals and Applications in the Preparation of Advanced Materials

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Received August 31, 1999

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I. Introduction

Olefin metathesis represents a comparably young area of chemistry. Originally strongly related to Ziegler−Natta chemistry, its basic principles started to be elucidated as late as in the early 1960s. In 1960 Truett, probably inspired by some previous patent disclosures, reported for the first time on the polymerization of bicyclo[2.2.1]hept-2-ene (norborn-2-ene, norbornene, NBE).[1] The finding that the system $WCl_6/AlEt_2Cl$/ethanol would not only polymerize cyclooctene but was also an efficient system for the disproportionation of 2-pentene shed more light on these types of reactions. Since the in-depth investigations carried out by Calderon et al., the expression "olefin metathesis" was used to describe this type of reaction.[2−4] The mechanism of ring-opening metathesis polymerization (ROMP) was finally elucidated by Dall'Asta et al. who provided evidence for the total cleavage of the double bond of the starting monomer during polymerization.[5] The originally proposed mechanism that suggested the existence of a metal carbene[6] was further supported by the work of Katz et al.[7,8] Consecutive investigations mainly carried out by Schrock et al.,[9−11] Grubbs et al.,[12−16] and Feast et al.[17−27] initiated further research on that area. A brief survey over the history of metathesis and metathesis polymerization has been given by Schrock[11] and Eleuterio.[28] The potential applications of metathesis-based reactions such as ROMP, acyclic diene metathesis polymerization (ADMET polymerization), alkyne

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10.1021/cr990248a CCC: $35.00

polymerization, and ring-closing metathesis (RCM) in materials science were soon recognized. Consequently, enormous efforts have been put into the development of new and more efficient catalytic systems. In the course of these investigations, a vast variety of different catalysts based on Ti, V, Nb, Ta, Cr, Mo, W, Re, Co, Rh, Ir, Ru, and Os have been investigated for their general applicability and utility in the above-mentioned metathesis-based reactions.[29−31]

This review intends to cover the synthesis as well as basic principles of modern, *well-defined* group VI and group VIII metal alkylidenes and their potential for use in ROMP, ADMET polymerization, and alkyne metathesis polymerization. In this context, the expression “well-defined” refers to catalytic systems, which are characterized by a *uniform* and *stoichiometric* composition and for which the actual propagating species is well-known and characterized. Consequently, both the chemistry of classical binary or ternary systems, e.g., $WCl_6/AlEt_2Cl$/ethanol, and other relevant techniques based on metathesis, such as ring-closing metathesis (RCM), have been neglected. Additionally, to stay within the definitions of this review, Arduengo-type carbenes will only be discussed in systems where they serve as two-electron donor ligands similar to phosphines. Instead, the main aspects of relevant applications in the preparation of “intelligent” and advanced materials via ROMP, ADMET, and alkyne polymerization will be reviewed.

II. Transition-Metal Alkylidenes as Initiators[32]

A. Group VI Transition-Metal-Based Initiators

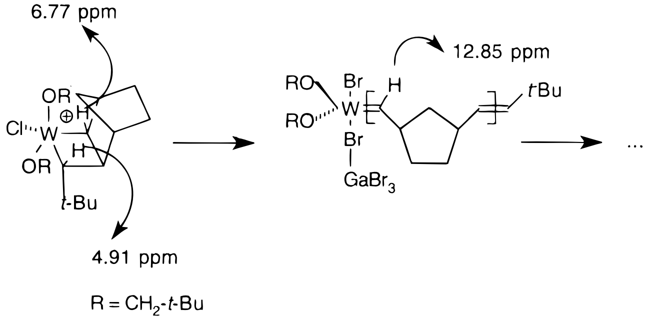
1. Chromium-Based Initiators

Very few reports on the successful use of chromium carbenes for ROMP have been reported so far. The only examples are the ROMP of 2,3-dihydrofuran catalyzed by $Cr(=CPh_2)(CO)_5$[33] as well as the ROMP of 2,3,4,5-tetrahydrooxypin-2-yl acetate.[34]

2. Tungsten-Based Initiators

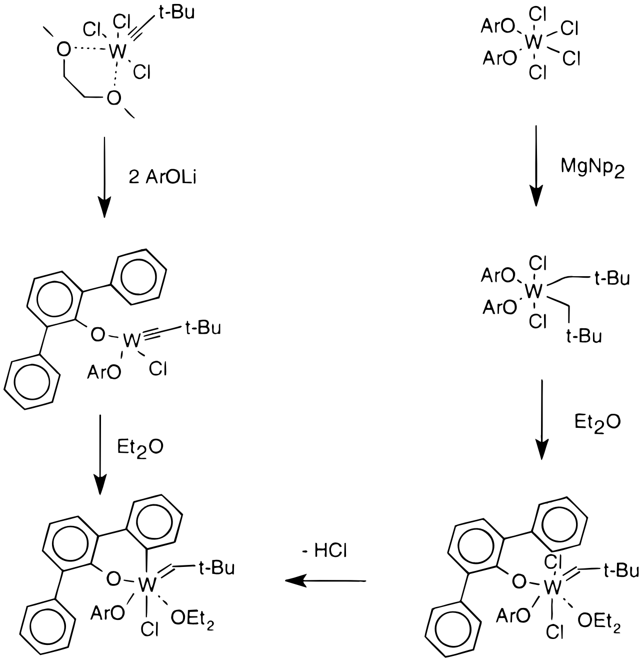
(a) Alkoxy−Akylidene Complexes. To contribute to the historical developments in ROMP, the chemistry of tungsten(VI) alkylidenes will be summarized first. After the reports of Casey et al. on tungsten(0) complexes,[35,36] the first well-defined tungsten(VI) alkylidenes, $W(=CR_2)(OCH_2\text{-}t\text{-}Bu)_2X_2$ and $W(=CR_2)(OCH_2\text{-}t\text{-}Bu)_3X$ (X = Cl, Br, I; R = *n*-Bu, *sec*-Bu, *t*-Bu, Ph, α,ω-cyclopentadienyl), were reported by J. A. Osborn and co-workers.[37,38] Upon addition of $GaBr_3$, $W(=CH\text{-}t\text{-}Bu)(OCH_2\text{-}t\text{-}Bu)_2Cl_2$ polymerizes a variety of substituted norbornenes. Using this compound, the “living” character (vide infra) of such a tungsten(VI)-based polymerization system was observed for the first time via ^1H NMR spectroscopy[39] and further supported by the preparation of *block*-copolymers. Additionally, by employing low-temperature techniques, an intermediate (cationic) tungstacyclobutane species[40] was observed (Scheme 1).[41−44] In consecutive studies, the equilibria that are relevant for ROMP to proceed efficiently have been studied in detail.[45]

Scheme 1. Observation of the Simultaneous Presence of Metal Alkylidenes and Metallacyclobutanes via ^1H NMR Spectroscopy

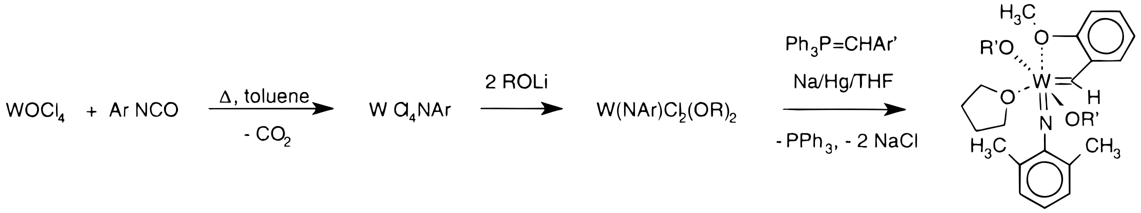


One of the first examples of Lewis-acid-free initiators based on tungsten(VI), $W(O\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)_2Cl_2(CH\text{-}t\text{-}Bu)(OR)_2$, (R = Et, *i*-Pr), which allowed the polymerization of substituted norbornenes, was reported by J. M. Basset and co-workers.[46] Additionally, Lewis-acid-free $W(=C(CH_2)_4)(OCH_2\text{-}t\text{-}Bu)_2Cl_2$ was reported to effectively polymerize substituted norbornenes such as *exo*-norborn-5-ene-2,3-dicarboxylic anhydride.[47,48] Finally, the synthesis of the aryloxy−alkyloxy tungsten alkylidene complex reported by Basset et al. needs to be mentioned (Scheme 2).[49] The synthesis may be accomplished via two independent routes. One entails the reaction of $W(C\text{-}t\text{-}Bu)Cl_3\cdot$dme with 2 equiv of ArOLi (Ar = $2,6\text{-}C_6H_3Ph_2$). The intermediary alkylidyne is believed to spontaneously isomerize to the desired alkylidene moiety. Alternatively, $WCl_4(OAr)_2$ is reacted with 2 equiv of dineopentylmagnesium (Np_2Mg). Elimination of neopentane and HCl again results in the formation of the desired catalyst. It has been reported to be highly active and stereoselective in the ROMP of 1-methylnorbornene to yield predominantly *cis*-polymers on a strong head-to-tail base.[50]

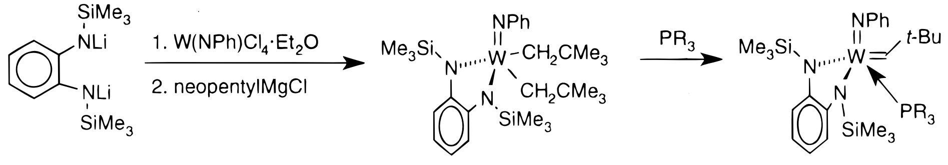
Scheme 2. Synthesis of a ROMP-Active Cyclometalated Aryloxy(chloro)neopentylidene Tungsten Complex



Scheme 3. Synthesis of a Tungsten Alkoxyimidoalkylidene Complex by Alkylidene Transfer from a Phosphorane to a Tungsten Imide

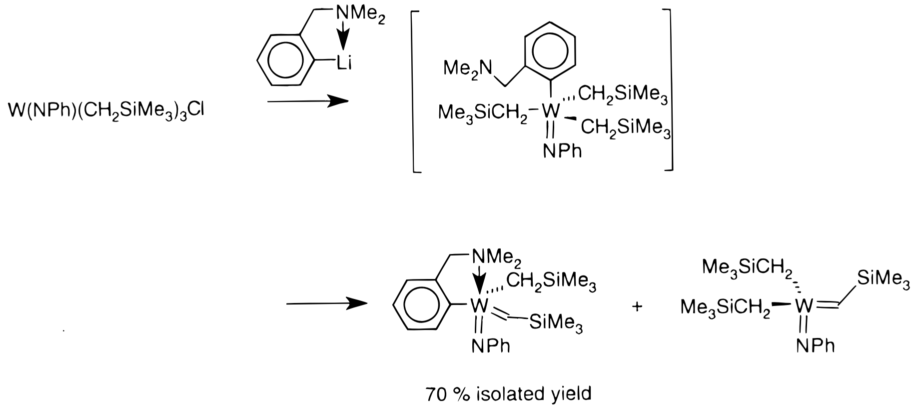


Scheme 4. Preparation of $W(NPh)(CHCMe_3)(TMS_2PDA)L$ ($L = PMe_3$)[a]



[a] PDA = *o*-phenylene diamide.

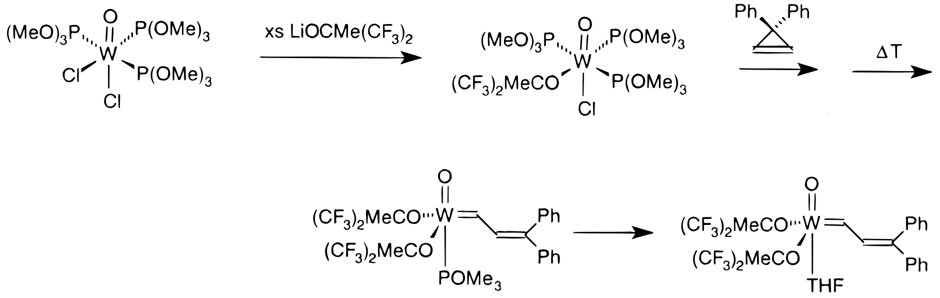
Scheme 5. Synthesis of $W(NPh)(CHSiMe_3)(CH_2SiMe_3)(2\text{-}NMe_2\text{-}CH_2C_6H_4)$



(b) Imido−Alkoxy−Alkylidene Complexes. As early as in 1986, titanacycles were found to polymerize NBE in a living manner.[51] The first living polymerization of cyclic strained olefins[52] such as norbornenes, norbornadienes (bicyclohept-2,5-dienes, NBDs), or the “FEAST monomer” 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene (TCDTF6) by $W(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)(CH\text{-}t\text{-}Bu)(OCMe(CF_3)_2)$[53] was reported in 1987.[54] The initiator may conveniently be prepared either by reaction of $W(NAr')(O\text{-}t\text{-}Bu)_2(CH_2\text{-}t\text{-}Bu)_2$ with PCl_5[55] or via base-catalyzed reaction of $W(C\text{-}t\text{-}Bu)Cl_3$ with $N(TMS)H\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3$ (TMS = trimethylsilyl).[56] Isolable metallacyclobutanes were reported to result from the reaction of this compound with ethylene, *tert*-butylethylene,[57] methyl acrylate, and *N*,*N*-dimethylacrylamide.[58] The synthesis of W−alkylidenes of the general formula $W(CH\text{-}t\text{-}Bu)(NAr')(OTf)_2$ (Tf = triflate) was first described in 1990 by Schrock and co-workers[59] and later adapted for the synthesis of the corresponding analogous molybdenum compounds (vide infra). Similar tungsten-based systems were elaborated by Grubbs and co-workers.[60] Starting from $WOCl_4$, addition of an aryl isocyanate followed by thermal treatment leads to the formation of a tungsten arylimidotetrachloride. Reaction with 2 equiv of an alkoxide followed by reduction in the presence of a phosphorane yielded the desired complex (Scheme 3). More recently, van der Schaaf reported on the photoinduced ROMP of NBE and dicyclopentadiene using $W(NPh)(OCMe(CF_3)_2)_2(CH_2SiMe_3)_2$ and $W(NPh)Cl(CH_2SiMe_3)_3$, respectively, as tungsten alkylidene precursors.[61] Unfortunately, the corresponding ROMP-active species were not isolated. Nevertheless, their existence was indirectly proven by reaction with an aldehyde and characterization of the resulting alkene. A diamido tungsten(VI)-based catalyst was reported by Boncella and co-workers.[62] It was prepared from the dilithio salt of *N*,*N*′-bistrimethylsilyl-protected *o*-phenylenediamine and $W(NPh)Cl_4(OEt_2)$. The conversion of the intermediate bisalkyl complex into the corresponding tungsten alkylidene requires the addition of an excess of base such as trimethylphosphine or triethylphosphine at elevated temperatures (Scheme 4). $W(NPh)(CHCMe_3)(TMS_2PDA)L$ (PDA = *o*-phenylenediamide, $L = PMe_3$) also effectively catalyzes the polymerization of NBE. Unfortunately, a nonstoichiometric initiation due to incomplete dissociation of the base was observed. Another tungsten-based complex $W(NPh)(CHSiMe_3)(CH_2SiMe_3)(2\text{-}NMe_2\text{-}CH_2C_6H_4)$ may be prepared via the synthetic protocol shown in Scheme 5.[63] It was reported stable up to $T \leq 80$ °C and turned out to be an efficient initiator for the polymerization of NBE yielding poly-NBE with a *cis*-content of >90%.

(c) Oxo−Alkoxy−Alkylidene Complexes. A tungsten oxoalkylidene complex $W(O)CHCHCPh_2(OCMe(CF_3)_2)_2 \cdot P(OMe_3)$ and its analogue $W(O)CHCHCPh_2(OCMe(CF_3)_2)_2 \cdot THF$ were reported to be active in the ROMP of NBE.[64] The synthetic route to

Scheme 6. Synthesis of $W(O)CHCHCPh_2(OCMe(CF_3)_2)_2 \cdot L^a$



[a] L = P(OMe3), THF.

these initiators entails the reaction of $W(O)Cl_2(P(OMe)_3)_3$ with $LiOCMe(CF_3)_2)_2$ and 2,2-diphenylcyclopropene (Scheme 6). This reaction of 2,2-diphenylcyclopropene with transition-metal complex was also used for the preparation of the Ru-based alkylidenes (vide infra). Another ROMP-active tungsten−oxo complex, $W(CH\text{-}t\text{-}Bu)(O)(PMe_3)_2(OAr)_2$, was obtained by reaction of $W(CH\text{-}t\text{-}Bu)(O)(PMe_3)_2Cl_2$ with $KO\text{-}2,6\text{-}Ph_2\text{-}C_6H_3$.[65] This complex was reported to be active in the ROMP of 2,3-bis(trifluoromethyl)-NBD and 2,3-dicarbomethoxy-NBD, producing highly tactic (>95%) polymers with a high *cis* contents (>95%). Finally, Boncella and co-workers reported on the use of the tris(3,5-dimethyl-1-pyrazolyl)borate (Tp′) ligand for the preparation of the tungsten oxoalkylidene complex W(O)(CH-*t*-Bu)(Cl)(Tp′), which was found to be an active ROMP catalyst for cyclooctadiene (COD) in the presence of aluminum chloride.[66]

3. Molybdenum-Based Initiators

(a) Imido−Alkoxy−Alkylidene Complexes. On the basis of the results obtained with well-defined tungsten(VI) initiators (vide supra), the synthesis of well-defined high-oxidation-state molybdenum alkylidenes was reported by Schrock and co-workers in 1990.[67] These and the analogous tungsten systems (vide supra) are now commonly named “Schrock catalysts”. The systems possess the general formula $M(NAr')(CHR)(OR')_2 \cdot L$, where M = Mo, W, Ar = phenyl or a substituted phenyl group, R = ethyl, phenyl, trimethylsilyl, CMe_2Ph, or *tert*-butyl, and R′ = CMe_3, CMe_2CF_3, $CMe(CF_3)_2$, $C(CF_3)_2$, aryl, etc. (Figure 1). The most commonly used and also commercially available systems are based on the neophylidene, the $2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3$-imido, the *tert*-butoxide, the hexafluoro-*tert*-butoxide, and the binaphtholate ligand. The synthesis of Mo-based compounds initially started from $Mo(C\text{-}t\text{-}Bu)Cl_3 \cdot DME$ (DME = dimethoxyethane), which was reacted with 1 equiv of TMS−NHAr′ to form $Mo(C\text{-}t\text{-}Bu)(NHAr')Cl_2 \cdot DME$.[68] This compound was transformed into $Mo(CH\text{-}t\text{-}Bu)(NAr')Cl_2 \cdot DME$ by reaction with 0.25 equiv of triethylamine. Due to the synthetic restrictions related with the formation of $Mo(CH\text{-}t\text{-}Bu)(NAr')Cl_2 \cdot DME$, an alternative route starting from $MoO_2Cl_2 \cdot 2THF$ was elaborated. Reaction of this compound with 2 equiv of TMS−NHAr′ in the presence of an auxiliary base, e.g., 2,6-lutidine, in DME resulted in the formation of $Mo(NAr')_2Cl_2 \cdot DME$. For convenience, the formation of $Mo(NAr')_2Cl_2 \cdot DME$ was later accomplished starting from ammonium molybdates[69] or sodium molybdate.[70] The entire reaction, which may be conducted in dimethoxyethane (DME) in virtually quantitative yields, is described by the following stoichiometry

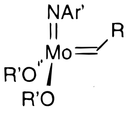


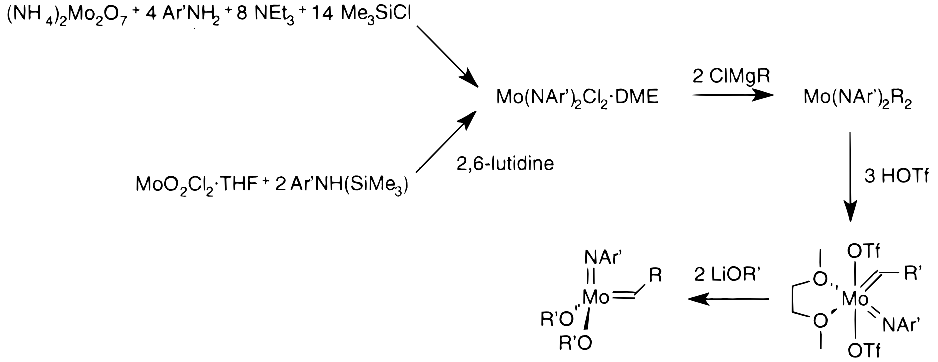
Figure 1. Schrock-type catalysts: M = Mo, W: Ar′ = phenyl, $2,6\text{-}Me_2\text{-}C_6H_3$, $2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3$, etc.; R = ethyl, phenyl, trimethylsilyl, CMe_2Ph, or *tert*-butyl; R′ = CMe_3, CMe_2CF_3, $CMe(CF_3)_2$, $C(CF_3)_2$, aryl, etc.

$$(NH_4)_2Mo_2O_7 + 4Ar'NH_2 + 8NEt_3 + 14Me_3SiCl \rightarrow 2Mo(NAr')_2Cl_2 \cdot dme + 8HNEt_3^+Cl^- + 2NH_4Cl + 7Me_3SiOSiMe_3$$

with Ar′ = a substituted aryl group. While a large variety of arylamines may be used, use of the corresponding alkyl analog is more or less restricted to sterically demanding amines such as *tert*-butylamine.

Similar bisimido complexes of the general formula $Mo(NAr')_2Cl_2 \cdot THF$ were reported by Osborn and coworkers.[71] They prepared molybdenum bis(2,6-diisopropylphenylimido) dichloride·THF by reaction of freshly sublimed MoO_2Cl_2 with 2,6-diisopropylphenylisocyanate in THF at 70 °C. Molybdenum bisimido dichlorides of the general formula $Mo(NAr)_2Cl_2 \cdot DME$ smoothly react with Grignard reagents such as neophyl- or neopentylmagnesium chloride to yield the corresponding molybdenum bisimidodialkyl complexes. Consecutive reaction with 3 equiv of triflic acid (HOTf) in DME yields the molybdenum imidoalkylidene bistriflates, which are conveniently transformed into a large variety of different Schrock-type catalysts by reaction with 2 equiv of a lithium alkoxide.[72] A broad variety of alkoxides such as *tert*-butoxide, trifluoro-*tert*-butoxide, hexafluoro-*tert*-butoxide, perfluoro-*tert*-butoxide, phenoxides, etc., may be used for these purposes. A summary of the entire reaction scheme is given in Scheme 7. In contrast to the corresponding Grubbs-type ruthenium carbenes ($Cl_2Ru(=CH_2)(PR_3)_2$), which were reported as stable in the solid estate (vide infra),[73] unsubstituted molybdenum carbenes (Mo−methylidenes)[74] such as $Mo(=CH_2)(NAr)(OR)_2$ were found to be unstable. The key intermediate of the general formula $Mo(NAr')(CHCMe_2R)(OTf)_2 \cdot DME$ pos-

Scheme 7. Synthesis of Mo-Based Schrock Catalysts[a]



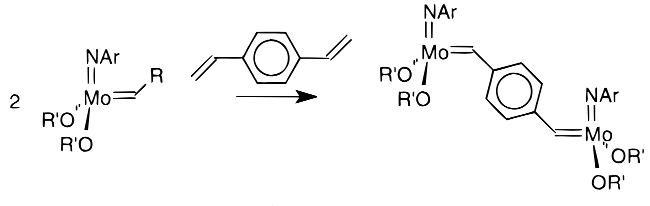
[a] Ar′ = phenyl, 2,6-Me_2-C_6H_3, 2,6-*i*-Pr_2-C_6H_3, etc.; R = ethyl, phenyl, trimethylsilyl, CMe_2Ph, or *tert*-butyl; R′ = CMe_3, CMe_2CF_3, $CMe(CF_3)_2$, $C(CF_3)_2$, aryl, etc.; Tf = triflate $(OSO_2CF_3)_2$.

