Molybdenum–NHC Complexes

DOI: 10.1002/anie.201404655

N-Heterocyclic Carbene, High Oxidation State Molybdenum Alkylidene Complexes: Functional-Group-Tolerant Cationic Metathesis Catalysts**

Michael R. Buchmeiser, Suman Sen, Jörg Unold, and Wolfgang Frey*

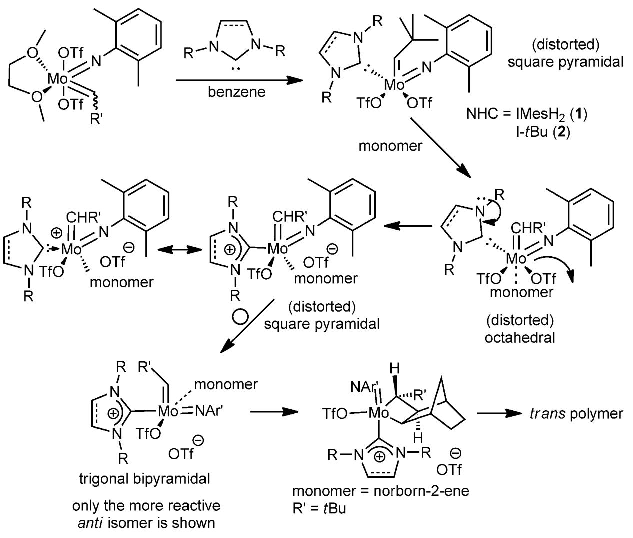
Dedicated to Prof. Richard R. Schrock on the occasion of his 70th birthday

Abstract: *We synthesized the first N-heterocyclic carbene (NHC) complexes of Schrock's molybdenum imido alkylidene bis(triflate) complexes. Unlike existing bis(triflate) complexes, the novel 16-electron complexes represent metathesis active, functional-group-tolerant catalysts. Single-crystal X-ray structures of two representatives of this novel class of Schrock catalysts are presented and reactivity is discussed in view of their structural peculiarities. In the presence of monomer (substrate), these catalysts form cationic species and can be employed in ring-closing metathesis (RCM), ring-opening metathesis polymerization (ROMP), as well as in the cyclopolymerization of α,ω-diynes. Monomers containing functional groups, which are not tolerated by the existing variations of Schrock's catalyst, e.g., sec-amine, hydroxy, and carboxylic acid moieties, can be used. These catalysts therefore hold great promise in both organic and polymer chemistry, where they allow for the use of protic monomers.*

Very few reports exist on cationic W[1] and Mo alkylidene complexes. The Mo alkylidenes include cationic Mo imidoalkylidene β-diketonate and β-diketiminates[2] as well as cationic Mo imidoalkylidene pyrrolide and Mo monoalkoxide complexes.[3] For cationic Mo imidoalkylidene monoalkoxide species, a low ring-closing metathesis (RCM) activity was reported with turnover numbers (TONs) less than 18. Despite this unsatisfactory status quo, however, cationic Schrock catalysts are of utmost interest since such catalytic systems could be used under biphasic or supported biphasic conditions including supported ionic liquid phase (SILP) conditions. Particularly the SILP approach has been demonstrated to allow metathesis reactions under continuous conditions, where the ionic catalysts are selectively dissolved in a polymer-supported ionic liquid, thereby offering access to products with unprecedented low metal contaminations, typically in the ppb regime.[4] Nonetheless, this approach has so far been limited to cationic Ru alkylidene complexes.

Nomura and Zhang reported the NHC-triggered α-hydrogen elimination in vanadium(V) complexes.[5] This result suggests that rather nucleophilic than basic NHCs should be suitable for preparing cationic Schrock catalysts. We anticipated that an NHC complex of one of Schrock's bis(triflate) progenitors, for example, $[Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CH\text{-}t\text{Bu})(OTf)_2(DME)]$ (DME = 1,2-dimethoxyethane) could indeed be a cationic one with the cationic charge dislocated between the NHC and molybdenum (see mesomeric structures in Scheme 1). And in fact, reaction of either 1,3-dimesitylimidazolin-2-ylidene ($IMesH_2$) or 1,3-di-*tert*-butylimidazol-2-ylidene (I-*t*Bu) with $[Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CH\text{-}t\text{Bu})(OTf)_2(DME)]$ resulted in the formation of the desired NHC-complexes **1** and **2** (Scheme 1).

Compound **1** (Figure 1) crystallizes in the orthorhombic system P_{bca}, $a = 1824.13(6)$ pm, $b = 2117.49(6)$ pm, $c = 2216.35(5)$ pm, $\alpha = \beta = \gamma = 90°$, $Z = 8$. In the solid state, the complex exists in its neutral form. The ligands adopt a distorted square pyramidal (SP) geometry with the Mo alkylidene unit in the apical position. The distance Mo–C30 is 187.3(3) pm and thus somewhat shorter than that found for



Scheme 1. Synthesis of catalysts **1** and **2**, formation of the cationic species in the presence of monomer, and *trans*-selectivity in ROMP.

---

[*] Prof. M. R. Buchmeiser, M. Sc. S. Sen, Dr. J. Unold
Institut für Polymerchemie, Universität Stuttgart
Pfaffenwaldring 55, 70550 Stuttgart (Germany)
E-mail: michael.buchmeiser@ipoc.uni-stuttgart.de
Homepage: http://www.uni-stuttgart.de/ipoc/msf/index_en.html
Dr. W. Frey
Institut für Organische Chemie, Universität Stuttgart
Pfaffenwaldring 55, 70550 Stuttgart (Germany)

[**] This work was supported by the Deutsche Forschungsgemeinschaft (DFG, contract Nr. BU2174/8-1). NHC = N-heterocyclic carbene.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201404655.

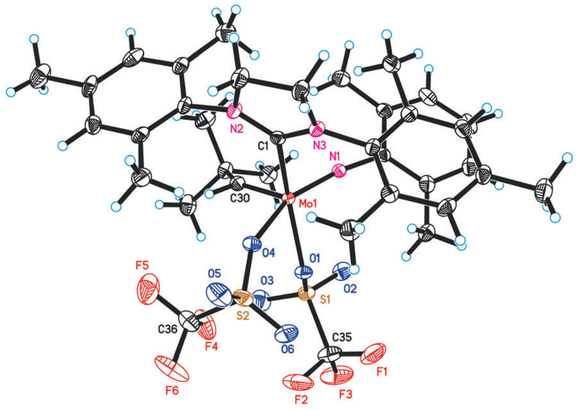


Figure 1. Single-crystal X-ray structure of **1**. Selected bond lengths [pm] and angles [°]: Mo1–N1 172.9(2), Mo1–C30 187.3(3), Mo1–O4 211.45(18), Mo1–O1 213.52(18), Mo1–C1 223.5(3); N1-Mo