Scheme 8. Synthesis of Molybdenum Alkylidenes as Elaborated by Osborn et al.

$$MoO_2Cl_2 \xrightarrow[-2\ CO_2]{2\ t\text{-BuNCO}} Mo(N\text{-}t\text{-Bu})_2Cl_2 \xrightarrow{2\ Li\text{-}CH_2\text{-}t\text{-Bu}} Mo(N\text{-}t\text{-Bu})_2(CH_2\text{-}t\text{-Bu})_2 \xrightarrow{2\ HOCH(CF_3)_2} Mo(N\text{-}t\text{-Bu})_2(NH_2\text{-}t\text{-Bu})(CH\text{-}t\text{-Bu})_2(OCH(CF_3)_2)_2$$

sesses a pseudohedral conformation with the imido and alkylidene ligand in a *cis* position and the two triflate groups in a *trans* position. The final catalysts of the type Mo(NAr′)($CHCMe_2R$)(OR')$_2$ possess a tetrahedral geometry. More recently, even silsesquioxanes have been reported as ligands.[75] It is worth noting that such a ligand exchange may also be performed in the course of the polymerization. Thus, starting the polymerization of 2,3-bis(trifluoromethyl)norborn-5-ene with Mo(NAr)(CHR)($OCMe_3$)$_2$, addition of $HOCMe(CF_3)_2$ leads to an alkoxide exchange and forms a living polymer containing the Mo(NAr)(CHR)($OCMe(CF_3)_2$)$_2$ moiety at the chain end. This approach offers access to *block*-copolymers with different *cis*−*trans* configurations for the resulting double bonds.[76] Generally speaking, tungsten and molybdenum Schrock carbenes are highly reactive initiators for the ROMP of a vast variety of cyclic alkenes such as substituted norbornenes, norbornadienes, 7-oxanorbornenes, cyclooctatetraenes (COTs), cyclooctadienes (CODs), etc., or polycyclic alkenes such as certain quadricyclanes.[77] Despite the fact that they are highly sensitive toward traces of oxygen or moisture, they possess a remarkable stability against various functionalities including cyano groups, esters, anhydrides, amides, ethers, amines, etc.[78−80]

Scheme 9. Synthesis of Binuclear Molybdenum Alkylidenes[a]



[a] Ar = 2,6-*i*-Pr_2-C_6H_3; R′ = $CMe(CF_3)_2$.

An alternative route to *N*-*tert*-butylimido-Mo-based systems of the type Mo(*N*-*t*-Bu)(CH-*t*-Bu)(OCH(CF_3)$_2$)$_2$ was reported by Osborn.[81] The synthetic protocol entails several interesting steps. Starting from MoO_2Cl_2, Mo(N-*t*-Bu)$_2Cl_2$ may be prepared by reaction with 2 equiv of *t*-BuNCO. Subsequent reaction with 2 equiv of $LiCH_2$-*t*-Bu yields Mo(*N*-*t*-Bu)$_2$(CH_2-*t*-Bu)$_2$. Addition of hexafluoroisopropyl alcohol yields Mo(*N*-*t*-Bu)(NH_2-*t*-Bu)(CH-*t*-Bu)(OCH(CF_3)$_2$)$_2$. The release of *tert*-butylamine may be induced by adding acetonitrile, which replaces the amine as a ligand. Interestingly enough, this reaction may only be accomplished with hexafluoroisopropyl alcohol (Scheme 8). Other less acidic alcohols show no reaction, while phenol derivatives result in the formation of dineopentyl derivatives. Finally, binuclear molybdenum alkylidenes are obtained by reaction of a Schrock carbene with α,*ω*-dienes such as divinylbenzene or with octatetraene (Scheme 9).[82]

Reactivity.[83] Addition of phosphines such as PMe_3 or amines such as quinuclidine to Mo(NAr)(CH-*t*-Bu)(OCMe(CF_3)$_2$)$_2$ allows, in analogy to W-based systems,[56] the observation and isolation of two isomeric adducts.[84] The attack of the ligand was found to preferably occur at the CNO face, a fact which is in accordance with recent calculations carried out for the attack of an alkene to such systems.[85] The one compound, in which the *tert*-butyl group points toward the imido ligand, is commonly called the *syn*-rotamer; the second compound with the *tert*-butyl group pointing away from the imido ligand is called the *anti*-rotamer (Figure 2). These two rotamers, whose reactivity and relative ratio are governed by the electronic nature of the alkoxide ligand, were found to be responsible for the structure of the final polymer if used in ROMP. In-depth investigations on the reactivity of these rotamers were carried out in order to shed some light onto the mechanism which is responsible for the formation of polymers with high *cis*- or *trans*-vinylene contents. Upon photolysis of a large variety of Mo-based Schrock carbenes in dif-

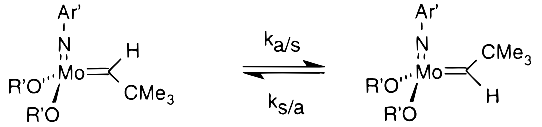


Figure 2. *anti*−*syn* interconversion in Mo-based Schrock carbenes: Ar′ = phenyl, 2,6-Me_2-C_6H_3, 2,6-*i*-Pr_2-C_6H_3, etc.; R′ = CMe_3, CMe_2CF_3, $CMe(CF_3)_2$, $C(CF_3)_2$, etc.

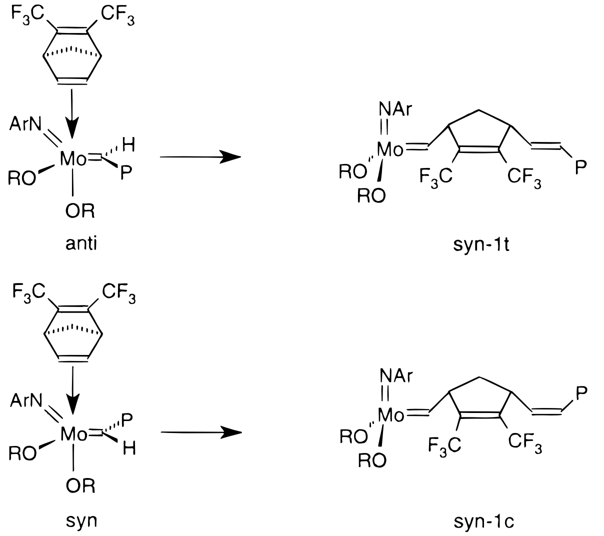
Table 1. *cis*−*trans* Contents and Tacticities of Polymers Prepared by ROMP Using Well-Defined Group VI Transition-Metal Alkylidenes[a] [88−93,177−181,431−435]

ref	compd no.	monomer	catalyst	double bond/ tacticity
93	**1**	(1*R*,2*S*,5*R*)-(−)-bis(menthyldicarboxy)-NBE	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	99% *cis*, isotactic
			Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)-((±)-BINO-SiMe$_2$Ph)$_2$·THF	99% *cis*, isotactic
93	**2**	(*R*)-(−)-bis(pentalactolyldicarboalkoxy)-NBE	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	99% *cis*, isotactic
			Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)-((±)-BINO-SiMe$_2$Ph)$_2$·THF	99% *cis*, isotactic
93, 432	**3**	(+)-*endo,exo*-5,6-dimethyl-NBE	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe(CF$_3$)$_2$)$_2$	85% *cis*, isotactic diads
93, 432	**4**	(±)-*endo,exo*-5,6-dimethyl-NBE	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe(CF$_3$)$_2$)$_2$	85% *cis*, isotactic diads
433	**5**	1,7,7-trimethyl-NBE	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	*trans*
93	**6**	(+)-*endo,exo*-5,6-dimethyl-NBE	Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	85% *cis*
177	**7**	1-methyl-NBE	W(OAr)Cl(CH-*t*-Bu-(*o*-(2-O-3-Ph-C$_6$H$_3$)-C$_6$H$_4$)	all-*cis*-all-HT
95	**8**	5,6-bis(trifluoromethyl)-NBD	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	98% *trans*, tactic
97	**9**	7-oxa-5,6-bis(trifluoromethyl)-NBD	Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	65% *trans*
97	**10**	5,6-bis(methoxycarbonyl)-NBD	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe$_3$)$_2$	95% *trans*, tactic
97	**11**	7-oxa-5,6-bis(methoxycarbonyl)-NBD	Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	30% *trans*
97	**12**	5,6-benzo-NBD	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe$_3$)$_2$	75% *trans*
97	**13**	7-oxa-5,6-benzo-NBD	Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	50% *trans*
97	**14**	5,6-diacetoxy-7-oxa-NBE	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe$_3$)$_2$	40% *trans*
431	**15**	11-(isopropylidene)benzo-NBD	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe$_3$)$_2$	>80% *trans*
431	**16**	11-(α-methylbenzylidene)benzo-NBD	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe$_3$)$_2$	all-*trans*
431	**17**	11-(α-phenylbenzylidene)benzo-NBD	Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	all-*cis*
434	**18**	7-oxa-NBE	W(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe(CF$_3$)$_2$)$_2$	all-*cis*, syndiotactic
434	**19**	*endo*-5-methoxymethyl-7-oxa-NBE	W(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe(CF$_3$)$_2$)$_2$	all-*cis*, syndiotactic
434	**20**	*exo,exo*-5,6-bis(methoxymethyl)-7-oxa-NBE	W(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe(CF$_3$)$_2$)$_2$	all-*cis*, syndiotactic
400	**21**	*cis*-3,4-bis(2-oxa-3-phenylpropyl)-CB	Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	70% *trans*
400	**22**	*cis*-3,4-bis(2-oxa-3-phenylpropyl)-CB	Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe(CF$_3$)$_2$)$_2$	92% *cis*
398	**23**	*cis*-bis(phenylmethyl)-CB-3,4-dicarboxylate	Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	60% *trans*
398	**24**	*cis*-bis(phenylmethyl)-CB-3,4-dicarboxylate	Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe(CF$_3$)$_2$)$_2$	91% *cis*
181	**25**	*exo*-*N*-*n*-alkyl-NBE-dicarboxyimide, $n = 6-11$	Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	97% *trans*, atactic
		exo-*N*-*n*-alkyl-NBE-dicarboxyimide, $n = 6-11$	Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	70% *cis*, atactic
181	**26**	*endo*-*N*-*n*-octyl-NBE-dicarboximide	Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	93% *trans*
			Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	57% *cis*
301	**27**	*N*-[*n*-(4-cyanobiphenyl-4′-yloxy)alkyl]-7-oxa-NBE-5,6-*exo*-dicarboximide	Mo(*N*-2,6-Me$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	*trans*
179	**28**	cyclooctadiene (COD)	W(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	80% *cis*
			Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	30% *cis*
			Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe(CF$_3$)$_2$)$_2$	15% *cis*
179	**29**	cyclopentene	W(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	55% *cis*
			Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	55% *cis*
179	**30**	cycloheptene	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	45% *cis*
			Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe(CF$_3$)$_2$)$_2$	20% *cis*
179	**31**	cyclooctene	W(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	90% *cis*
			Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	30% *cis*
			Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe(CF$_3$)$_2$)$_2$	15% *cis*
179	**32**	cyclodecene	W(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	20% *cis*
			Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	17% *cis*
			Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe(CF$_3$)$_2$)$_2$	5% *cis*
179	**33**	cyclododecene	W(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	20% *cis*
			Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe$_3$)$_2$	15% *cis*
			Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_3$)(OCMe(CF$_3$)$_2$)$_2$	15% *cis*
180	**34**	*N*, *N*-bis(ethoxycarbonyl)-2,3-diaza-NBE	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe$_2$(CF$_3$))$_2$	31% *trans*
			Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	16% *trans*
180	**35**	*N*, *N*-bis(butoxycarbonyl)-2,3-diaza-NBE	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe$_3$)$_2$	86% *trans*
			Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe$_2$(CF$_3$))$_2$	34% *trans*
			Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	16% *trans*
180	**36**	*N*-phenyl-2,3-diaza-NBE-2,3-dicarbimide	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	11% *trans*
180	**37**	*N*-methyl-2,3-diaza-NBE-2,3-dicarbimide	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	13% *trans*
435	**38**	(−)-*endo*-norbornen-2-yl acetate	Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$	95% *cis*

[a] NBE = norbornene; NBD = norbornadiene; CB = cyclobutene; HT = head to tail.

ferent coordinating and noncoordinating solvents (toluene, THF), photostationary *syn*–*anti* mixtures containing up to 35% of the *anti*-rotamer were obtained.[86] Taking advantage of the different chemical shifts of the H_α-alkylidene resonances in both isomers (characterized by α-agostic interactions with the Mo core and typically found between 11 and 13 ppm), the first-order rates of conversion of the *anti*-rotamer to the *syn*-rotamer were determined by ^1H NMR spectroscopy. These investigations revealed, that the rate of interconversion strongly depends on the alkoxide. Thus, $k_{a/s}$ is 10^8 times higher in Mo(NAr)(CHR′)$(OR)_2$ if R = *tert*-butoxide than in the case where R = $CMe(CF_3)_2$. A comparison of these data obtained in toluene with those obtained in THF revealed a decrease for both $k_{a/s}$ and $k_{s/a}$, which was even more pronounced in the case of more electron-withdrawing alkoxides such as $OCMe(CF_3)_2$. These findings were consistent with the expected stronger binding of THF by a more electrophilic metal core along with the fact that a coordinating ligand must be lost from a five-coordinate species in order to allow interconversion.[84] SCF-Xα-SW calculations were carried out on simplified analogues $Mo(NH)(CH_2)(OH)_2$ and confirmed the contribution of the alkoxide oxygen 2p orbitals to most other orbitals.[87] Consequently, their influence on the *syn*–*anti*-interconversion and reactivity of these complexes[88] was obvious. In contrast to the living polymerizations carried out with Mo–bis(hexafluoro-*tert*-butoxide)-based initiators which were found to yield all-*cis* polymers with only 75% tacticity,[88] the living polymerizations which resulted from Mo–bis(*tert*-butoxide)-derived initiators lead to the formation of all-*trans*, highly tactic polymers (Table 1).[89] The tacticity of such polymers was suggested to be controlled by the chirality of the alkylidenes β-carbon (chain end control). Thus, among both rotamers of the Mo-initiator Mo(NAr)(CHR)$(OCMe(CF_3)_2)_2$, the *anti*-rotamer turned out to be the more reactive one in the reaction with bis(trifluoromethyl)norbornadiene (NBDF6), leading to a *syn* first insertion product. The configuration of the double bond was determined as *trans* (*anti* → *syn*, *trans*). In contrast, the *syn*-rotamer produces a *syn* first insertion product with a *cis*-configured double bond (*syn* → *syn*, *cis*) (Scheme 10).[90] Since little *anti* form is present under equilibrium conditions (without irradiation) in Mo(NAr)(CHR)$(OCMe(CF_3)_2)_2$ and *syn* to *anti* conversion is slow (ca. 10^{-5}/s), *cis*-polymers are proposed to form from the *syn* species of a catalyst via olefin attack on the CNO face of the initiator.[85] In a *tert*-butoxide system, where interconversion is relatively fast (ca. 1/s), it was proposed that the *anti* form was the only propagating alkylidene species. This proposal was further supported by studies carried out by Feast and co-workers.[91] Using highly unreactive monomers such as 1,7,7-trimethylnorbornene, only the reaction of the *anti*-rotamer at a very slow, monomer concentration-independent rate was observed. Additionally, the calculated rate constant was essentially identical with the one for *syn*–*anti* conversion. The high dependency of the *cis*–*trans* contents of a polymer on the temperature as found for the polymerization of NBDF6 or DCMNBD with Mo(*N*-2-*t*-Bu-C_6H_4)($CHCMe_2Ph$)(2,2′-[4,4′,6,6′-*t*-$Bu_4(C_6H_2)_2]O_2$) again underlined the importance of *syn*–*anti* conversion with respect to the time-scale of the polymerization.[92] Thus, the careful choice of an alkoxide in these systems offers an attractive access to polymers with either *cis*- or *trans*-configured double bonds as well as to highly tactic polymers.[93] To be capable of preparing polymers which are >99% *cis* and >99% tactic, the use of chiral alkoxide ligands was elaborated.[94–96] Table 2 gives an overview over the corresponding chiral ligands, the investigated monomers, and the polymer properties. 7-Oxanorbornene and 7-oxanorbornadiene derivatives were found to form observable and even isolable molybdametallacycles. Thus, 7-oxa-2,3-(bistrifluoromethyl)-norbornadiene reacts with Mo(*N*-2,6-*i*-Pr_2-C_6H_3)-($CHCMe_3$)$(OCMe_3)_2$ to form a remarkably stable metallacycle (Scheme 11).[97] A similar tungstametallacycle may be observed in the reaction of 2,3-bis-(trifluoromethyl)norbornadiene with W(*N*-2,6-*i*-Pr_2-C_6H_3)($CHCMe_3$)$(OCMe_3)_2$.[89] An interesting approach that uses Schrock Mo–alkylidenes for imine metathesis will not be neglected. Mo(*N*-2,6-*i*-Pr_2-C_6H_3)-($CHCMe_3$)$(OCMe_3)_2$ cleanly reacts with pyrroline to yield the corresponding first insertion product.[98] Despite the fact that the reaction comes to an end at this point and imine ROMP may hardly be realized, some further developments in imine metathesis may be expected.

Scheme 10. Reaction of *syn*- and *anti*-Rotamers in ROMP[a]



[a] Ar = 2,6-*i*-Pr_2-C_6H_3, 2,6-Me_2-C_6H_3; R = *t*-Bu, $CMe(CF_3)_2$.

(b) Oxo–Imido Complexes. The enormous degree of dependence of the reactivity of well-defined transition-metal alkylidene complexes of the type Mo(CHR)(NAr)$(OR')_2$ (where Ar = 2,6-*i*-$Pr_2C_6H_3$, for example) toward olefins on the nature of the OR′ group suggested a similar influence of the imido group. Keeping the qualitative correlation between olefin metathesis activity and the electron-withdrawing ability of certain alkoxides in mind, synthesis of the corresponding Mo–hexafluoro-*tert*-butylimido complexes was attempted. Nevertheless, as a consequence of the low basicity of fluorinated alkylamines, only a mixed molybdenum oxo–imido complex, Mo-

Table 2. Chiral Alkoxides, Initiators, Monomers, and Properties of the Resulting Polymers[a]

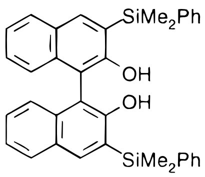
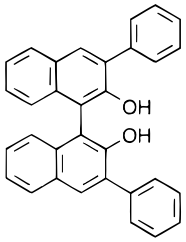
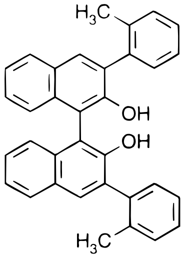
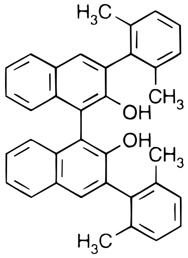
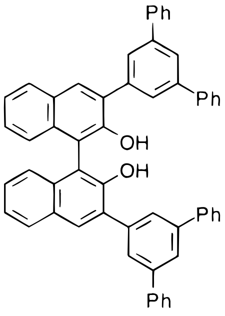
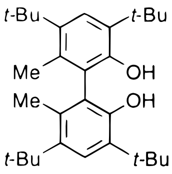
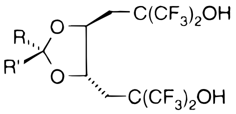
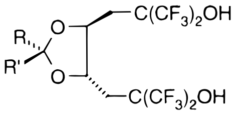
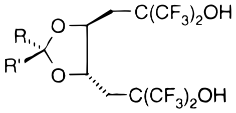
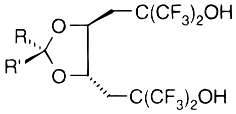
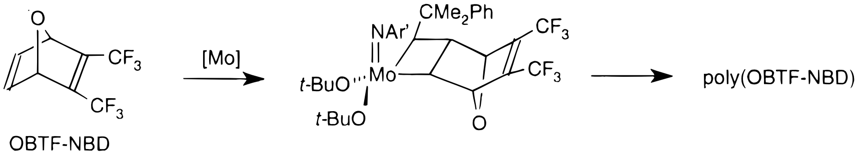
#	ligand (R)	initiator $Mo(NAr)(CHCMe_2Ph)(OR)_2$	monomer	polymer properties % cis [%]
1		Ar = 2,6-Me_2-C_6H_3	NBDF6	> 99
			DMMNBE	> 99
		Ar = 2,6-*i*-Pr_2-C_6H_3	NBDF6	71
			DMMNBE	93
2		Ar = 2,6-Me_2-C_6H_3	NBDF6	95
			DMMNBE	70
		Ar = 2,6-*i*-Pr_2-C_6H_3	NBDF6	> 99
			DMMNBE	> 99
3		Ar = 2,6-Me_2-C_6H_3	NBDF6	93
			DMMNBE	83
		Ar = 2,6-*i*-Pr_2-C_6H_3	NBDF6	98
			DMMNBE	98
4		Ar = 2,6-Me_2-C_6H_3	NBDF6	99
			DMMNBE	91
		Ar = 2,6-*i*-Pr_2-C_6H_3	NBDF6	98
			DMMNBE	99
5		Ar = 2,6-Me_2-C_6H_3	NBDF6	93
			DMMNBE	84
		Ar = 2,6-*i*-Pr_2-C_6H_3	NBDF6	98
			DMMNBE	> 99
6		Ar = 2,6-*i*-Pr_2-C_6H_3	NBDF6	96
			DMMNBE	-
		Ar = 2-*t*-Bu-C_6H_4	NBDF6	44
			DMMNBE	54

Table 2 (Continued)

#	ligand (R)	initiator	monomer	polymer properties
		$M(NAr)(CHCMe_2Ph)(OR)_2$		% cis [%]
7		M = Mo Ar = 2,6-*i*-Pr_2-C_6H_3	-	synthesis only
8		$W(CHCHCOCH_2CH_2CH_2O)(O)$ $Cl_2[P(OMe)_3]$	-	synthesis only
9		W(η²-diphenylcyclopropene)(O) $Cl_2[P(OMe)_3]_2$	-	synthesis only
10		$W(CHCHCPh_2)(NAr)$ $Cl_2[P(OMe)_3]_2$ Ar = 2,6-*i*-Pr_2-C_6H_3	-	synthesis only

[a] NBDF6 = 2,3-bis(trifluoromethyl)norbornadiene; DMMNBE = (+)-(2*S*,3*S*)-2,3-bis(dimethoxymethyl)norborn-5-ene.[94,95,436]

Scheme 11. Formation of Molybdacyclobutane Species[a]



[a] OBTF-NBD = 7-oxa-bis(trifluoromethyl)norbornadiene; [M] = Mo(NAr′)(CHCMe₂Ph(O-*t*-Bu)₂; Ar′ = 2,6-*i*-Pr₂-C₆H₃.

$(O)(NCMe(CF_3)_2)Cl_2pyridine_2$, and its derivative, $Mo(NCMe(CF_3)_2)$(*N*-2,6-*i*-Pr_2-C_6H_2)Cl_2Py_2, could be prepared (Figure 3).[99] It is worth mentioning that such oxoimido complexes of molybdenum are in contrast to osmium-[100,101] or tungsten-based systems[102] (vide supra) quite rare. These findings are in accordance with the fact that the preparation of Mo−triflates of the general formula $Mo(NAr)(CHR)((OTf)_2{\cdot}DME$ (Tf = triflate) also fails in the case where Ar = C_6F_5, C_6-3,5-$(CF_3)_2$. Similar mixed imido complexes of the general formula $Mo(NAr)(NR)Cl_2{\cdot}DME$ were obtained by reaction of Mo(*N*-*t*-Bu)$_2$$Cl_2{\cdot}DME$ with a mixture of hexfluoroaniline and adamantylamine (Ar = C_5F_5, R = adamantyl).[70]

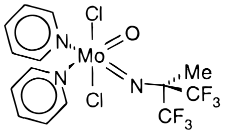


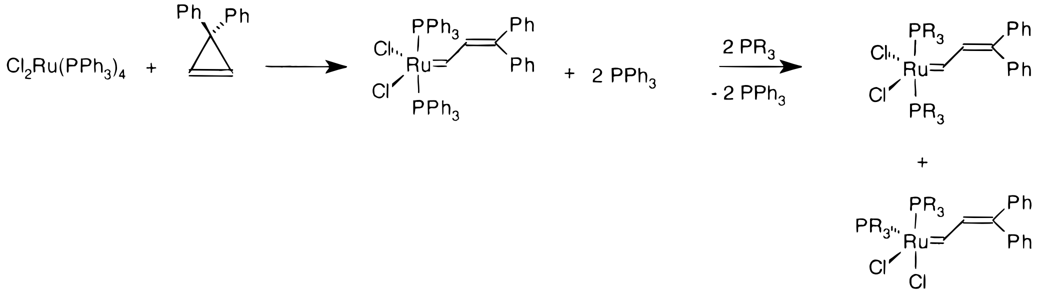
Figure 3. Structure of a molybdenum oxo−imide based on hexafluoro-*tert*-butylamine.

B. Group VIII Transition-Metal-Based Initiators

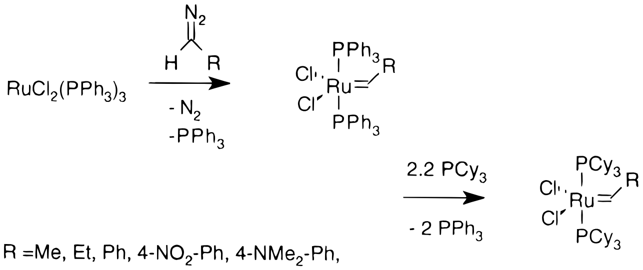
1. Ruthenium-Based Initiators

Ruthenium salts such as $RuCl_3{\cdot}xH_2O$, ruthenium(II) tosylates, have been known to effectively catalyze ROMP of several cycloalkenes for quite some time. Despite the characterization of several olefin−ruthenium(II) complexes,[103−106] the actual catalytic species in such systems was still ill-defined. Nevertheless, the fact that ruthenium-based systems did effectively catalyze the ROMP even in aqueous systems[107,108] or in the presence of other protic functional groups (alcohols, carboxylic acids, etc.)[104,105,109−114] initiated an intense search for well-defined, functional-group-tolerant ruthenium systems,[115] mainly conducted by the group of R. H. Grubbs. In 1992, this group described the synthesis of the first well-defined ruthenium alkylidene (Scheme 12).[116] Thus, reaction of $Cl_2Ru(PPh_3)_3$ or $Cl_2Ru(PPh_3)_4$, respectively, with 2,2-diphenylcyclopropene in benzene or methylene chloride yields the desired ruthenium carbene complex in quantitative yield. Typical alkylidene resonances for H_α and C_α are observed at $\delta = 17.94$ and

Scheme 12. Preparation of the First Well-Defined Ruthenium Alkylidenes

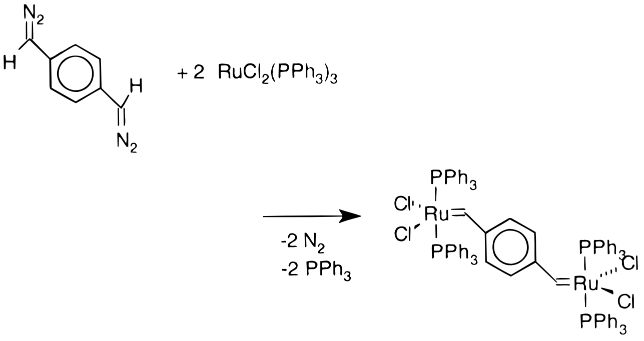


Scheme 13. Preparation of Grubbs Catalysts



R =Me, Et, Ph, 4-NO_2-Ph, 4-NMe_2-Ph, 4-Me-Ph, 4-MeO-Ph, 4-Cl-Ph, 4-Br-Ph

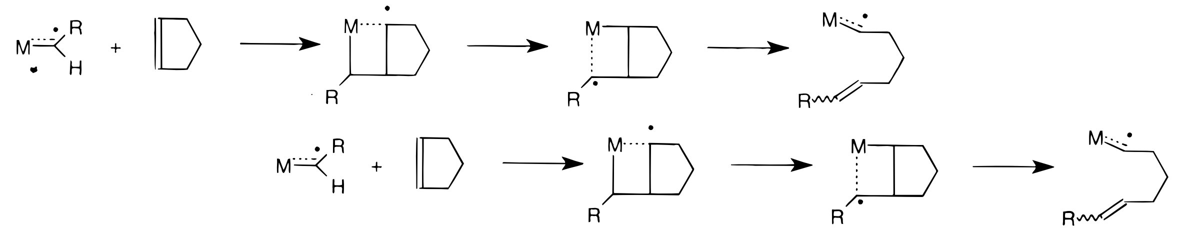
Scheme 14. Synthesis of the Bimetallic Ruthenium Catalyst $(PR_3)_2Cl_2Ru({=}CH{-}p{-}C_6H_4{-}CH{=})Ru(PR_3)_2Cl_2$



288.9 (both in C_6D_6). Despite a ratio of $k_i/k_p < 1$, the compound was reported to be an efficient initiator for the polymerization of NBE. The rather low activity of the bis(triphenylphosphine) derivative for cyclic olefins other than NBE, such as bicyclo[3.2.0]-hept-6-ene or *trans*-cyclooctene, was successfully enhanced by phosphine exchange with more basic analogues, e.g., tricyclohexylphosphine and triisopropylphosphine (Scheme 12).[117] It is worth mentioning that the resulting compounds of the general formula $Cl_2Ru(CHCHCPh)_2(PR_3)_2$ (R = cyclohexyl, isopropyl) exist in two isomeric forms as shown in Scheme 12. An alternative route to ruthenium alkylidenes that avoids the preparation of 2,2-diphenylcyclopropene was elaborated by Schwab and Grubbs.[73,124] The synthetic protocol entails the reaction of $RuCl_2(PPh_3)_3$ with an diazoalkane (Scheme 13). The resulting compounds of the general formula $Cl_2Ru(CHR)(PR_3)_2$ (R = Ph, $CHCPh_2$), now well-known as the Grubbs catalyst, may be prepared in high yields. In analogy, a bimetallic species may be prepared (Scheme 14)[132] which gives access to the formation of ABA *block*-copolymers. Ruthenium-based Grubbs catalysts turned out to be highly efficient in the ROMP of various substituted cyclic olefins such as norbornenes, bicyclo[3.2.0]heptene,[125] and 7-oxanorbornenes[126] in the presence of cationic surfactants[127] as well as for low-strain olefins such as cyclooctenes.[128] Interestingly enough, the polymerization of 7-*tert*-butoxybicyclo[2.2.1]hepta-2,5-diene with $Cl_2Ru(CHPh)(PCy_3)_2$ does not lead to the desired polymer but to cyclic products and regeneration of the initiator. So far, this exclusive cyclization has only been observed for this particular monomer.[131]

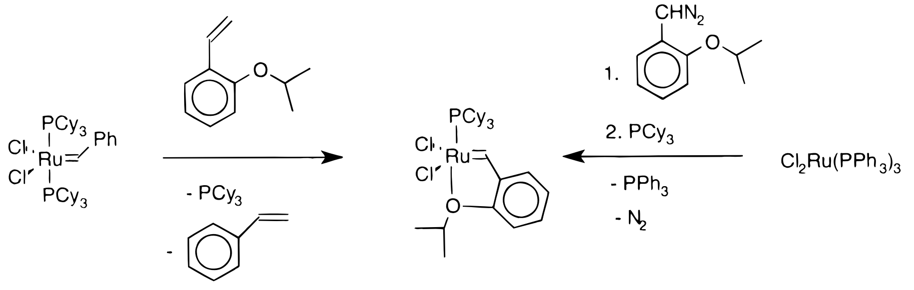
Reactivity. Compared to molybdenum- or tungsten-based Schrock catalysts, the reactivity of ruthenium-based systems is different. While reactivity slightly increases in the order I < Br < Cl,[118] it may more efficiently be enhanced via the phosphines than by the nature of the alkylidene moiety[73] or by substitution of the chlorides by other more electron-withdrawing groups.[119] The thermodynamics and, in particular, the importance of σ-donation related with the exchange of phosphines, the influence of electronic as well as steric effects, of this type of compounds have been studied in detail.[120] The stability as well as the reactivity order that may be deduced therefrom is $PPh_3 < PBz_3 < PCyPh_2 < PCy_2Ph < P\text{-}i\text{-}Bu_3 < P\text{-}i\text{-}Pr_3 < PCy_3$. Phosphine exchange from the parent bis(triphenylphosphine) systems into the more reactive bis(tricyclohexylphosphines) may either be performed consecutively or in situ. The influence of different phosphines on the reactivity of ruthenium-based systems of the general formula $Cl_2Ru(CHCHCPh)_2(PR_3)_2$ was additionally investigated in the ring-closing metathesis (RCM) of dipropargylmalonate.[118] These investigations again revealed increasing reactivity in the order I < Br < Cl and $PPh_3 < P\text{-}i\text{-}PPr_2Ph < PCy_2Ph < P\text{-}i\text{-}Pr_3 < PCy_3$. In principle, two different mechanisms were postulated on the basis of these experiments: An associative mechanism with both phosphines on the metal center and the dominant dissociative mechanism with only one phosphine attached to the ruthenium core. The latter one was further supported by the finding that the addition of CuCl as a phosphine scavenger resulted in significantly elevated catalytic activities. Both mechanisms and the existence of both mono- and diphosphine adducts, respectively, were confirmed by quantum molecular dynamics studies.[121] These studies also confirmed the importance of the use of sterically crowded phosphines for the preparation of highly active ruthenium alkylidenes as they lead to longer and consequently less stable Ru−P bonds. The important effect of phosphine size and basicity on metathesis performance[118,120] was

Scheme 15. Radical-Based Polymerization Mechanism of Ruthenium-Based Grubbs Catalysts[a]



[a] M = Ru; R = Ph.

Scheme 16. Preparation of a Chromatographically Recoverable Ruthenium Alkylidene



further underlined by the finding that even small changes in the PCy_3 ligand allow the fine-tuning of this catalytic system. Thus, the use of the $PCy_2CH_2SiMe_3$ ligand allows the synthesis of the initiator $Ru(CHPh)Cl_2(PCy_2CH_2SiMe_3)_2$ that turned out to be highly active in the polymerization of norbornene imides.[133] Generally speaking, ROMP of norbornenes and norbornadienes using ruthenium-based systems results in the formation of polymers that predominantly contain *trans*-vinylene units. Another important point that needs to be addressed in any catalytic system is its stability. Investigations carried out with a large variety of mono- and binuclear ruthenium alkylidenes revealed significant differences between the more stable alkylidenes and the rather unstable methylidenes.[153] Thus, alkylidene decomposition requires phosphine dissociation and is predominantly second order while methylidene decomposition turned out to follow primarily first-order kinetics. Probably for steric reasons, no ethylene formation resulting from bimolecular decomposition is observed with methylidenes. Finally, monophosphine or, generally speaking, monoligand adducts were found to be highly unstable. Since such monoadducts have been proposed to be the actual catalytic species in metathesis-based reactions, the utility of any catalyst strongly depends on the ratio of the rate of catalysis to the rate of decomposition. Consequently, catalyst design has to focus on accelerating the catalytic process instead of accelerating both processes. For purposes of completeness, investigations of the actual catalytic cycle in the reaction of $Cl_2Ru(CHPh)(PCy_3)_2$ with cyclic olefins carried out with substituted cyclobutenes have to be mentioned.[122] Recently, evidence obtained for the formation of persistent radical anions in the reaction of $Cl_2Ru(CHPh)(PCy_3)_2$ with dienes and even simple alkenes was provided by ESR measurements.[123] While the actual nature of the radical anions still needs to be identified, a new radical-based mechanism has been proposed (Scheme 15).

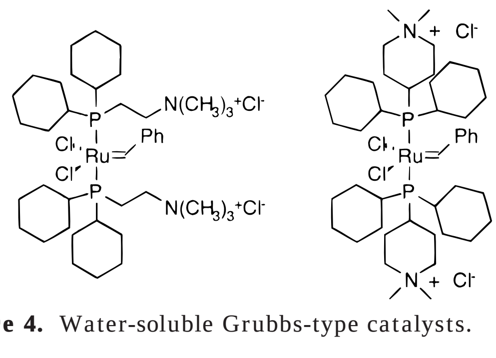
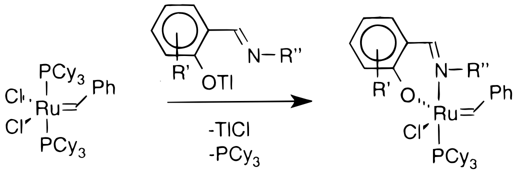


Figure 4. Water-soluble Grubbs-type catalysts.

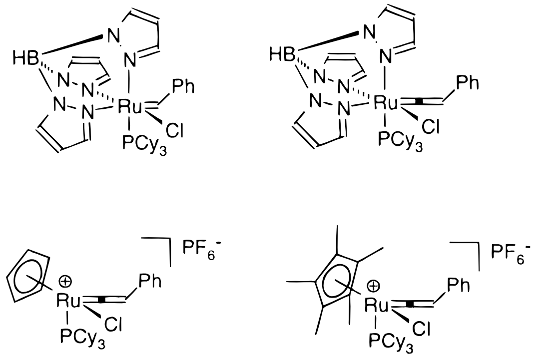
Scheme 17. Synthesis of Schiff-Base-Ligated Ruthenium Carbenes[a]



[a] $R' = H$, 4-NO_2, 6-Me-4-NO_3; $R'' = 2,6$-*i*-Pr_2-C_6H_3, 2,6-Me_2-4-MeO-C_6H_3, 2,6-Me_2-4-Br-C_6H_3, 2,6-Cl_2-4-CF_3-C_6H_3, 2,6-*i*-Pr_2-4-NO_2-C_6H_3.

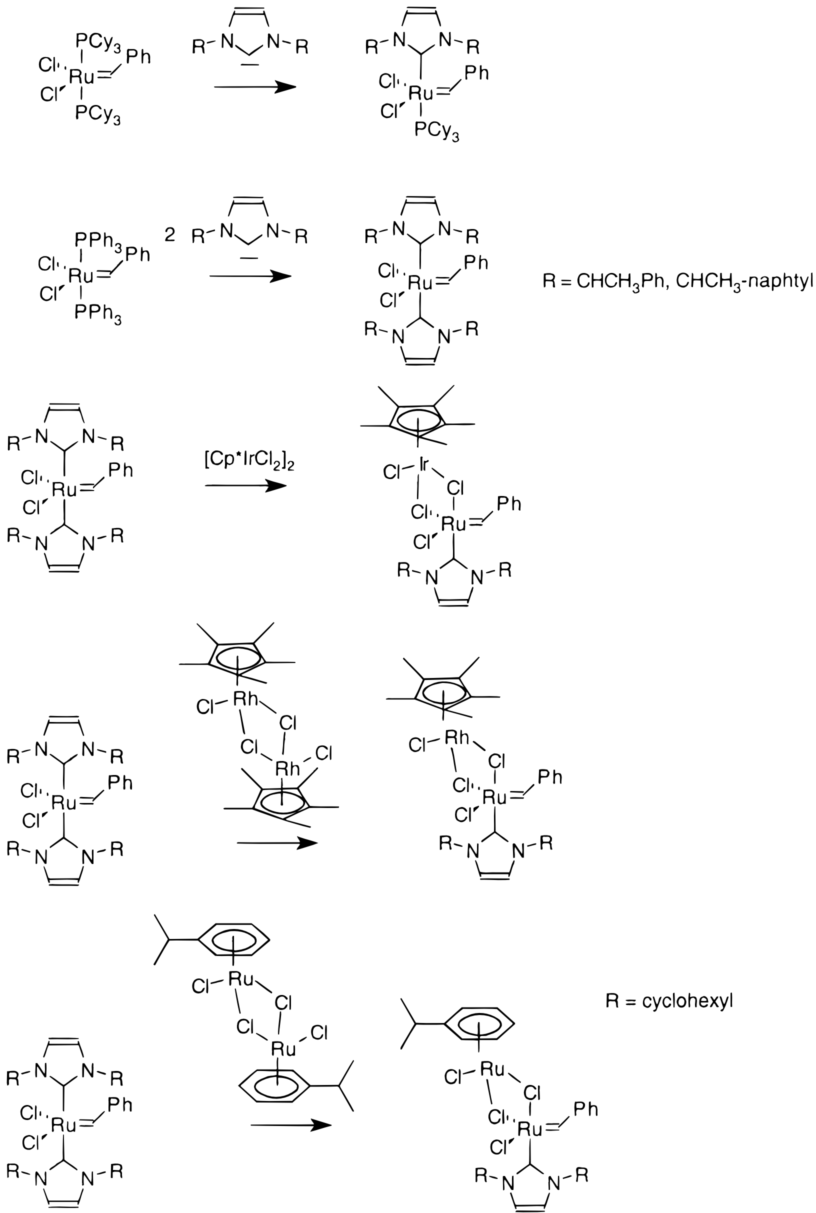
Ligand Variation. The reaction of diazo compounds with ruthenium arene complexes has been used lately for the in situ generation of ruthenium alkylidenes from $[RuCl_2(p\text{-cymene})]_2$, tricyclohexylphosphine, and trimethylsilyldiazomethane.[134] The resulting initiators were again found to polymerize 2,3-difunctionalized norbornadienes and their 7-oxa analogues with high *trans*-stereoselectivity.[135,136] Finally, following the diazo approach, the synthesis of an internally oxygen-chelated ruthenium alkylidene has to be mentioned (Scheme 16). Thus, reaction of $Cl_2Ru(PPh_3)_3$ with 2-isopropoxyphenydiazomethane and PCy_3 leads to the formation of $Cl_2Ru(CH\text{-}2\text{-}i\text{-}Pr\text{-}O\text{-}C_6H_4))(PCy_3)$. Alternatively, this compound, which turned out to be highly stable and even chromatographically recyclable, may be prepared by reaction of $Cl_2Ru(CHPh)(PCy_3)_2$ with 2-isopropoxystyrene. So far, this compound has only been used in RCM.[137] More recently, the synthesis of entirely water-soluble analogues has been reported (Figure 4).[129,130] These

Scheme 18. Tris(pyrazolyl)borate-, Cyclopentadienyl- (Cp), and Pentamethyl-Cp-Based Grubbs-Type Catalysts



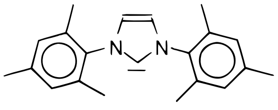
water-soluble systems have also been investigated in terms of their stability vs Brønsted acids such as DCl.[138] Interestingly enough and in contrast to the behavior of “classical” water-soluble systems such as $RuCl_3\cdot xH_2O$, addition of an acid does not interfere with the ruthenium alkylidene but effectively protonates one phosphine group, thus generating a more active monophosphine complex. The corresponding monophosphine adducts were found to be stable and quantitatively initiate ROMP of cyclic olefines. Interestingly, the same monophosphine adducts were found to be the active species in the ROMP in the gas phase.[139] Another structural variation in the synthesis of well-defined ruthenium carbenes represents the use of bidentate Schiff-base ligands (Scheme 17),[140] tris(pyrazolyl)borate (Tp), cyclopentadienyl (Cp), and pentamethylcyclopentadienyl (pentamethyl-Cp) ligands (Scheme 18).[141] In this context it is worth mentioning that molybdenum alkylidenes prepared from the Tp ligand of the formula Mo(Tp)($CHCMe_2Ph$)(N-2,6-i-Pr_2-C_6H_3)(OTf) require a cocatalyst ($AlCl_3$) in order to be ROMP active.[142] A synthetic protocol consisting of the reaction of $Cl_2Ru(CHR)(PPh_3)_2$ with imidazoline-2-ylidene[148,149] was used for the generation of another type of ruthenium-based system.[150] Generally, these imidazoline-2-ylidene-derived sys-

Scheme 19. Synthesis of Chiral *N*-Heterocyclene-Based Mono- and Binuclear Ruthenium Carbenes



tems were found to possess higher ROMP activities. By this approach, chirally substituted mononuclear as well as binuclear ruthenium alkylidenes[151] that were again found to possess enhanced ROMP activity compared to mononuclear ruthenium alkylidenes[152] may be prepared (Scheme 19). Other imidazol ligands, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene(IMes), 1,3-bis(4-methylphenyl)imidazol-2-ylidene (ITol), and 1,3-bis(4-chlorophenyl)imidazol-2-ylidene (IpCl), were successfully used for the preparation of mixed-ligand ruthenium carbenes of the general formula $Cl_2Ru(CHPh)(IMes)(PR_3)$, R = Cy, Ph (Scheme 20)[154−156] and $Cl_2Ru(CHCHCPh_2)(IMes)(PR_3)$, $Cl_2Ru(CHPh)(ITol)(PR_3)$, $Cl_2Ru(CHPh)(IpCl)(PR_3)$.[155] Despite the missing data on the ROMP activity of this class of compounds, the triphenylphosphine-containing systems (R = Ph) were found to possess the highest RCM activity. A class of cationic ruthenium allenylidenes, which has been reported recently by Fürstner and Dixneuf,[157] possesses similar high RCM activity. These cationic species are accessible by reaction of (p-cymene)$RuCl_2(PR_3)$ with a 1-prop-2-ynol, preferably with 1,1-diphenylprop-2-ynol (Scheme 21). A dicationic ruthenium vinylidene complex that was also reported to be active in the ROMP of NBE may be prepared from $[RuCl_2(N,N',N)(PPh_3)]$ and 2 equiv of $AgBF_4$ (N,N′,N = 2,6-bis[(dimethylamino)methyl]-pyridine) (Figure 5).[143] Another Grubbs-type catalyst containing a bridged diphosphino ligand was reported by Hofmann and co-workers (Scheme 22).[158] This system was reported to be active in the metathesis polymerization of NBE. Nevertheless, polymer yields were found to be comparably low (42%). Additionally M_w/M_n values of 2.75 suggested unfavorable ratios of k_i/k_p, resulting in a polymerization system where only a small part of the initiator initiates while a major part remained inactive.

Scheme 20. Structure of 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) Ligand



IMes

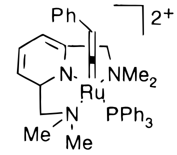
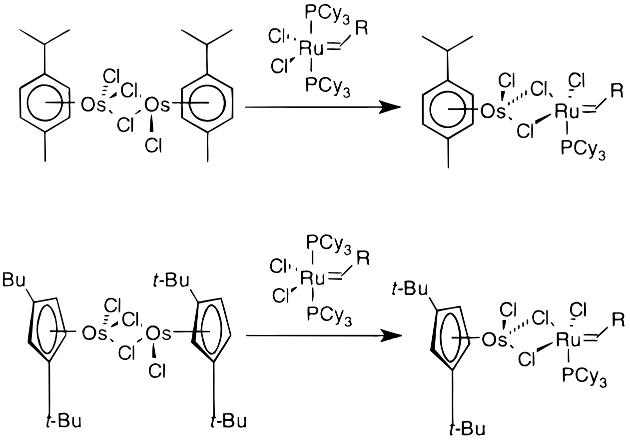


Figure 5. Structure of 2,6-bis(dimethylaminomethyl)-pyridine (N,N′,N) based Ru(N,N′,N)(CCHPh).

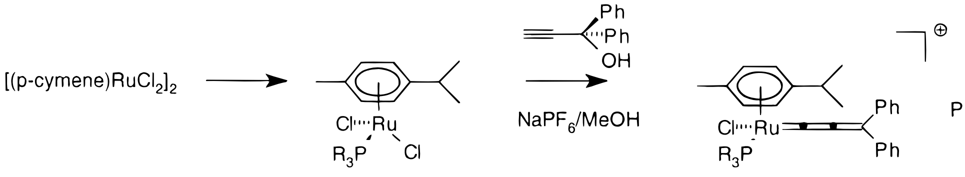
Heterobimetallic ruthenium alkylidenes, which may be prepared by reaction of $Cl_2Ru(PCy_3)_2(CHR)$ with $[Ru(p\text{-cymene})Cl_2]_2$, $[Os(p\text{-cymene})Cl_2]_2$, and $[Rh(\textit{tert}\text{-butylcyclopentadienyl})Cl_2]_2$, respectively, were reported to possess significantly elevated activities in the ROMP of 1,5-cyclooctadiene (COD) and 2,2-bis(trifluormethyl)norbornene.[144] The most active compounds obtained so far are the bimetallic complexes (p-cymene)RuCl(μ-Cl)$_2$RuCl(CHPh)(NHC) and (Cp*)RhCl(μ-Cl)$_2$RuCl(CHPh)(NHC) (NHC = N-heterocyclic carbene, Cp* = pentamethylcyclopentadienyl)[145,146] (Scheme 23). It is worth mentioning that the same compounds have been reported to be highly active in ring-closing metathesis (RCM).[147] The reactivity of such systems increases in the order Ru < Os < Rh. Assuming that the coordination of the second metal center to the bridging chlorides directly influences their electron-withdrawing capability, this

Scheme 23. Synthesis of Heterobimetallic Ruthenium Carbenes[a]



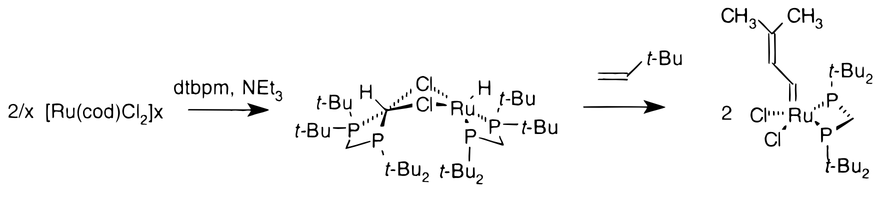
[a] R = Ph.

Scheme 21. Synthesis of RCM-Active Cationic Ruthenium Allenylidenes[a]



[a] R = cyclohexyl, phenyl, i-Propyl.

Scheme 22. Synthesis of $[(\eta^2\text{-dtbpm})Cl_2Ru{=}CH{-}CH{=}CMe_2]$[a]



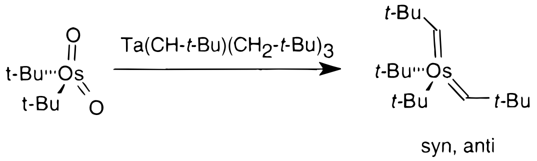
[a] dtbpm = di-$tert$-butyldiphosphinomethane.

finding is consistent with the observed order of activity I < Br < Cl in the mononuclear complexes.[118]

2. Osmium-Based Initiators

Reaction of dineopentylosmiumdioxide with 2 equiv of $Ta(CHR)(CH_2R)_3$ was reported to result in the formation of osmium dineopentylbisneopentylidene (Scheme 24).[100,159] The interconversion of the two isomeric forms (*syn*–*anti* and *anti*–*anti*) of this compound was postulated to proceed via an osmium trineopentylneopentylidene. So far, no reports on the ROMP activity of these complexes have been given.

Scheme 24. Synthesis of Well-Defined Os(VI) Alkylidenes



3. Platinum-Based Initiators

Quite recently, a platinum(II) vinylidene complex was reported. Its synthesis was accomplished by reaction of $Pt(PPh_3)_2(CH_3)(CCR)$ with triflic acid and tetrafluoroboric acid, respectively, to give the resulting cationic Pt(II) complex, $(CH_3)(PPh_3)_2Pt({=}C{=}CHR)]^+ X^-$ ($X = BF_4^-$, $CF_3SO_3^-$).[160] No data on the catalytic activity of this complex, which has not been isolated but whose structure has been proven by NMR experiments, have been reported so far.

III. Applications

Three polymerization techniques, ROMP, ADMET polymerization, and alkyne polymerization, that may be carried out with the catalytic systems described above will be addressed. Despite their relatively recent addition to the armor of synthetic methods, they already faced extensive exploitation in the manufacture of speciality polymers. In particular, the great control over polymer structure in all its ramifications which is provided by ROMP and ADMET polymerization offers an attractive access to the fine-tuning of polymer properties and function. In particular, the unique backbones that may be generated from norbornenes, norbornadienes, cyclobutenes, cyclooctenes, cyclooctadienes, -trienes, and -tetraenes, and barrelenes as well as alkynes let ROMP-based polymers appear as highly attractive materials for modern technology.[161–167] In the following sections some selected applications in various areas will be presented. Where applicable, special considerations will be given to the corresponding initiator system used for synthesis.

A. Living Polymerizations

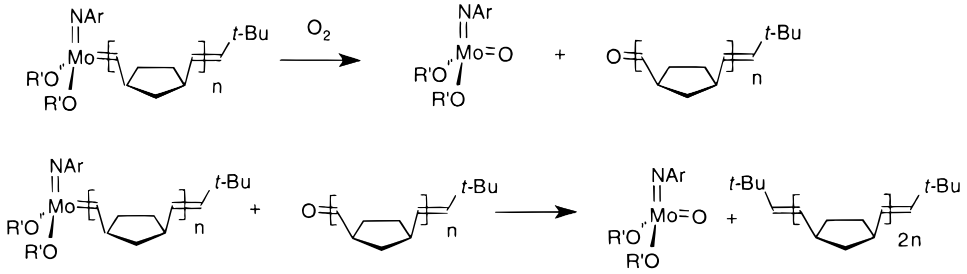
The term “living” polymerization[168–173] is appropriate for systems that do not show any chain termination or chain transfer. Nevertheless, such living systems are not immortal. The generally accepted definition of a living polymerization is as that of a chain polymerization proceeding without termination or transfer. Within this definition, initiation may be quantitative and instantaneous; nevertheless, these two features are not a basic requirement. Widely accepted probes for the livingness of a system are low values for M_w/M_n (polydispersity, PDI) and a linear relationship between M_n and the number of equivalents of monomer added to such a system.[174] To be able to “rank” living systems in terms of their mortality, Matyjaszewski provided a quite useful tool.[175] His rankings are based on the ratios of the rate constants of chain transfer, propagation, and chain termination. Six different classes of living polymerizations were defined on the basis of an arbitrarily defined minimum lifetime, where ≤ 10% of the living polymer chains are deactivated. The 10% limit was chosen as it represents an amount of deactivated polymer that may conveniently be detected and quantified by means of GPC.

Molybdenum- or tungsten-based polymerization systems sometimes result in a bimodal molecular weight distribution. This may result from a nonstoichiometric initiation which leads to two sets of propagating species, the (unwanted) termination of a certain percentage of the living polymer chains during propagation or the reaction of living polymer termini after polymerization with carbonyl-terminated oligomers. This dioxygen-initiated post-polymerization bimolecular dimerization[176] may be described as shown in Scheme 25. One of the main advantages of living polymer systems lies in the controlled preparation of well-defined polymers with respect to molecular weight and polydispersity (PDI) as well as in the synthesis of *block*- and *graft*-copolymers.

B. Polymer Tacticity

Until now, a large variety of functional norbornenes, norbornadienes, and other cyclic olefins has been polymerized by different transition-metal alkylidenes.[177–181] For convenience, a summary of the

Scheme 25. Dioxygen-Initiated Post-Polymerization Bimolecular Dimerization[a]



[a] Ar = 2,6-Me_2-C_6H_3, 2,6-*i*-Pr_2-C_6H_3, etc.; R′ = *tert*-butyl, $CMe_2(CF_3)$, $CMe(CF_3)_2$, etc.

corresponding monomers, initiators, and polymer properties in terms of *cis*–*trans* configuration and tacticity is given in Table 1. For the influence of the catalytic system on the resulting tacticity in the corresponding polymer vide supra.

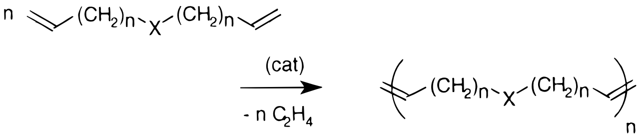
C. Acyclic Diene Metathesis (ADMET) Polymerization

1. Mechanism

ADMET represents a versatile tool for both polymerization and depolymerization.[182] To stay within the thematic limits of this review, only ADMET polymerization will be discussed in this section. Combinations of ADMET with other polymerization techniques as well as further applications are presented in following sections if applicable.

Generally speaking, ADMET polymerization is carried out with α,ω-dienes. The general reaction sequence is shown in Scheme 26. The actual driving force of this reaction is the formation of ethylene that is permanently removed from the reaction mixture. Since ethylene requires the involvement of a metal methylidene, this intermediary species needs to possess a certain stability.[183] Other elimination products resulting from the use of other (functional) dienes have to be removed in order to avoid polymerization–depolymerization equilibria.[184] Since well-defined Mo-, W-, as well as Ru-based carbenes avoid the formation of carbocationic species,[185] a large variety of homo- and copolymers may be prepared according to the general ADMET scheme. Due to the comparably reduced reactivity, the use of Ru-based systems generally requires larger amounts of catalyst.[186] Structural restrictions are present in that substituted α,ω-dienes such as 2,5-dimethyl-1,5-hexadiene or 2-methyl-2,5-hexadiene do not react at all even with Lewis-acid-free, highly active tungsten or molybdenum Schrock carbenes nor do they give rise to more complex reaction pathways including cross-metathesis reaction of intermediary formed *internal* double bonds.[187–189] Since α,ω-dienes containing functional groups such as ethers or thioethers exhibit a significantly different reactivity vs Mo- and Ru-based initiators, these effects have been studied in detail. Investigations revealed that, in particular, Ru-based initiators that follow a dissociative mechanism[118] show an enhanced tendency toward cyclization reactions. Besides the favorable entropy and enthalpy factors, Π-complexation from the neighboring olefin seems to play an important role. Among the vast variety of Mo-based Schrock carbenes, Mo(*N*-2,6-Me_2-C_6H_3)($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$ has been proposed to be the most reactive initiator.[190]

Scheme 26. General Reaction Scheme for ADMET Polymerization[a]



[a] For X and *n* refer to text.

2. Applications

Besides the large variety of pure hydrocarbon-based polymers that are available via ADMET polymerization,[191–195] functionalized polymers are of particular interest. Alcohol-functionalized polymers are accessible by ADMET polymerization of the corresponding alcohol-functionalized dienes ($n = 3$, X = CHOH, CCH_3OH, $CHCH_2OH$) using $Cl_2Ru(CHR)(PCy_3)_2$ as an initiator.[196,197] Main-chain metal-containing polymers may conveniently be prepared from tin- ($n = 3$; X = Bu_2Sn),[198,199] silicon- ($n = 1$ and 4; X = $SiClCH_3$, $SiCl_2$),[200,201] germanium- ($n = 2$ and 3; X = $GeMe_2$, $GeEt_2$),[201a] and boron- ($n = 3$ and 4; X = O–B(CH_3)-O, O–B(Ph)-O)[202] containing dienes using Mo-based Schrock catalysts. Similarly, cubane-containing polymer backbones may be prepared from 1,4-bis(homoallyl)cubane.[203] Unsaturated polyesters[204,205] and unsaturated polyacetals may be prepared from ethylenediundecenoate and bis(5-methenoxy)methylbenzene,[206,207] respectively. In analogy, unsaturated poly[carbo(dimethyl)silanes],[208,209] poly(carbosiloxanes),[210–214] and oligo(chlorocarbosilanes) may be synthesized. ADMET polymerization also represents a highly attractive alternative to polymers that are usually only accessible via polycondensation reactions. Thus, unsaturated polyesters[215,216] and polycarbonates[217,218] may be synthesized. Unsaturated poly(ethers)[219,220] and poly(thioethers)[221–223] are also accessible via ADMET homo- and copolymerization. Unsaturated, ADMET-based poly(ethers) may further be epoxidized,[224] a reaction that has also been used lately for the chemical transformation of NBE-based ROMP polymers.[225] Homo- and copolymers with metallocenes in the main chain have been prepared from 1,1′-divinylferrocene and 1,1′-divinylferrocene and 1,9-decadiene, respectively.[226] While diallylamine does not allow the preparation of the corresponding amine-functionalized polymers via ADMET, dienes containing the *N*-phenyl group ($n = 2$ and 3; X = N–Ph)[227,228] readily form the corresponding polymers. In analogy, ethylene oxide- ($n = 2$–6; X = $(O-C_2H_4-O)^m$, $m = 2$–5)[229] and THF- ($n = 4$, X = O–$(CH_2)_4$–O)[230,231] segmented polymers may be prepared. The former ones may be hydrogenated using tosylhydrazide in refluxing toluene to yield perfectly alternating poly(ethylene-*co*-ethylene oxide) (PE-PEO copolymers).[232,233] Segmented copolymers represent interesting materials for applications as blend compatibilizers, surfactants, and thermoplastic elastomers. ADMET copolymerization of monomers shown in Figure 6 allows the preparation of such segmented polymers, e.g., polyurethane-segmented materials.[234,235] ADMET polymerization of 1,9-decadiene followed by reduction yields perfectly linear PE.[236,237] Consequently, ADMET polymers of α,ω-dienes carrying internal methyl groups may be hydrogenated to generate PE containing perfectly spaced methyl groups.[238,239] Main-chain ferroelectric liquid-crystal oligomers have been prepared from a biphenyl-derived monomer (Figure 7). $Cl_2Ru(PCy_3)_2CHCHPh_2$ was successfully used for ADMET polymerization of this monomer. Interestingly and in contrast to Mo-based Schrock carbenes, the Ru core did not seem to be affected by the redox-

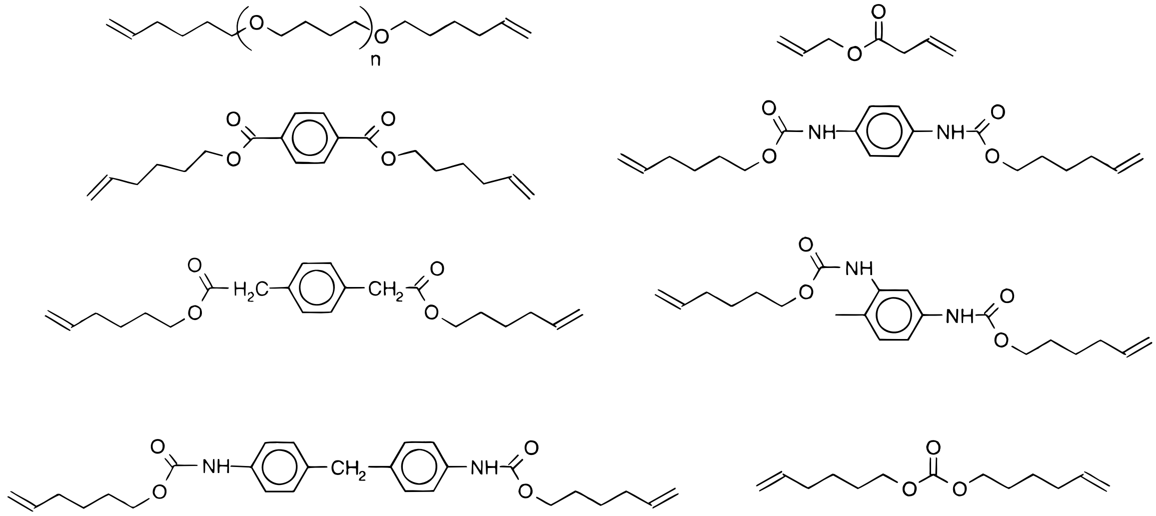


Figure 6. Ester, urethane, poly-THF, and carbonate diene comonomers for ADMET copolymerization.

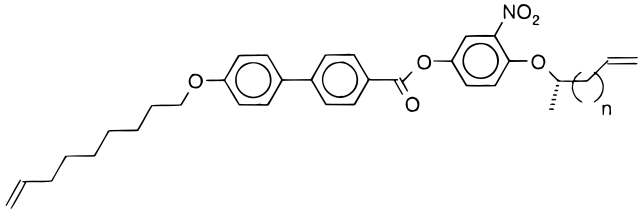


Figure 7. ADMET-active monomer for the synthesis of main-chain ferroelectric LC oligomers; $n = 2-4$.

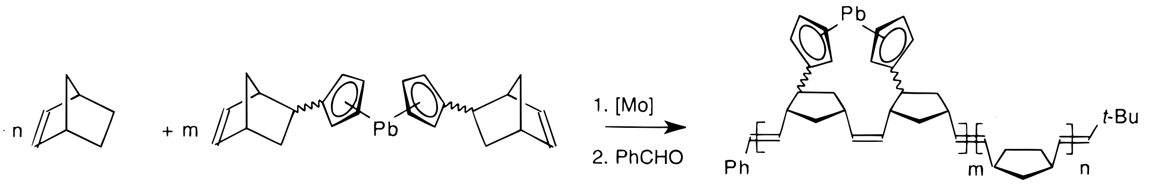
active nitro group. Perfectly alternating copolymers may be obtained from ADMET polymerization of monomers such as 5-methyl-1,5,9-decatriene, 5,6-dimethyl-1,5,9-decatriene, and 5,6-diphenyl-1,5,9-decatriene[240] using the tungsten Schrock carbene W(N-2,6-i-Pr_2-C_6H_3)($CHCMe_2Ph$)($CMe(CF_3)_2$)$_2$.

Nonconjugated analogues of poly(*p*-xylylene) (PPX), which are of particular interest because of their intriguing properties, have been prepared from bis-(1,4-pent-4-ene)benzene[241,242] and diallylbenzene.[243] Poly(*p*-phenylene butylene) polymers that are obtained by hydrogenation of the parent ADMET polymer poly(diallylbenzene) represent high melting polymers that permit conventional processing techniques as opposed to PPX. Conjugated main-chain polychromophores prepared by ADMET have been reported by Bazan et al.[244] Thus, reaction of bis-(vinylthienyl)tetramethyldisilane with Mo(N-2,6-i-Pr_2-C_6H_3)($CHCMe_2Ph$)($OCMe_3(CF_3)_2$) yielded polymers with up to 20 thienylene units in the main chain. The polymers showed the expected interchromophore cooperativity.

D. Synthesis of Nanoclusters

The high tolerance of Schrock-type catalysts of the general formula Mo(NAr′)($CHCMe_2Ph$)(OR)$_2$, NAr′ usually being N-2,6-i-Pr_2-C_6H_3, vs a large variety of functional groups allowed the polymerization of various 2,3-substituted norbornenes carrying chelating groups. These chelating groups were subsequently used to bind transition metals. The corresponding metal-containing monomers were used for the synthesis of a series of side-chain metal-containing polymers,[245] which significantly differ from the long known main-chain metal-containing polymers.[246] Such side-chain metal-containing polymers were used for the preparation of metal microdomains. Thus, small particles of PbS were prepared by H_2S treatment of poly[($C_7H_9CH_2C_5H_4$)$_2$Pb] microdomains of a *block*-copolymer film of copoly(bis(norbornene-2-ylcyclopentadienyl)lead-*b*-NBE). The latter one was prepared via the living ROMP of bis(norbornene-2-ylcyclopentadienyl)lead initiated by Mo(N-2,6-i-$Pr_2C_6H_3$)(CH-t-Bu)($OCMe_3$)$_2$ followed by the addition of NBE. The living system was finally terminated with benzaldehyde (Scheme 27). In a similar approach, tin-,[247,248] lead-, and zinc-containing poly(norbornenes) have been prepared. Starting from *endo,exo*-2,3-di(tosylatomethyl)norbornene, *endo,exo*-2,3-di(*tert*-butylaminomethyl)norbornene was prepared. The corresponding tin, lead, and zinc complexes were successfully polymerized by Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)($OCMe_3$)$_2$ in a living manner. TEM investigations of the corresponding microphase-separated *block*-copolymers revealed *block*-size-dependent morphologies. Following this generally applicable approach, a large variety of metal-containing polymers have been synthesized. Generally speaking, mainly NBE-based cyclopentadienyl, amido, phosphino, ether-, and carboxylate ligands were used for these purposes. Table 3 gives an overview over the

Scheme 27. Preparation of Copoly(bis(norbornene-2-ylcyclopentadienyl)lead-*b*-NBE)



metals, the corresponding ligands, and the properties of the final materials.[247,249−257]

E. Electroluminescent, Photoluminescent, and Other Luminescent Materials

Poly(NBE)-based electroluminescent polymers have been prepared from 1,4-bis[2-(3,4,5-trimethoxyphenyl)ethenyl]benzene-derivatized norbornenes (Figure 8).[258] Single layers of this polymer, which may conveniently be prepared using Mo(N-i-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OC-t-Bu)$_2$ as an initiator show a λ_{max} (emission) of 475 nm with quantum yields of up to 0.55%. Blue-light-emitting electroluminescent polymers based on a NBE-substituted diphenylanthracene chromophore (e.g., NBDPA-1)[259] (λ_{max} = 450 nm) as well as on a NBE-bound oxadiazole (e.g., NBBPO-2) (Figure 9) were used for the fabrication of electroluminescent devices. These consist of an Al cathode and an indium−tin oxide (ITO) anode. In between, alternating layers of a polycationic precursor to PPV (20 layers) and poly(styrene-4-sulfonate) (SPS, 5 layers) were deposited by spin-coating techniques. Self-assembly leads to the formation of a stable "platform", where each layer is held in place by ionic interaction. Finally, suitable NBE-based polymers were spin coated onto this platform. A schematic drawing of the device is shown in Figure 10. In the case where copolymers of both compounds with a DP of 50 were used, the emittence of 675 nm blue light was observed with an output power of 675 nW. For technical reasons, ionic polymers containing suitable groups for light emission and electron transport are desirable. Since poly-NBE-based polymers possess a large amount of double bonds that may further be derivatized, these types of materials were subject to polymer transformation.[225] Sulfonation using SO$_3$−dioxane yielded the corresponding sulfonated polymer. Epoxidation and subsequent reduction were carried out using *m*-chloroperbenzoic acid and LiAlH$_4$, respectively. These polymer transformations were used to synthesize sulfonated and hydroxylated diphenylanthracene-, oxadiazole-, and *p*-triphenylene-substituted poly(norbornenes), which were again used for the construction of light-emitting devices (Scheme 28).

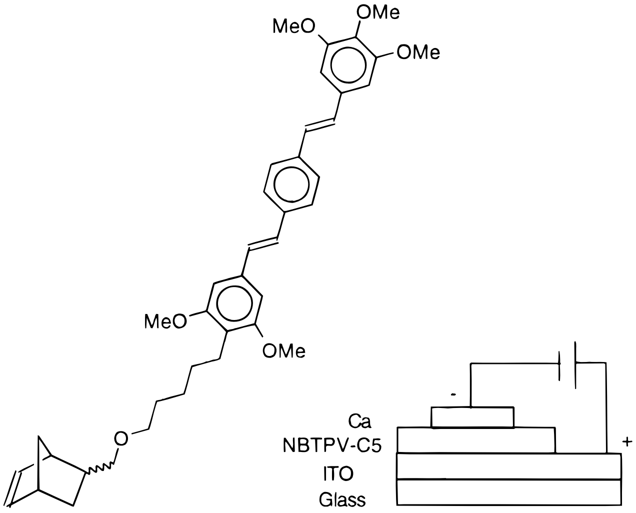


Figure 8. Blue-light-emitting electroluminescent (EL) polymer precursor based on NBTPV-C5 and schematic drawing of the EL device.

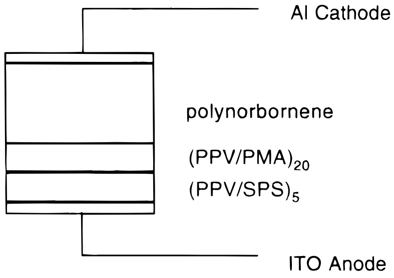
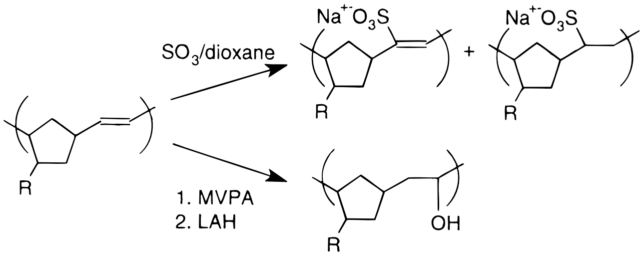


Figure 10. Electroluminescent device based on diphenylanthracene and oxadiazolenorbornene polymers. ITO = indium−tin oxide.

Scheme 28. Sulfonation and Epoxidation of Substituted Poly(norbornenes)[a]



[a] MCPA = *m*-chloroperbenzoic acid; LAH = lithium aluminumhydride; R = diphenylanthracene, oxadiazole, *p*-triphenylene.

block-Copolymers of PPV prepared from 9-((*tert*-butyldimethylsilyl)oxy)-[2.2]-paracyclophan-1-ene and poly(2,3-bis(trifluoromethyl)norbornadiene) units were reported by Bazan and co-workers (Scheme 29).[260] The *block*-copolymers show a λ_{max}(excitation) of 400 nm, similar to PPV. Copolymers of [2.2]paracyclophane-1,9-diene (PCPDE) with COD prepared by the Grubbs catalyst W(CHAr′)(NAr)[OCMe(CF$_3$)$_2$]$_2$·THF (Ar′ = o-CH$_3$−O−C$_6$H$_4$; Ar = 2,6-Me$_2$C$_6$H$_3$) were found to consist of separated −C$_6$H$_4$−CH═CH units homogeneously distributed along the polymer chain.[261,262] Oligomers of divinylbenzene prepared via ADMET polymerization have been reported to be useful for the preparation of copolymers containing

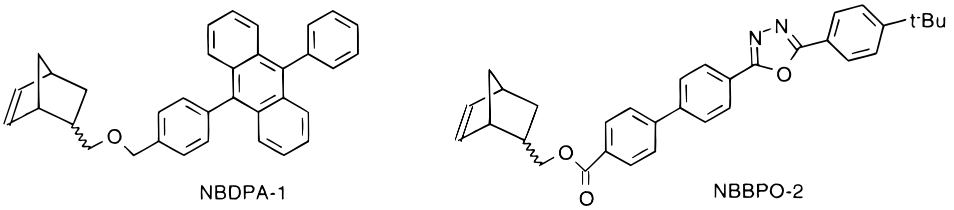


Figure 9. Structure of NBDPA-1 and the electron-transport monomer NBDPA-2 used for the preparation of blue-light-emitting devices.

Table 3. NBE-Based Chelating Systems for the Preparation of Metal-Containing Polymers[a]

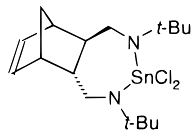
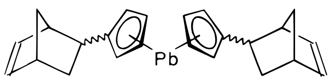
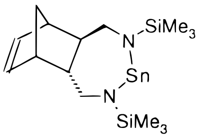
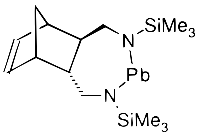
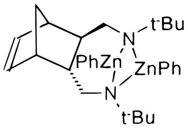
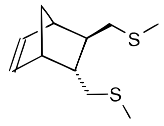
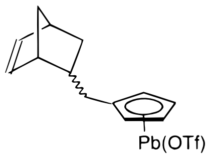
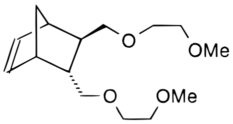
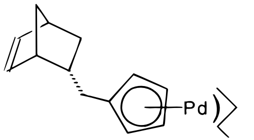
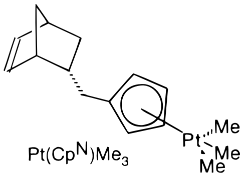
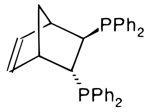
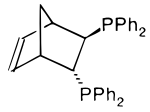
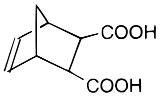
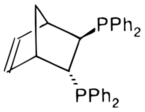
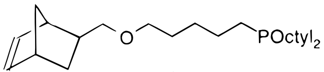
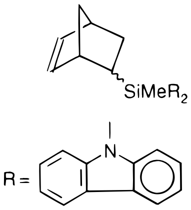
metal	complex	catalyst (Ar = 2,6-i-Pr_2-C_6H_3)	copolymer	polymer properties
Sn	 Sn(bTAN)Cl_2	M(NAr)(CH-*t*-Bu)$(OR)_2$ M = Mo, W R = *t*-Bu	$[Sn(bTAN)Cl_2]_{16}$-NBE_{111} $[Sn(bTAN)Cl_2]_9$-NBE_{19} $[Sn(bTAN)Cl_2]_{25}$-NBE_{120}	spherical cylindrical lamellar morphology, D = 190 Å
Pb		Mo(NAr)(CH-*t*-Bu)$(OR)_2$ R = *t*-Bu	Pb(bSAN)n-NBE_{200} n = 5, 10, 20	microphase-separated morphology
Sn	 Sn(bSAN)	Mo(NAr)(CH-*t*-Bu)$(OR)_2$ R = *t*-Bu	$Sn(bSAN)_{25}$-MDT_{177}	lamellar, D = 210 Å
Pb	 Pb(bSAN)	Mo(NAr)(CH-*t*-Bu)$(OR)_2$ R = *t*-Bu	$Pb(bSAN)_{20}$-MDT_{176}	lamellar morphology D = 125 Å
Zn	 $(ZnPh)_2$(bTAN)	Mo(NAr)(CH-*t*-Bu)$(OR)_2$ R = *t*-Bu	$[(ZnPh)_2(bTAN)Cl_2]_{80}$-$MTD_{250}$	lamellar morphology D = 340 Å
Zn	 7-S	Mo(NAr)(CH-*t*-Bu)$(OR)_2$ R = *t*-Bu	$(7\text{-}S)_{74}MTD_{220}$-74 $ZnPh_2$	lamellar
Pb	 Pb(CpN)$(OTf)_3$	Mo(NAr)($CHCMe_2Ph$)$(OR)_2$ R = *t*-Bu	$(Pb(CpN)OTf)_3$-MDT_{382}	spherical
Cd	 5-O	Mo(NAr)(CH-*t*-Bu)$(OR)_2$ R = *t*-Bu	$(5\text{-}O)_{80}MTD_{220}$-80 Cd $[(3,5\text{-}CF_3)_2\text{-}C_6H_3]$	lamellar
Pd	 Pd(Cp^N)(PA)	Mo(NAr)(CH-*t*-Bu)$(OR)_2$ R = *t*-Bu	$Pd_{50}MTD_{113}$ $Pd_{10}MTD_{163}$	lamellar spherical

Table 3 (Continued)

metal	complex	catalyst (Ar = 2,6-i-Pr_2-C_6H_3)	copolymer	polymer properties
Pt	 $Pt(Cp^N)Me_3$	Mo(NAr)(CH-*t*-Bu)$(OR)_2$ R = *t*-Bu	$Pt_{40}MTD_{200}$	cylindrical
Ag	 NORPHOS	Mo(NAr)(CH-*t*-Bu)$(OR)_2$ R = *t*-Bu	$[Ag_2(Hfacfac)_2(NORPHOS)]_{60}$-$MTD_{300}$	180 Å microdomains
Au	 NORPHOS	Mo(NAr)(CH-*t*-Bu)$(OR)_2$ R = *t*-Bu	$[Au_2Me_2(NORPHOS)]_{20}$-MTD_{300}	cylindrical
Cu	 NOR-COOH	Mo(NAr)(CH-*t*-Bu)$(OR)_2$ R = *t*-Bu	NOR-$COOH_{50}MTD_{400}$	Cu oxidized to CuO absorbs at λ = 650 nm
CdSe	 NORPHOS	Mo(NAr)(CH-*t*-Bu)$(OR)_2$ R = *t*-Bu	$NORPHOS_{20}MTD_{300}$	increased electronic passivation by polymers during formation of CdSe from $CdMe_2$ and Se=P$(Octyl)_3$
CdSe	 NOR-O-P	Mo(NAr)(CH-*t*-Bu)$(OR)_2$ R = *t*-Bu	NOR-O-$P_{20}MTD_{300}$	increased electronic passivation by polymers during formation of CdSe from $CdMe_2$ and Se=P$(Octyl)_3$
Cd		$Cl_2Ru(CHPh)(PCy_3)_2$	$(NOR\text{-}SiMeR_2)_{200}$-$(NOR\text{-}CH_2OH)_{200}$	phase separation, selective reaction of alcohol-functionalized microdomains with $CdMe_2$.

[a] MTD = methyltetracyclododecene.[245,249−256,437]

controllable sequence lengths of PPC units.[263] Ring-opening metathesis copolymerization has been used successfully for the enhancement of the solubility of PPV-containing copolymers.[264] A series of triarylamine-containing NBE-based polymers was prepared using $Cl_2Ru(CHPh)(PCy_3)_2$ as an initiator[265] and used as hole transport layers (HTLs). Spin casting was used for the fabrication of the LED devices. The influence of structural differences on the ultimate performance was investigated systematically (Table 4).

The high versatility and tolerance of the molybdenum-based Schrock-type catalysts was again underlined by the preparation of NBE-based ferrocene- and phenothiazene-containing homo- and *block*-copolymers with pyrene end groups. The latter ones were introduced into the living polymer chain by reaction with 1-pyrene-carboxaldehyde. The corresponding polymers were investigated for their quenching properties of the pyrene end-group emission.[266] Finally, poly(benzobarrelene)-based materials have been prepared.[267−269] Table 4 gives an overview over the

Table 4. Polynorbornene- and Poly(benzbarrelene)-Based Luminescent Polymers[167−176,326]

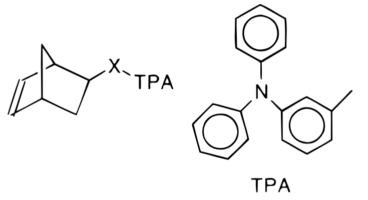
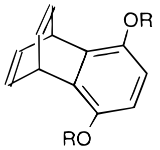
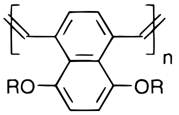
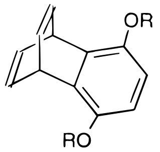
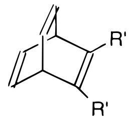
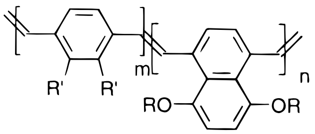
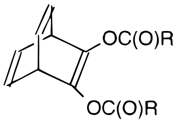
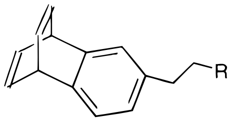
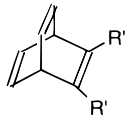
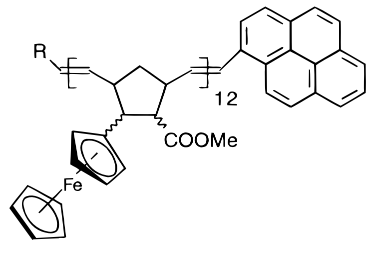
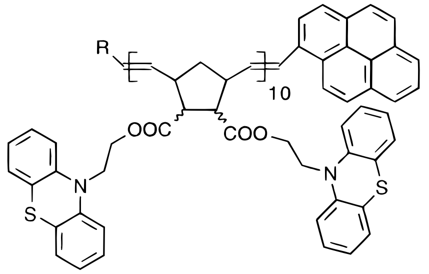
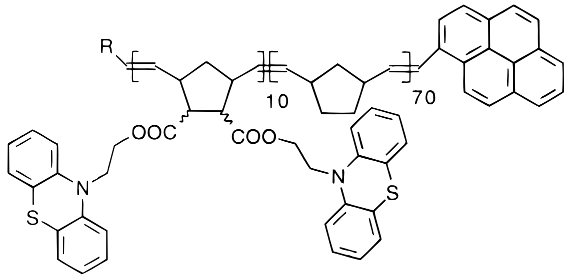
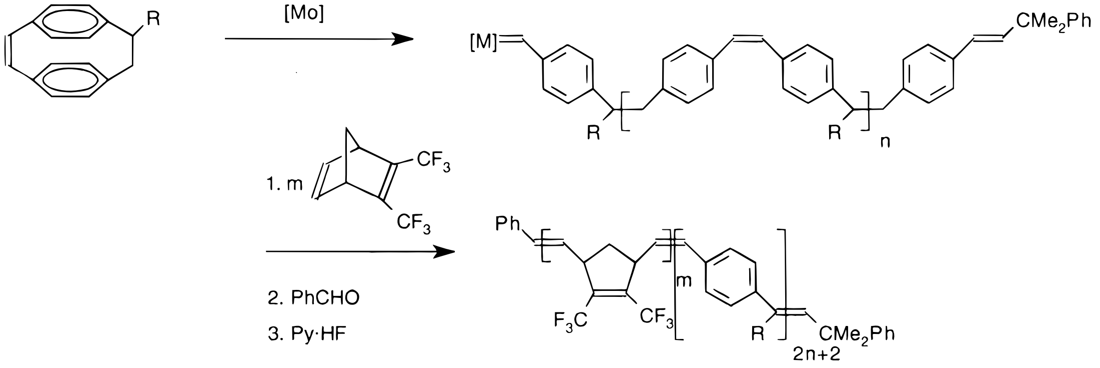
entry	monomer	initiator	properties
1	 X = $COO(CH_2)_6$; $COOCH_2CH_2$; COO; CH_2O; $CH_2O(CH_2)_6$	$Cl_2Ru(PCy_3)_2(CHPh)$	X = $COO(CH_2)_6$: 240 cd/m^2 @ 11 V X = $COO(CH_2)_2$: 800 cd/m^2 @ 10 V X = COO: 1030 cd/m^2 @ 14 V X = CH_2O: 850 cd/m^2 @ 8 V X = $CH_2O(CH_2)_6$: 2580 cd/m^2 @ 8 V
2	 R = ethyl, 2-ethylhexyl, octyl	$Mo(NAr)(CHCMe_2Ph)(OR)_2$ R = $CMe(CF_3)_2$	 2-ethylhexyl: λ_{max} (emission) = 534 nm octyl: λ_{max} (emission) = 541 nm
3	 R = ethyl, 2-ethylhexyl, octyl 	$Mo(NAr)(CHCMe_2Ph)(OR)_2$ R = $CMe(CF_3)_2$	 ethyl: λ_{max} (emission) = 571 nm 2-ethylhexyl: λ_{max} (emission) = 492 nm octyl: λ_{max} (emission) = 581 nm
4		$Mo(NAr)(CHCMe_2Ph)(OR)_2$ R = $CMe(CF_3)_2$	-
5	 R = butyl, nonyl	$Mo(NAr)(CHCMe_2Ph)(OR)_2$ R = $CMe(CF_3)_2$	El_{max} = 620 nm, 40 cd/m^2
6	 R = $COOCH_3$, COO-t-Bu	$Mo(NAr)(CHCMe_2Ph)(OR)_2$ R = $CMe(CF_3)_2$	water soluble (R = COONa) PL_{max} = 501 nm
7		Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$	pyrene-emission quenching quenching factor = 30

Table 4 (Continued)

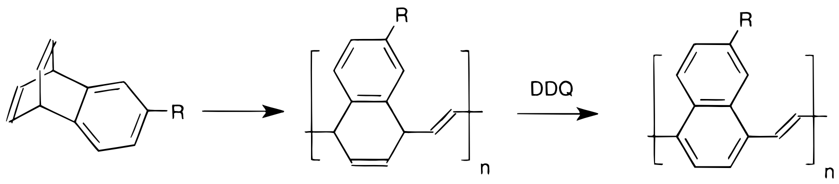
entry	monomer	initiator	properties
8		Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$	pyrene-emission quenching quenching factor = 110
9		Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$	pyrene-emission quenching quenching factor = 7

Scheme 29. Light-Emissive Copoly(*p*-phenylenevinylene-*b*-bis(trifluoromethyl)norbornadiene)[a]



[a] R = *tert*-butyldimethylsilyloxyl; [Mo] = Mo(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OCMe(CF$_3$)$_2$)$_2$.

Scheme 30. ROMP of Alkyl-Substituted Benzobarrelenes[a]



[a] R = hexyl, undecyl; DDQ = 2,3-dichloro-5,6-dicyano-*p*-quinone.

corresponding monomers, initiators, and polymer properties. The poly(1,4-hexa-2,5-dienylenevinylene) precursors that are formed by ROMP of the starting substituted barrelenes may be converted into the corresponding poly-*p*-phenylenevinylene (PPV) analogues via base-catalyzed thermal elimination or via oxidation by DDQ (Scheme 30). Soluble PPP derivatives were obtained from 2,3-dicarboxybarrelenes.[270] Finally, the synthesis of NBE-based polymers containing pendant carbazole moieties via ROMP using Cl$_2$Ru(CHPh)(PCy$_3$)$_2$ was reported. *block*-Copolymers with trimethylsilyl- (TMS) protected NBE−methanol showed microphase separation and selective reaction of the alcohol-functionalized domains with dimethyl cadmium.[271]

F. Telechelic and Ditelechelic Polymers

Polymers prepared by ROMP using molybdenum- or tungsten-based carbenes may conveniently be end-functionalized by reaction with an appropriate aldehyde (Scheme 31).[272] This “Wittig-like” capping reaction proceeds smoothly and quantitatively and has been used for the preparation of a series of end-functionalized polymers and star polymers[273] (vide infra). Interestingly, α,β-unsaturated ketones were reported to be entirely unreactive.[274] Alternatively,

Table 5. Monomers, Initiators, and Polymer Properties of NBE-Based Liquid-Crystalline Polymers[a]

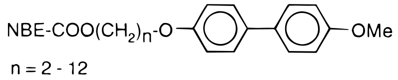
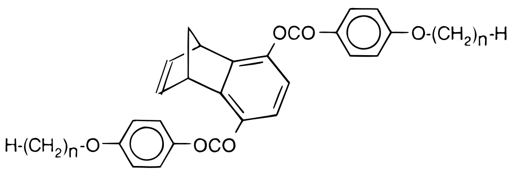
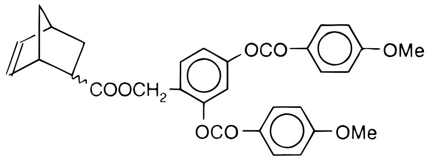
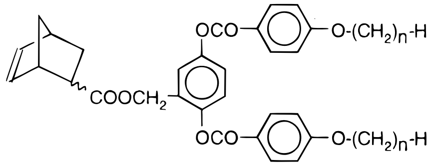
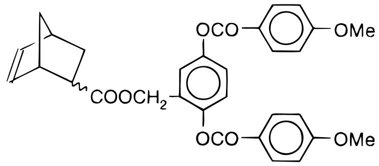
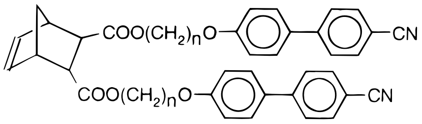
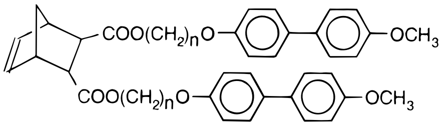
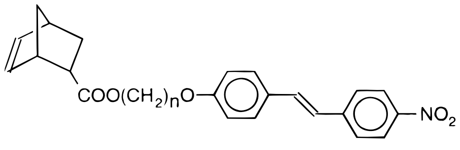
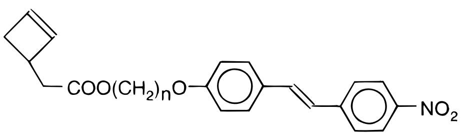
#	monomer (NBE = norbornene)	initiator (Ar=2,6-*i*-Pr_2-C_6H_3)	polymer properties
1	 NBEBIPO	Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$	n = 4, DP = 16 nematic (77 °C). $(NBEBIPO)_{300}MTD_{20}$ n = 6 anisotropic (87°C)
2		Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$	n = 7, monomer: nematic (77.4°C) polymers: enantiotropic nematic mesophases
3		Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$	polymers: enantiotropic nematic mesophases
4		Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$	n = 6, monomer: nematic (75.6 °C) polymers: enantiotropic nematic mesophases
5		Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$	polymers: enantiotropic nematic mesophases
6		Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$	n = 5, nematic n = 11, smectic
7		Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$	n = 6 smectic n = 10 smectic
8	 NBE-NSTILB	$Cl_2Ru(CHPh)(PCy_3)_2$	nematic
9	 CB-NSTILB	$Cl_2Ru(CHPh)(PCy_3)_2$	smectic
10	NBE-NSTILB-*co*-CB-NSTILB	$Cl_2Ru(CHPh)(PCy_3)_2$	smectic

Table 5 (Continued)

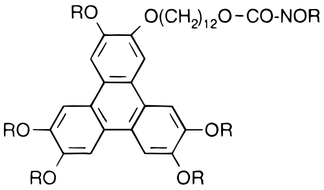
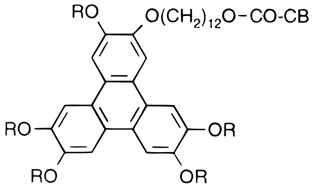
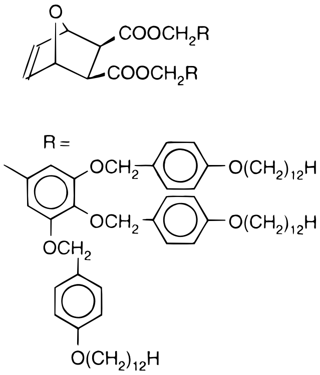
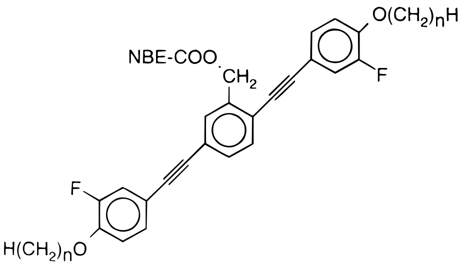
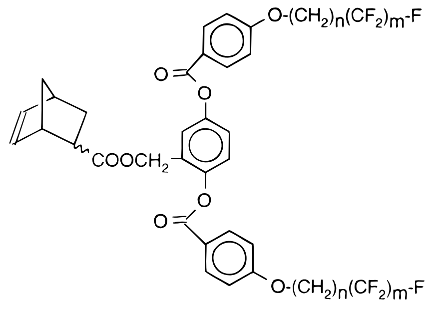
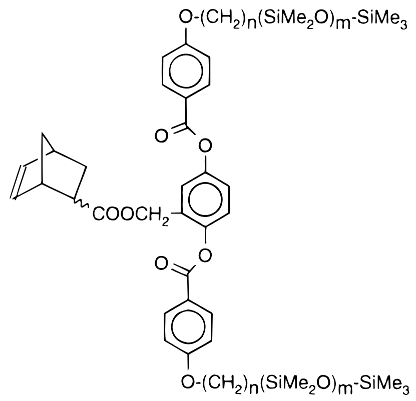
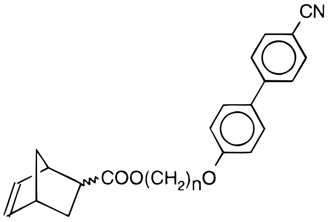
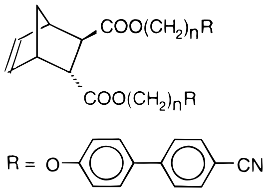
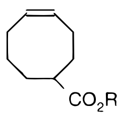
#	monomer (NBE = norbornene)	initiator (Ar=2,6-*i*-Pr_2-C_6H_3)	polymer properties
11		$Cl_2Ru(CHPh)(PCy_3)_2$	R = $C_{10}H_{21}$: enantiotropic discotic hexagonal mesophases R = C_5H_{11} :no LCs
12		$Cl_2Ru(PCy_3)_2(CHPh)$	R = $C_{10}H_{21}$: enantiotropic discotic hexagonal mesophases R = C_5H_{11} :no LCs
13		$Cl_2Ru(CHPh)(PCy_3)_2$	enantiotropic hexagonal colunar (Φ_h)
14	 n = 1 - 12	Mo(NAr)(CHCMe_2Ph)(O-*t*-Bu)$_2$	n = 1 - 12: enantiotropic nematic mesophase
15		Mo(NAr)(CHCMe_2Ph)(O-*t*-Bu)$_2$	smectic C, smectic A

Table 5 (Continued)

#	monomer (NBE = norbornene)	initiator (Ar=2,6-*i*-Pr_2-C_6H_3)	polymer properties
16		Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$	smectic C
17		Mo(NAr)(CHCMe$_3$)(O-*t*-Bu)$_2$	n = 7, smectic (80 °C)
18		Mo(NAr)(CHCMe$_3$)(O-*t*-Bu)$_2$ Mo(NAr)(CHCMe$_3$)(O-CMe$_2$(CF$_3$))$_2$ Mo(NAr)(CHCMe$_3$)(O-CMe(CF$_3$)$_2$)$_2$	n = 2-6 nematic n = 7-12 smectic
19	 R = $(CH_2)_{11}O(C_6H_4)_2CN$	Mo(NAr)(CHCMe$_3$)(O-CMe(CF$_3$)$_2$)$_2$	nematic (-5 < T < 53 °C)

[a] DP = degree of polymerization; MTD = methylcyclododecene; CB = cyclobutene.[290−300,303−306]

Scheme 31. End-Functionalization of Living Mo-Based Schrock Catalyst-Initiated Polymers[a]

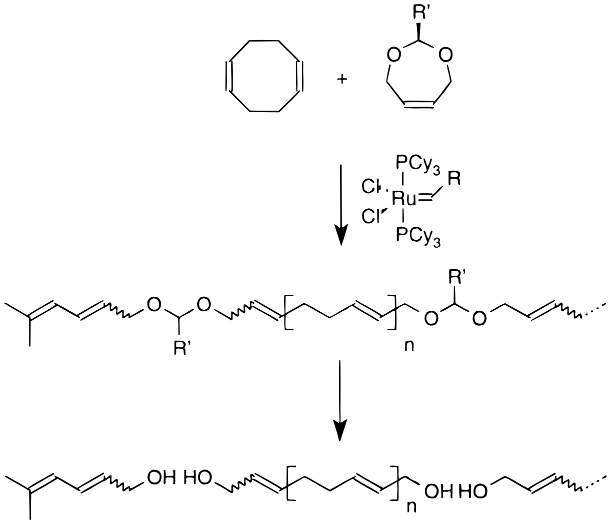
$$Mo(NAr)(CHP)(OR')_2 + R''CHO \longrightarrow \mathbf{PCH{=}CHR''} + M(O)(NAr)(OR')_2$$

[a] Ar′ = phenyl, 2,6-Me_2-C_6H_3, 2,6-*i*-Pr_2-C_6H_3, etc.; R′ = CMe_3, CMe_2CF_3, $CMe(CF_3)_2$, $C(CF_3)_2$, etc.; R″ = phenyl, ferrocenyl, *tert*-butyl, etc.; P = polymer.

such an end functionalization may also be achieved by reaction of the starting Schrock initiator with a terminal alkene, e.g., *p*-dimethylaminostyrene, prior to polymerization.[82] A second approach for the end functionalization of polymers lies in the use of chain-transfer agents (CTAs),[275] which have been investigated on a theoretical basis in the case of the Mo-based ROMP of NBE using neohex-1-ene as a CTA.[276,277] While 4-substituted cyclopentenes were reported to be rather unsuitable for these purposes,[278] living polymers obtained from the polymerization of COD[279] with W(NPh)(CHAr)(OCMe(CF_3)$_2$)$_2$ react with but-2-ene-1,4-diol-bis(*tert*-butyldimethylsilyl)ether to give α,*ω*-ditelechelic dihydroxy-poly-COD (hydroxy-telechelic polybutadiene, HTPBD). Protection of the diol may be avoided by using $Cl_2Ru(CHCHCPh_2)(PR_3)_2$ as a catalyst.[280,281] Reaction of COD with $Cl_2Ru(CHCHCPh_2)(PCy_3)_2$ in the presence of 1,4-diacetylbut-2-en-1,4-diol followed by hydrolysis of the polymer yields α,*ω*-bis-HTPBD.[282] The same type of polymer was obtained by reaction of COD with *cis*-4,7-dihydro-1,3-dioxepin and *cis*-4,7-dihydro-2-phenyl-1,3-dioxepin, respectively (Scheme 32).[283]

The formation of cyclic products during the ROMP of COD and cyclooctene, respectively, represents an important side reaction. Recent investigations revealed a kinetic control over this process which is driven by back-biting reactions of the growing polymer chains.[279,284] Finally, the use of ADMET chemistry for the preparation of α,*ω*-ditelechelic polymers needs to be addressed. Using tungsten- and molybdenum-based Schrock carbenes as well as ruthenium-based Grubbs catalysts, silicon-terminated ADMET polymers, e.g., derived from 1,9-decadiene, have been prepared.[285,286] Similarly, telechelic polyacetylenes prepared from hexa-2,4-diene[287] and 2,4,6-octadiene[288] as well as silicon-terminated telechelic oligo-

Scheme 32. Preparation of Hydroxytelechelic Polybutadiene HTPBD[a]



[a] R = Ph, CHCPh$_2$; R′ = H, Ph.

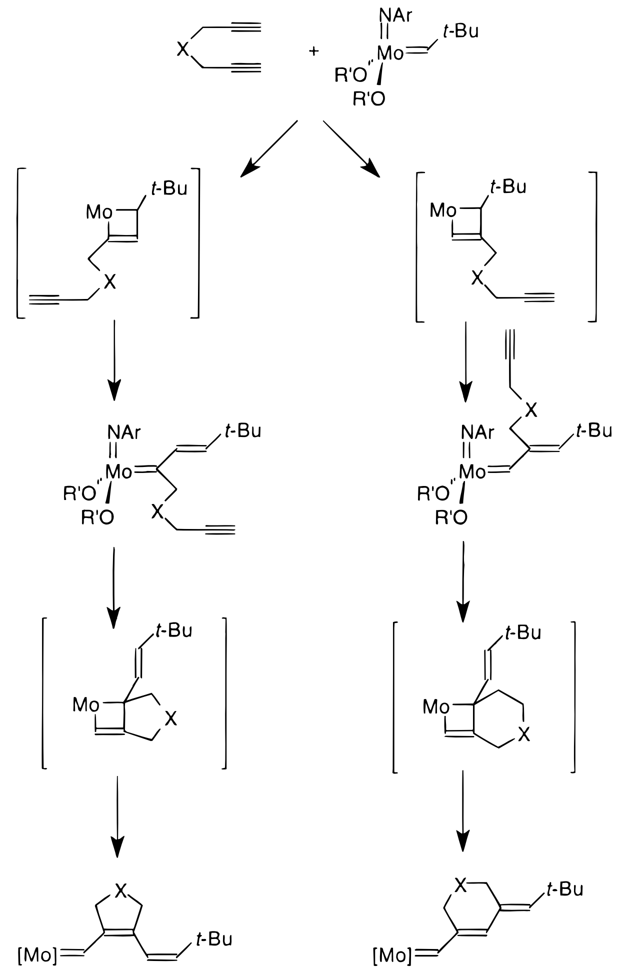
mers prepared from 1,9-decadiene and 5-hexenylchlorodimethylsilane[285] are accessible.

G. Liquid-Crystalline Materials

A comprehensive review about the engineering and preparation of side-chain liquid-crystalline polymers by living polymerization methods including ROMP has been given recently.[289] Consequently, only the more recent contributions shall be covered briefly. One convenient approach for the preparation of side-chain liquid-crystalline materials entails the ROMP of norbornenes carrying mesogenic side groups in the 5- or in the 5- and 6-positions. Both molybdenum[290−302] and ruthenium-based initiators[303−306] have already been employed for the preparation of LC polymers. Table 5 gives an overview over the corresponding monomers, initiators, and polymer properties.

H. Conjugated Materials

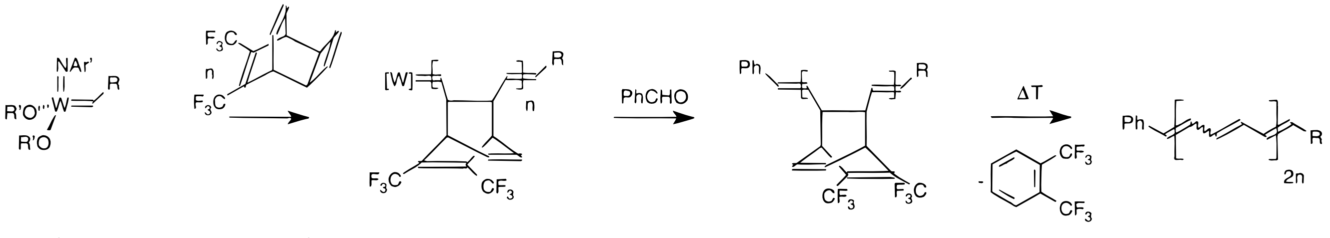
Scheme 34. Mechanisms for α- and *β*-Insertion and Their Influence on the Polymer Structure of Poly(dipropargylmalonate)[a]



[a] Ar = phenyl, 2,6-Me$_2$-C$_6$H$_3$, 2,6-*i*-Pr$_2$-C$_6$H$_3$, etc.; R′ = CMe$_3$, CMe$_2$CF$_3$, CMe(CF$_3$)$_2$, C(CF$_3$)$_2$, etc.; X = C(COOC$_2$H$_5$)$_2$.

In principle, conjugated materials may be directly synthesized either via metathesis polymerization of 1-alkynes, via ROMP of (substituted) cyclooctatetraene (COT), or via ROMP of polyene precursors (e.g., by the Durham route[307−311]). The first direct polymerization of acetylene to yield black untreatable unsubstituted polyacetylene was achieved with W(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CH-*t*-Bu)(OC-*t*-Bu)$_2$.[312] To obtain soluble polymers, polyenes were prepared via the ROMP of a polyene-precursor, e.g., 7,8-bis(trifluoromethyl)tricyclo[4.2.2.$0^{2,5}$]deca-3,7,9-triene (TCDTF6) using well-defined Schrock-type catalysts (e.g., W(*N*-2,6-*i*-Pr$_2$-C$_6$H$_3$)(CH-*t*-Bu)(OC-*t*-Bu)$_2$).[313,314] The desired polyene is generated from the prepolymer by thermal treatment (Scheme 33). Polyenes prepared by this route have been demonstrated to possess a finite potential window of high conductivity upon treatment with liquid sulfur dioxide or upon electrochemical reduction in THF.[315] The high degree of reaction control in this polymerization even allows the synthesis of oligomeric polyenes and their separation by RP-HPLC.[308] Isomerization of the *cis*−*trans* mixtures to an all-*trans* form becomes easier with increasing number of double bonds; nevertheless, polyenes containing more than 17 double bonds are rather unstable and show a high tendency toward cross-linking. In contrast, copolymers of this compound

Scheme 33. Preparation of Polyenes via the Durham Route[a]



[a] Ar′ = 2,6-*i*-Pr$_2$-C$_6$H$_3$; R = R′ = *t*-Bu.

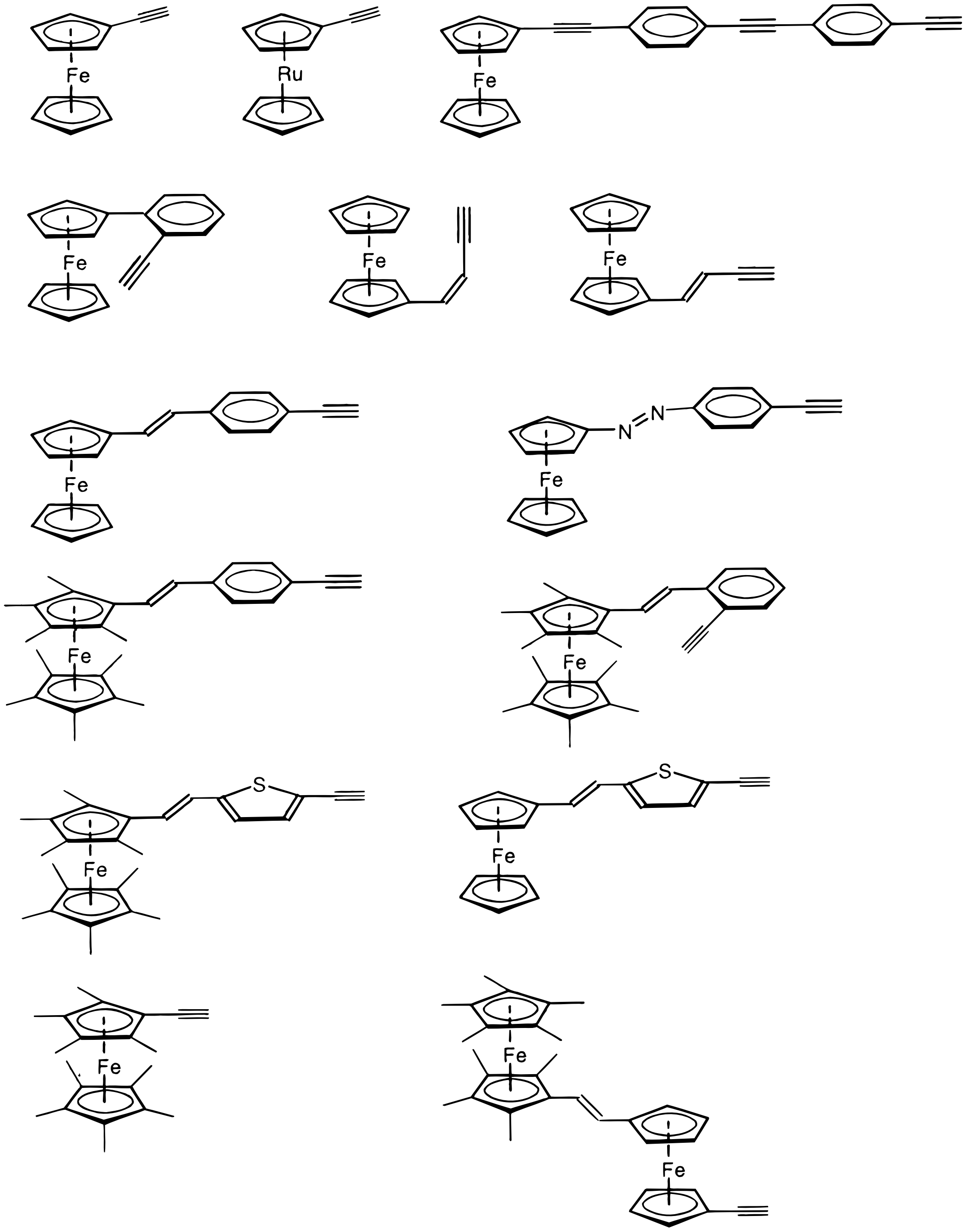
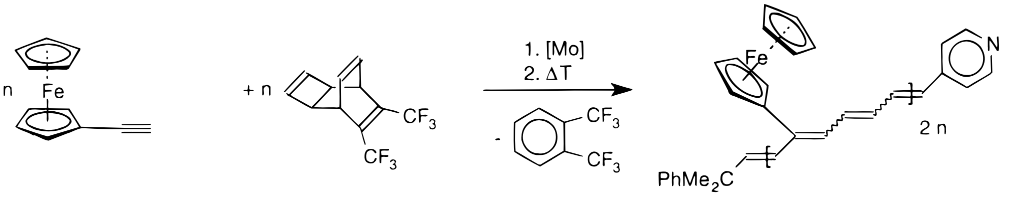


Figure 11. Metallocenyl-substituted 1-alkynes polymerized via metathesis polymerization.

with other monomers (e.g., NBE[316,317] or ethynyl ferrocene[318]) appear to be highly stable. Films prepared from poly-NBE-*block*-polyacetylene were reported to show microphase separations as revealed by small-angle X-ray scattering (SAXS).[319] In the case of polyacetylene prepared from homopolymers of TCDTF6, UV−Vis and Raman scattering[320] revealed a linear dependency of the lowest energy electronic absorption peak and the frequency of the Raman bands vs $1/n$ (n = number of double bonds) for $n > 7$.[321] Films of poly-TCDTF6 were casted onto platinum surfaces and heated to induce the thermal formation of polyacetylene with molecular weights of 400−6500 D, corresponding to a $\mathrm{DP_{HCCH}}$ of 15−250.[322] The polymer films showed a linear increase in conductivity up to a DP of roughly 60, after which conductivity leveled off. Radical cations of such polyenes with 3−13 double bonds were generated radiolytically in a Freon matrix and investigated by electronic absorption spectroscopy.[323] Finally, Langmuir−Blodgett films of conducting diblock copolymers have been prepared by ROMP from 2,3-bis(trimethylsilyloxycarbonyl)norbornene and 7,8-benzotricyclo[4.2.2.0^{2,5}]deca-3,7,9-triene via the Durham route.[311]

In contrast to unsubstituted acetylene, the polymerization of differently substituted 1-alkynes and di-1-alkynes may be carried out conveniently using Schrock-type catalysts. Dipropargylmalonate and derivatives thereof may be cyclopolymerized in a living manner using Mo(N-2,6-i-$\mathrm{Pr_2}$-$\mathrm{C_6H_3}$)(CH-t-Bu)($\mathrm{OCMe(CF_3)_2)_2}$. The resulting conjugated polymer

Scheme 35. Preparation of Highly Conjugated Copolymers from Ethynyl Ferrocene[a]



[a] [Mo] = Mo(N-2,6-Me_2-C_6H_3)($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$.

contains both five- and six-membered rings, resulting from competitive α and β insertions (Scheme 34).[324,325] In accordance with the concept of "small" alkoxides elaborated for α insertion (vide infra),[326,327] a catalyst containing large carboxylate groups, (Mo(N-2-*tert*-buylphenyl)(CH-*t*-Bu)(O_2CCPh_3)$_2$), was found to produce a dipropargylmalonate-polymer which solely contained six-membered rings.[328] Polyacetylenes with pendant metallocenyl side groups have been prepared by metathesis polymerization of the corresponding 1-alkynes.[318,329,330] The structures of these metallocene-based monomers are given in Figure 11. These monomers turned out to be very useful probes for the insertion chemistry into Mo-based Schrock catalysts. The initial model developed by Schrock and coworkers,[326] which was based on the findings that "small" alkoxides lead to α insertions whereas larger alkoxides favored β insertion, had to be extended. In this context, *o*-ferrocenylphenylacetylene turned out to possess a "critical" size. The reaction of this compound with Mo−carbenes of the general formula Mo(N-2,6-R_2-C_6H_3($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$ proceeded via α insertion for R = Me yet via β insertion with R = *i*-Pr, thus underlining the importance of the steric nature of the 2,6-substituents of the imido group in the approach of the terminal alkyne at the CNO face of the initiator. Additionally, using 4-(ferrocenylethynyl)-4′-ethynyltolan,[331,332] the living character of an alkyne metathesis polymerization which proceeded via β-insertion was demonstrated for the first time.[330] In the case of linear *n*-alkyl-substituted alkynes, the mode of insertion was reported to be governed solely by the electronic nature of the alkoxide. Thus, fluorinated alkoxides lead to β insertion while the *tert*-butoxide ligand favored α insertion.[333,334] In terms of the effective conjugation length (N_{eff}), polyenes based on metallocenyl-substituted alkynes are characterized by 1,3-interactions. Nevertheless, a higher degree of conjugation characterized by UV−Vis absorption maxima (λ_{max}) of up to 520 nm was achieved by the preparation of copolymers, e.g., those of ethynyl ferrocene and TCDTF6, employing the Durham route (Scheme 35).[318]

Interestingly enough, *ortho*-substituted phenylacetylenes carrying bulky substituents (e.g., trimethylsilyl,[327] ferrocenyl[329]) or charged end groups[335] turned out to have a high tendency for the formation of higher conjugated polyenes compared to their *p*-substituted analogues. Recently, the influence of the pendant metallocene groups on the conjugated polymer backbone of poly(ethynylmetallocenes) in terms of transfer of electron density have been studied by ^{57}Fe Mössbauer spectroscopy.[336] In this context, the proposed electron-density transfer was supported by significantly elevated values for the isomeric shift (IS) of the pendant ferrocene groups in the polymer. Conjugated polymers containing metallocenes in the main chain may be obtained by ROMP of vinylene-,[337] butadien-1,4-diyl-,[338] or 1-*tert*-butylbutadien-1,4-diyl-bridged[339,340] *ansa*-ferrocenes using Mo(NAr)-($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$ or W(NAr)(CH-2-MeO-Ph)($OCMe(CF_3)_2$)$_2$·THF as initiators (Figure 12).

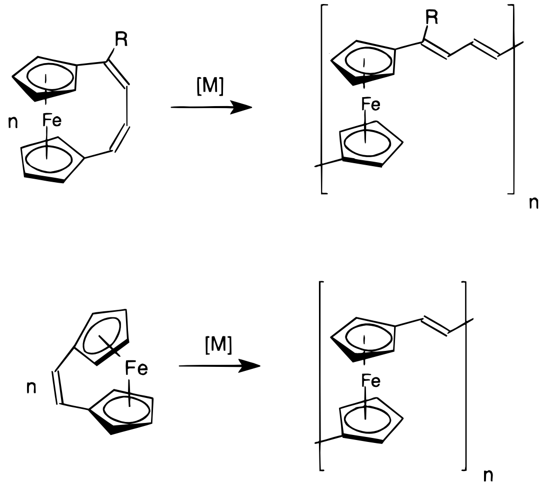
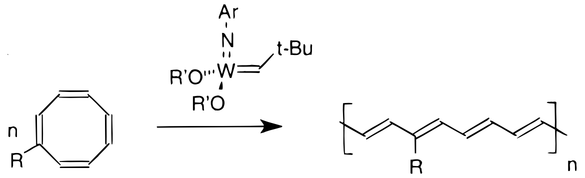


Figure 12. ROMP of ferrocenophanes: R = *t*-Bu; [M] = Mo(NAr)($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$, W(NAr)(CH-2-MeO-Ph)($OCMe(CF_3)_2$)$_2$·THF.

A third access to soluble polyenes lies in the ROMP of cyclooctatetraene (COT) derivatives.[341−343] COTs are readily polymerized by W- and Mo-based Schrock carbenes to yield substituted polyenes (Scheme 36). As evidenced by UV−Vis spectroscopy, these materials which are synthesized in a predominately *cis* form are highly conjugated with values for λ_{max} of up to 538 nm (R = *n*-octadecyl). Thermal *cis*−*trans* isomerization is possible and may be monitored via UV−Vis spectroscopy. The resulting predominately all-*trans* polymers show values for λ_{max} of up to 634 nm (R = neopentyl). Upon doping of these materials with iodine, conductivities of up to 50 S/m may be achieved.[344] Trimethylsilyl-substituted COT[345] forms transparent polymers, which may be casted onto n-doped silicon (n-Si). Upon treatment with iodine, surface barrier solar cells may be prepared.[346] Soluble,

Scheme 36. Synthesis of Conjugated Polyenes from (Substituted) COT[a]



chiral COT-derived polyacetylenes may be prepared in a similar manner using chirally substituted COTs.[347] The backbone $\pi-\pi^*$ transition of these polymers show a circular dicroism which is generated by the chiral side groups which twist the backbone in predominately one sense (Figure 13). In contrast to solution, the voltammetric characterization of spin-cast, polymeric substituted COTs revealed reversible oxidation and reduction.[348] Variation of the substituents results in a change for oxidative and reductive doping of 0.3 V. In course of these doping steps, one electron per approximately 13−15 double bonds is added and removed, respectively.

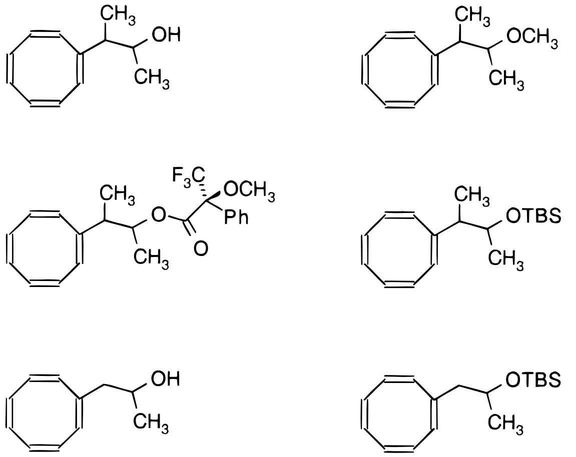
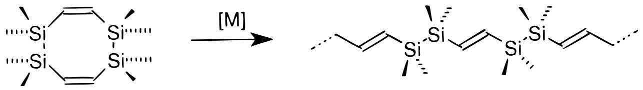


Figure 13. Chiral COT derivatives for the synthesis of chiral polyacetylenes.

An interesting approach to conjugated materials was reported by Lee and co-workers. ROMP of the tetrasila-analogue of cyclooctadiene (COD) yields a hybrid polyacetylene−polyorganosilane copolymer where conjugation is based on a $\sigma-\pi$ network (Scheme 37).[349] PPV analogues, poly(1,4-naphthylenevinylenes) (PNVs), have been prepared by ROMP of benzobarrelenes (Scheme 30).[350] N-Alkyl-substituents were used to solubilize the resulting polymer and to enhance film-casting properties. Upon doping using nitrosonium tetrafluoroborate in acetonitrile, the resulting polymer showed conductivities of up to 15 S/cm.

Scheme 37. Synthesis of a Hybrid Polyacetylene−Polyorganosilane Copolymer via ROMP[a]



[a] [M] = e.g., Mo(N-2,6-i-Pr_2-C_6H_3)($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$.

Finally, conjugated polymers may be prepared by ROMP of norbornene−bis(S-methyl dithiocarbonate) and bis(S-methyl carbonate) followed by thermal decomposition (Scheme 38)[351,352] as well as by ADMET polymerization of conjugated monomers such as 2,4-hexadiene and 2,4,6-octatriene.[353]

I. Materials for Nonlinear Optics (NLO)

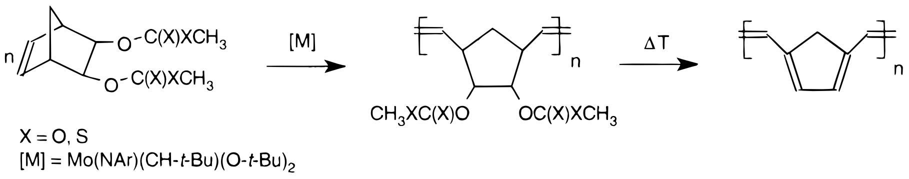
NBE and 7,8-bis(trifluoromethyl)tricyclo[4.2.2.0^{2,5}]-deca-3,7,9-triene may be used to generate ABA-triblock copolymers of NBE (A-block) and polyacetylene (B-block) via the Durham route[308,310] (Scheme 39).[354,355] The two poly-NBE blocks sufficiently solubilize the triblock copolymer. The resulting highly conjugated copolymers were prepared with 4−16 double bonds and showed increasing values for $\gamma(2w/p)$ with increasing effective conjugation (N_{eff}), which could additionally be enhanced via thermal isomerization of the alternating *cis*−*trans*-polyene structure into an all-*trans* polymer. Similar results were obtained with an ABA-triblock copolymer obtained from MTD, hexa-2,4-diene-1,6-dial, and but-2-ene-1,4-bis-(diethylphosphonate) (Scheme 40).[355]

Finally, second-order NLO devices were prepared from *p*-substituted *N*-phenylnorbornene-5,6-dimethyleneimines (Figure 14).[356] The polymers prepared using $Cl_2Ru(CHPh)(PCy_3)_2$ as a catalyst were investigated by hyper-Rayleigh scattering measurements of β_o in chloroform. These data were correlated with molecular dynamics calculation on the backbone tacticity. The calculations, which were in good agreement with the experimental data for β_o, suggested a syndiotactic structure, where each chromophore contributes coherently to the hyperpolarizability.

J. Electroactive Polymers

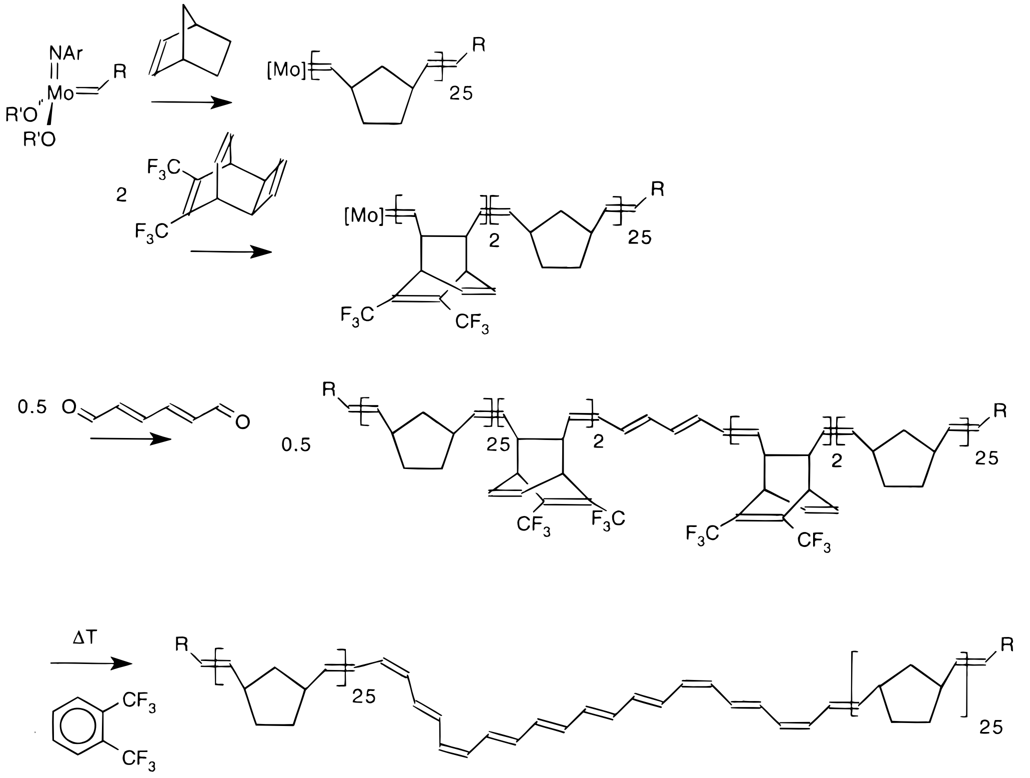
Schrock-type carbenes such as Mo(N-2,6-i-Pr_2-C_6H_3)($CHCMe_3$)(O-t-Bu)$_2$ were found to be redox-stable within a range from −2.1 to +1 V. Consequently, redox-active monomers that have a redox potential within this range may conveniently be polymerized via ROMP to give the corresponding redox-active polymers. Phenothiazene-containing homopolymers and copolymers thereof with NBE as well as ferrocene-substituted poly(norbornene)s were prepared by ROMP using Mo(N-2,6-i-Pr_2-C_6H_3)-($CHCMe_3$)(O-t-Bu)$_2$ and Mo(N-2,6-i-Pr_2-C_6H_3)(CH-ferrocenyl)(O-t-Bu)$_2$, respectively (Figure 15).[357,358] The electrochemical independence of the redox centers was demonstrated by solution voltammetry. Termination of living polymers of these ligands with 4-bromomethyl- and 4-fluorobezaldehyde as well as with 4-pyridylcarbaldehyde gave access to a surface attachment of these redox-active homo- and copolymers.[359] The synthetic protocol entails the reaction

Scheme 38. Synthesis of Poly(cyclopentadienylenevinylene)[a]



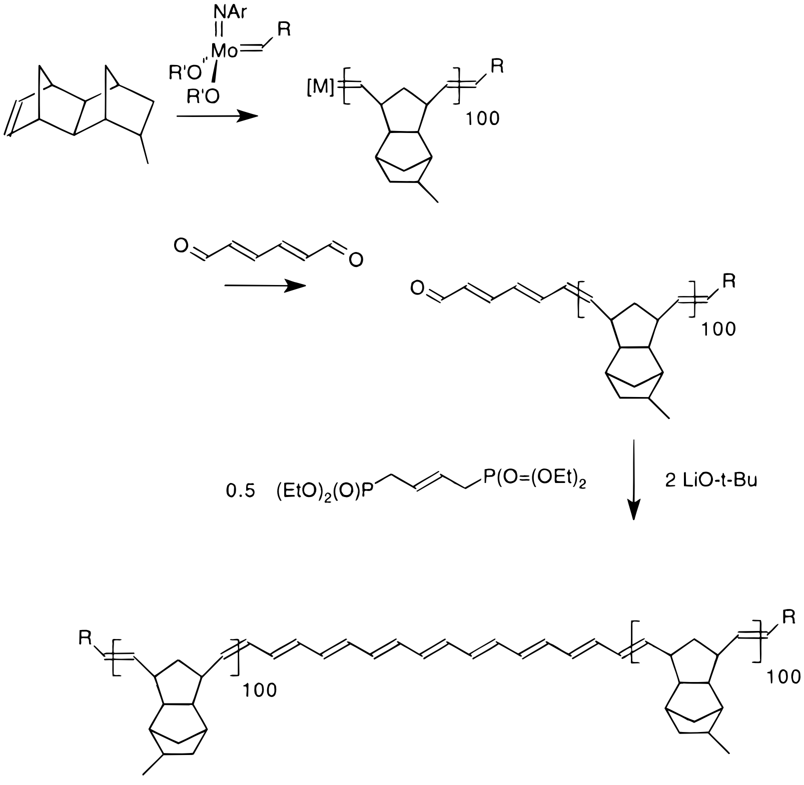
[a] Ar = 2,6-i-Pr_2-C_6H_3.

Scheme 39. Synthesis of a Highly Conjugated ABA Triblock Copolymer[a]



[a] Ar = 2,6-*i*-Pr$_2$-C$_6$H$_3$; R = R′ = *t*-Bu.

Scheme 40. Synthesis of MTD-Based ABA-triblock copolymer[a]



[a] Ar = 2,6-*i*-Pr$_2$-C$_6$H$_3$; R = R′ = *t*-Bu.

of benzyl chloride or pyridine surface-derivatized electrodes with these polymers, which become attached by formation of the corresponding ion pair. Pt, In_2SnO_3, and n-Si electrodes were derivatized with $Si(OEt)_3$-containing polymers.

K. Beaded and Surface-Derivatized Materials

More recently, ROMP has been used for the preparation of beaded materials with well-defined surface chemistry. Living polymers of functional monomers,

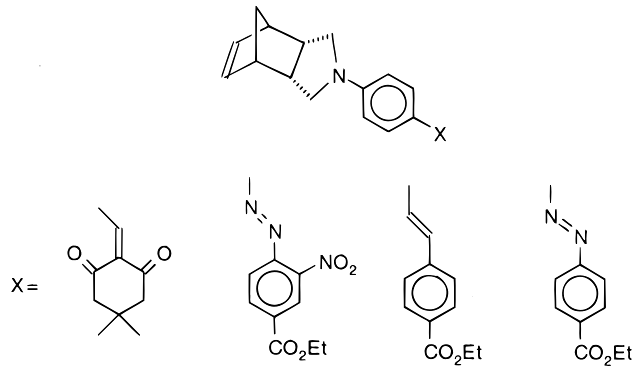


Figure 14. *p*-Substituted *N*-phenylnorbornene-2,3-dimethyleneimimines.

e.g., norbornene-2,3-dicarboxylic anhydride and norbornene-2-(*N*,*N*-dipyrid-2-yl)carbamide, were cross-linked in a precipitation-type polymerization to form 40−60 μm beads (Scheme 41).[360−362] Pd-loaded poly(norbornene-2-(*N*,*N*-dipyrid-2-yl)carbamide)-based resins have been used successfully in heterogeneous Heck-type coupling reactions.[363] In contrast to the 5-methacroyl-cyclooctene-based systems used by Grubbs and co-workers,[364,365] 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo,endo*-dimethanonaphthalene and related compounds served as cross-linkers, compounds which had already been used by Schrock and co-workers for the synthesis of (amphiphilic) star *block*-copolymers.[366,367] The resulting materials were used for the selective extraction of organic compounds[368,369] from water and volatile compounds from air.[370] Transition metals such as mercury and palladium[371] were extracted with copolymers of 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo,endo*-dimethanonaphthalene and norbornene-2-dipyridylamide. Norbornene-2,3-dicarboxylic acid-based copolymers were used for the selective extraction of lanthanides from complex mixtures such as rock digests.[372] These digests were prepared by dissolving granite, basalt, and andesite rocks in a $LiBO_2$ melt, which was consecutively dissolved in nitric acid. Finally, their use as on-line ion-exchange materials in LC-MS of oligonucleotides has to be mentioned.[373]

Adsorbed monolayers have already been used for block segregation purposes of diblock copolymer monolayers on surfaces.[374] Such adsorbed monolayers of functionalized diblock copolymers (e.g., imidazol-containing ligands) may serve as adhesion promotors, biosensors, biomembranes, etc.[374] Another application lies in the use of ROMP-based *block*-copolymer. Thus, copolymers of 7-oxanorbornene-2,3-dicarboxylic anhydride (ONDCA) and NBE, repectively, may be covalently attached to vinylated silica surfaces via radical copolymerization of the ROMP polymer vinylene groups with the surface vinyl groups using AIBN (Figure 16). The resulting materials have been

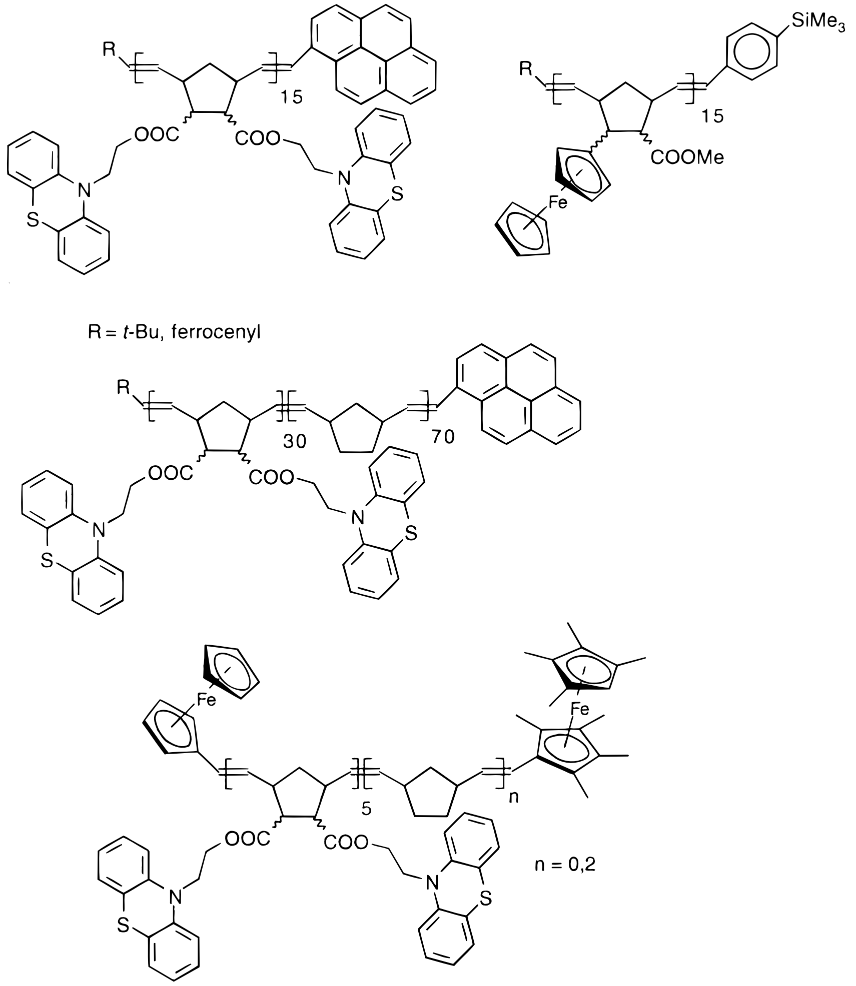
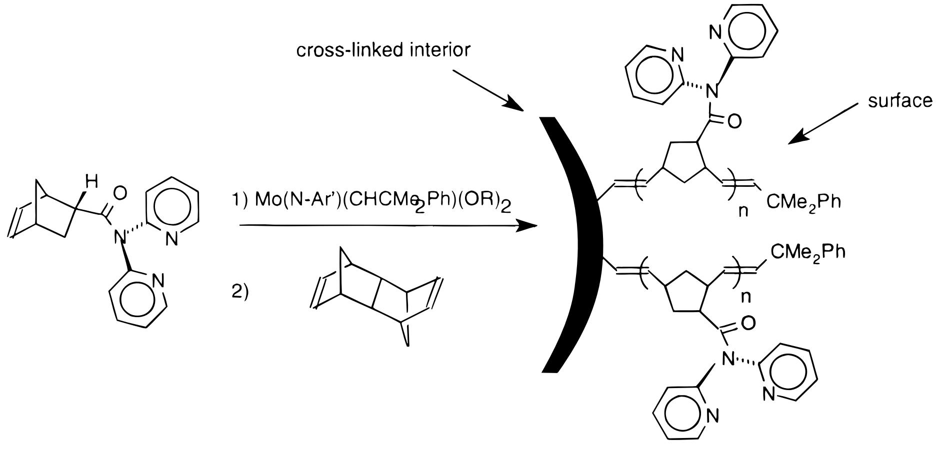


Figure 15. Structures of electroactive ferrocene- and phenothiazene-based polymers.

Scheme 41. Representative Example for Dipyridyl Amide-Functionalized Polymer Beads for the Selective Binding of Hg(II) and Pd(II) Prepared via Ring-Opening Metathesis Precipitation Polymerization and for the Preparation of Heterogeneous Supports for Heck-Type Couplings, Respectively[a]



[a] Ar′ = 2,6-i-Pr_2-C_6H_3; R = $CMe(CF_3)_2$.

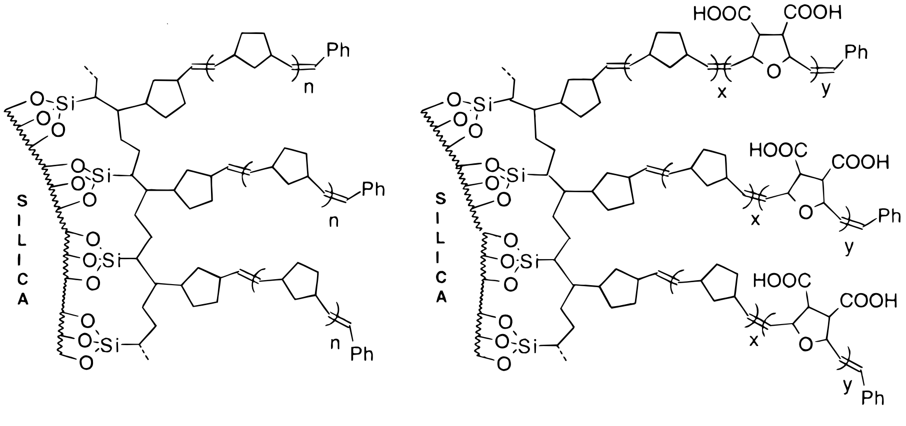


Figure 16. Structure of coated silica for HPIC and for the extraction of radioactive lanthanides: (A) poly-NBE coating, (B) poly(7-oxanorbornene-2,3-dicarboxylic acid)-*block*-poly-NBE coating.

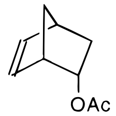
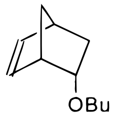
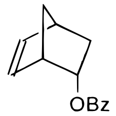
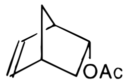
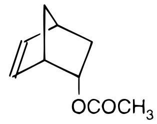
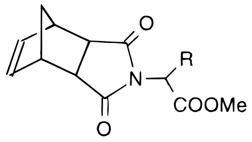
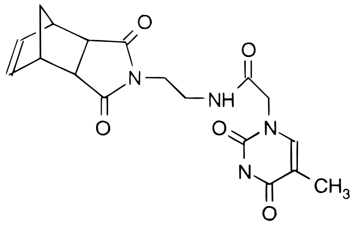
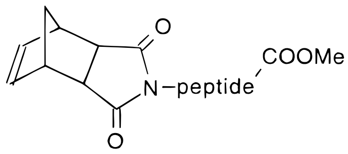
used successfully in HPIC of isomeric anilines, lutidines, and hydroxyquinolines[375] as well as for selective (on-line) extraction of (radioactive) lanthanides.[376] ROMP-based graft-copolymers may be prepared from NBE-derivatized silica or poly(styrene-*co*-divinylbenzene) supports and have been used successfully for the synthesis of chiral HPLC supports.[377] Recently, we elaborated a straightforward route for the preparation of ROMP-based, functionalized monolithic separation media.[378] Three steps were required for the synthesis of such functionalized monoliths: (1) Generation of a continuous matrix by ring-opening metathesis copolymerization of NBE and the cross-linker 1,4,4a,5,8,8a-hexahydro-1,4,5,8-*exo,endo*-dimethanonaphthalene in the presence of the porogenic solvents 2-propanol and toluene within the separation device (column) using $Cl_2(PCy_3)_2Ru(=CHPh)$; (2) consecutive “in situ” derivatization with a suitable ROMP-active monomer. Due to the living character of this polymerization technique, parts of the initiator remain active and the fraction that is covalently bound to the surface of the rod may be used for further derivatization. Thus, pumping solutions of a ROMP-active monomer over the column allows its grafting onto the surface of the monolith. The broad applicability of the concept of in situ functionalization was demonstrated by the derivatization of monoliths with a series of ROMP-active monomers such as NBE-cyclodextrin derivatives. Investigations by electron microscopy revealed that the resulting rods consist of spherical, agglomerated microglobules. By choosing adequate polymerization conditions, the diameters of the microglobules may be varied within 0.6−30 μm, achieving narrow particle size distributions (±20%).

Metal particles with diverse polymer brushes or with chemically tailorable shell properties may be prepared by the following approaches. The metal surface was derivatized by a surface-anchoring group. In the case of gold, terminal thiol groups, e.g., present in ω-(*exo*-5-norborn-5-ene-2-oxy)decan-α-thiol, are reacted with $HAuCl_4$ under reducing conditions. Copolymerization of these surface-anchored NBE groups with other functional monomers such as *N*-methyl-7-oxanorbornene-2,3-dicarbimide, 2,3-bis(*tert*-butyldimethylsilyloxymethyl)-norbornene,[379] or 2-ferrocenylcarboxylnorbornene[380] yields the desired surface-derivatized metal (Au) particles.

L. Chiral Polymers

In principle, chiral ROMP-based polymers may be generated by the use of a suitable enantiomerically

Table 6. Values for $[\alpha]_D^{20}$ Obtained for Poly-1−Poly-8 Using Mo(NAr′)CHR)(OR′)$_2$ as the Initiator[a] [382−388]

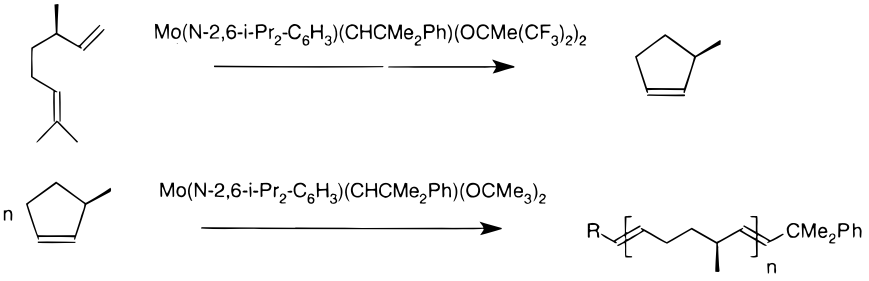
#	Monomer	$\alpha\frac{20}{D}$ (deg)	M_w/PDI
1		42.8	197000/1.67
2		54.54	224000/3.40
3		87.23	173000/1.36
4		-23.71	57000/1.50
5		88.63	188000/1.23
6		R = Me, *exo*: D: +34 R = Me, *exo*: L: -31 R = Me, *endo*: D: +54 R = Me, *endo*: L: +52 R = CHMeEt, *exo*: L: -57 R = CHMeEt, *endo* L: -49	M_n = 20500/1.16 M_n = 27100/1.27 M_n = 19600/1.18 M_n = 21400/1.28 M_n = 13300/1.27 M_n = 67700/1.4
7		n.d.	2500/1.07
8		peptide = Gly-Phe-Phe: +24	9500/1.04

[a] Ar = N-2,6-i-Pr$_2$-C$_6$H$_3$; R = CMe$_2$Ph, −t-Bu; R′ = −t-Bu, CMe(CF$_3$)$_2$.

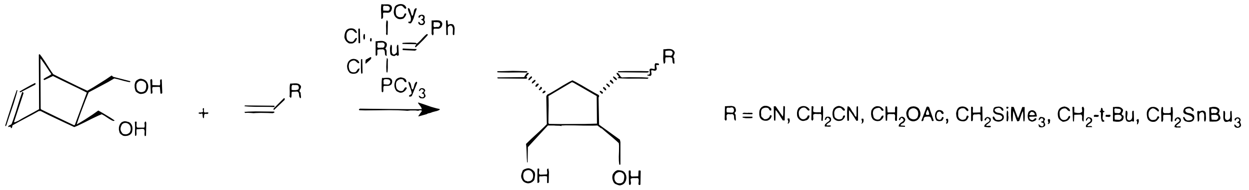
pure monomer (e.g., based on NBE) or via the introduction of additional chiral elements into the polymer chain starting from an achiral monomer. One access to chiral monomers is represented by unsymmetrically 2,3-disubstituted norbornenes which may be isolated in high enantiomeric excess (ee) via enzymatic resolution. Thus, the polymerization of monomers 1−5 using Mo(NAr)(CH-t-Bu)(O-t-Bu)$_2$ results in the formation of polymers with high optical rotation[381] (Table 6).

Another type of chiral polymer may be prepared from enantiomerically pure methyl-*N*-(1-phenethyl)-

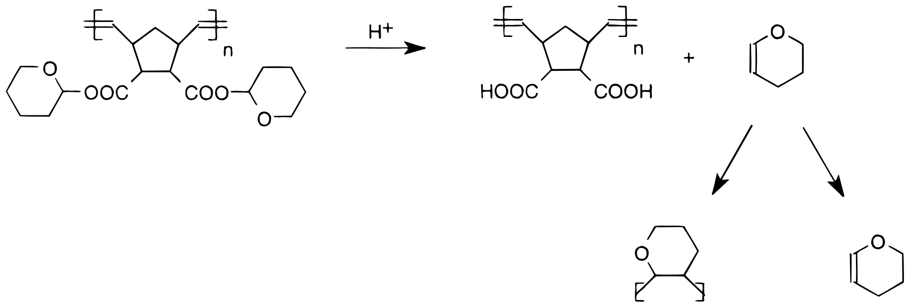
Scheme 42. Tandem RCM-ROMP for the Preparation of Chiral Polymers



Scheme 43. Ruthenium-Catalyzed Cross-Coupling



Scheme 44. Decomposition of Photoresist Polymers via H^+ Generated by UV Light



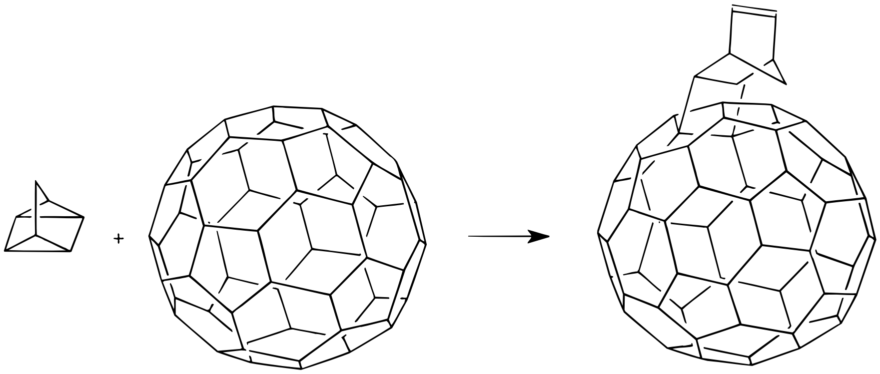
2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate and (1-phenylethyl)-*N*-(1-phenethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxamide, which may conveniently be synthesized through an asymmetric Lewis-acid-catalyzed Diels–Alder reaction.[382,383] Poly(methyl-*N*-(1-phenethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate was additionally characterized by electrospray ionization mass spectrometry (ESI-MS).[384] Using initiators of the general formula Mo(*N*-2,6-*i*-Pr_2-C_6H_3)(CH-*t*-Bu)(OR) (R = *t*-Bu, $CMe_2(CF_3)$, CMe-$(CF_3)_2$), chiral polymers may be prepared. For purposes of completeness, it must be mentioned that for both monomers, ratios of k_i/k_p, which may be calculated from the ^1H NMR data,[89] were found to be $\ll 1$ with all initiators.

An interesting approach to chiral polymers was reported by Sita.[385] A synthetic protocol consisting of a tandem diene metathesis cyclization/ROMP was applied (Scheme 42). Thus, (−)- and (+)-*β*-citronellene were converted into enantiomerically pure (3*R*)- and (3*S*)-3-methylcyclopentene via ring-closing metathesis (RCM) using Mo(*N*-2,6-*i*-Pr_2-C_6H_3)($CHCMe_2$-Ph)$(OCMe(CF_3)_2)_2$. ROMP was accomplished using Mo(*N*-2,6-*i*-Pr_2-C_6H_3)($CHCMe_2Ph$)$(OCMe_3)_2$ resulting in the formation of chiral polymers with high optical rotation. Chiral polymers may additionally be synthesized by the ROMP of α-amino acid- or peptide-derived norbornene-2,3-dicarbimides (Table 6).[386−388]

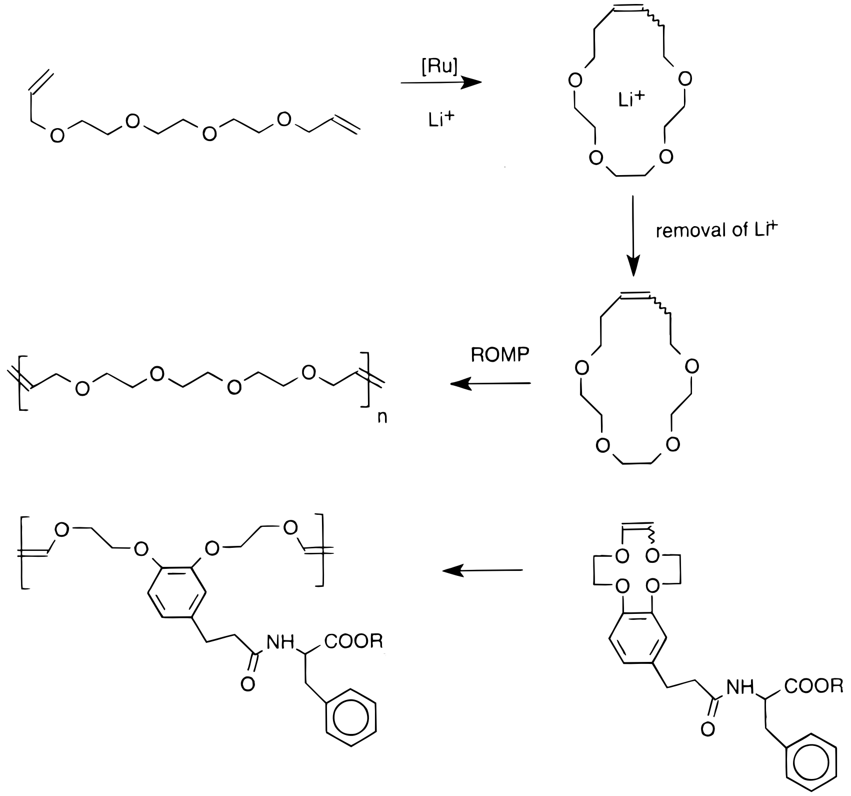
M. Other Functional Polymers

One of the first applications of ROMP polymers such as poly(7-oxanorbornene)-2,3-dicarboxylic acids and amides was their use as water additives for water treatment.[402] Additionally, ROMP may be used for the preparation of "advanced materials" such as carbohydrate-functionalized polymers. Both molybdenum-based initiators as well as ruthenium-based initiators were found suitable for these purposes. While $Cl_2Ru(CHCHCPh_2)(PCy_3)_2$ may be used for the polymerization of both (*exo*-norborn-5-ene-2-carboxamido)-2-deoxy-D-glucopyranose and its protected analogues, (*exo*-norborn-5-ene-2-carboxamido)-2-deoxy-1,3,4,6-tetra-*O*-acetyl-D-glucopyranose),[389] the use of Mo(*N*-2,6-*i*-Pr_2-C_6H_3)($CHCMe_2Ph$)$(OCMe_3)_2$ requires O-protection in any case.[390] Carbohydrates may be also be attached by a C-glycoside linker to either 7-oxanorborn-5-ene-2,3-dicarboxylic acid[391] or to (enantiomerically pure) (*R*)-(+)-7-oxabicyclo[2.2.1]hept-5-ene-*exo*-2-carboxylic acid[392] for the formation of selectin-inhibiting neoglycoplymers.[393] Functionality-tolerant initiators such as $Cl_2Ru(CHPh)(PCy_3)_2$ have to be used. In a similar approach, vancomycin was bound to a norbornene-2,3-dicarbimide (Figure 17). The polymers were prepared using again Cl_2Ru-$(CHPh)(PCy_3)_2$ and showed significantly enhanced potency against vancomycin-resistant enterococci (VREs). An alternative approach to pseudopolysaccharides lies in the use of hydrogenated ROMP polymers of 7-oxanorborn-5-ene-2,3-diol. The synthetic protocol involves the ROMP of acetonide or acetal-protected 7-oxanorborn-5-ene-2,3-diol using either Mo(*N*-2,6-*i*-Pr_2-C_6H_3)($CHCMe_3$)$(OCMe_3)_2$ or $Cl_2Ru(CHPh)(PCy_3)_2$ followed by catalytic hydration. Deprotection and subsequent treatment with chlo-

Scheme 45. C_{60}-Derivatized NBE



Scheme 46. Preparation of Functionalized Polyethers via RCM-ROMP[a]



[a] [Ru] = $Cl_2Ru(CHCPh)(PCy_3)_2$.

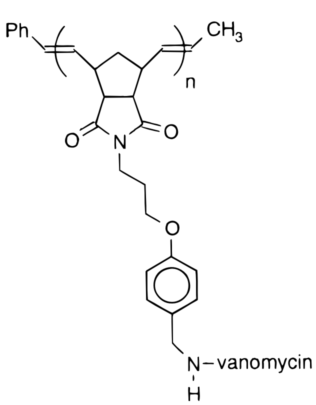
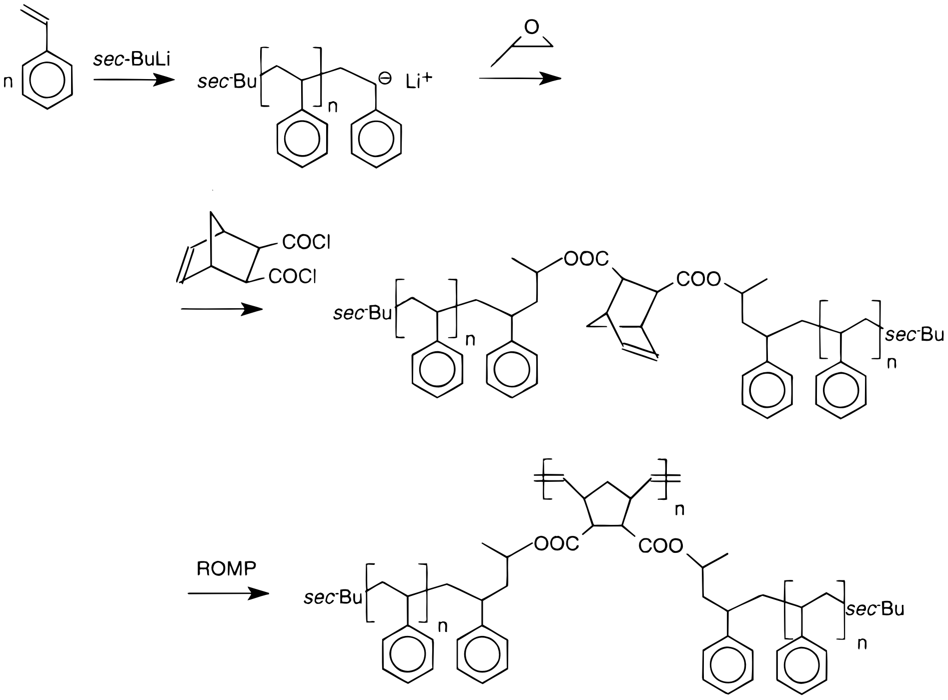


Figure 17. Vancomycin-derivatized ROMP polymer.

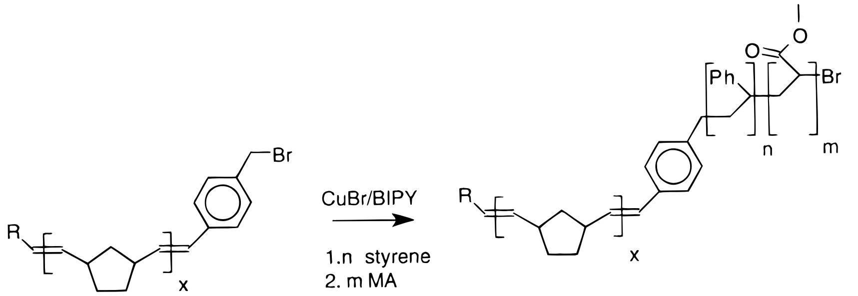
rosulfonic acid yields the corresponding poly(hemisulfonates).[394] Finally, a general and widely applicable access to well-defined saccharide-functionalized polymers lies in the reaction of a poly(norborn-5-ene-*exo*-2-carboxylic acid *N*-hydroxysuccinimide ester) with the corresponding saccharide.[395] Generally speaking, this approach offers access to biologically active, multivalent displays and may be used, e.g., in the investigation of blood agglutination.

Besides substituted NBEs, cyclobutene[396] and substituted cyclobutenes[397] may also effectively be polymerized by ROMP using both Mo- and Ru-based systems.[165,166,398−401] In terms of materials science, ROMP of 1-methylcyclobutene appears to be highly attractive as it offers access to highly stereoregular polyisoprenes.[397] Thus, the use of Mo(N-2,6-i-Pr_2-C_6H_3)($CHCMe_3$)($OCMe_2(CF_3)$)$_2$ yields polymers which are 100% *cis* and show 100% head-to-tail connectivity. Hydrated ROMP polymers of 3-methylcyclobutene and 3,3-dimethylcyclobutene are interesting equivalents of poly(ethylene-*alt*-propylene) and poly(ethylene-*alt*-isobutylene).[399]

Scheme 47. Coupling of Living Anionic with Living ROMP

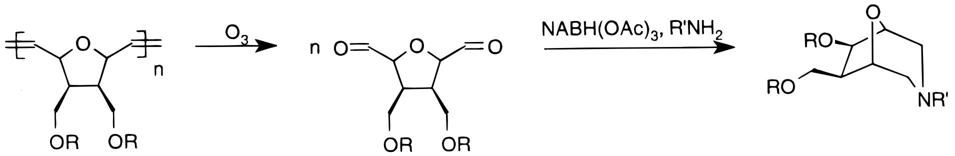


Scheme 48. Coupling of ROMP with Atom-Transfer Radical Polymerization (ATRP)[a]



[a] R = initiator-derived end group.

Scheme 49. Polymer Backbone Disassembly via Ozonolysis[a]



[a] R = methyl, 4-bromobenzyl; R′ = butyl, benzyl.

N. Other Applications

Selective cross-coupling of monosubstituted olefins with strained, cyclic olefins, e.g., 5,6-disubstituted norbornenes, 7-oxanorbornenes,[403] and cyclobutenes,[404] may be achieved in high yields using $Cl_2Ru(CHPh)(PCy_3)_2$ as the catalyst (Scheme 43). Nevertheless, to accomplish such reactions in a highly stereoslective way, the use of chiral Mo-based Schrock carbenes seems highly favorable.[405] This reaction offers access to tetrasubstituted cyclopentanes and tetrahydrofuranes. Polymacromonomers with *comb*-polymer structure were prepared from (ω-norbornenyl polystyrene), α- and ω-norbornenyl-polybutadiene, and α-norborn-2-enyl-polyethylenoxide macromonomers, e.g., using $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe_3)_2$ as an initiator.[406−410] Similarly, ROMP of α-norbornenyl-poly(ϵ-caprolactone) macromonomers using $[RuCl_2(p\text{-cymene})]_2PCy_3/(CH_3)_3Si{-}CHN_2$[411] as well as of phosphazene-functionalized norbornenes using $Cl_2Ru(CHPh)(PR_3)_2$ have been reported.[412] Unimolecular micelles and associative thickeners have been proposed as possible applications for this type of polymers. Novak and co-workers reported on the ROMP of 3,4-disubstituted cyclobutenes by Schrock-type catalysts.[398,400,401,413] Recently, the successful use of poly(norbornen-2-ene)-based materials as positive photoresists was reported.

Polymers based on *exo,endo*-di(tetrahydropyranyl)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate and *exo,exo*-di(tetrahydropyranyl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate were used for chemical amplification using 2,6-dinitrobenzyltosylate as a photoacid generator (Scheme 44).[414] The acid—generated at $\lambda = 254$ nm—leads to the hydrolysis of the polymer, which is consecutively removed with tetrabutylammonium hydroxide (TBAH). Boron-containing monomers, e.g., *exo*-B-5-norborn-2-enylborabicyclononane, may be used to generate boron-containing polymers via ROMP using $W(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)(CHCMe_3)(OR)_2$ ($R = CMe_3$, $CMe(CF_3)_2$). These polymers may be treated with hydrogen peroxide/sodium hydroxide to yield the corresponding hydroxyl-functionalized polymers.[415−417] Poly(norbornenes) containg C_{60} are accessible by ROMP of the corresponding C_{60}-norbornene derivative (Scheme 45) using $M(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)(CHCMe_3)(OCMe(CF_3)_2)_2$.[418]

Polyethers and functionalized polyethers may be prepared via a consecutive RCM−ROMP approach (Scheme 46).[419,420] Lithium is added as a template in order to facilitate ring formation via RCM. The attachment of biologically relevant peptides offers some potential use in biomedical applications such as tissue engineering and drug delivery. Additionally, the synthesis of poly(5-siloxydeltacyclene) and poly(deltacyclene) via ROMP has to be mentioned.[421] Another interesting topic is the polymerization of dicyclopentadiene (DCPD). The mechanism of the polymerization of DCPD and, in particular, its cross-linking has been a subject of controversy for some time. Investigations carried out by Grubbs et al.[422] and Wagener et al.[423,424] using both classical WCl_6-based and well-defined W- and M-based Schrock carbenes revealed that DCPD polymerizes with these well-defined systems to produce *linear* poly(DCPD). Nevertheless, at high monomer concentrations or with classical WCl_6-based systems, thermal-induced cross-linking occurs. NMR investigations revealed that this cross-linking occurs via olfin addition rather than via a metathesis-based mechanism.

Coupling of living anionic polymerization and living ROMP may be achieved by terminating living anionic polymer chains with norborn-2-ene-5-carboxylic chloride[425] or norbornene-2,3-dicarboxylic chloride.[426,427] This end-functionalized polymer may then be polymerized via ROMP (Scheme 47).

Another type of *block*-copolymer was obtained by conversion of living ROMP into controlled atom-transfer radical polymerization (ATRP).[428] The approach involves the termination of a living ROMP polymer with a *p*-bromomethylbenzaldehyde. This prepolymer may be initiated using CuBr/2,2-dipyridyl and used for *block*-copolymer formation with styrene and methyl acrylate (Scheme 48). Finally, the preparation of 7-oxabicyclo[2.2.1]hept-2-ene-5,6-dimethanol-derived ROMP polymers and their use for the preparation of *N*-alkyl-3-aza-8-oxabicyclo[3.2.1]octane-6,7-dimethanol derivatives via ozonolytic scission (Scheme 49) for the synthesis of 1,4-azoxepanes[429] as well as the preparation of ROMP dendrimer[430] have to be mentioned.

IV. Acknowledgment

Financial support was provided by the Austrian National Science Foundation (FWF Vienna, Project Number P-12963-GEN) and the “Jubiläumsfond der Österreichischen Nationalbank”, Vienna, Austria (Project Number 7489).

V. References

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CR990248A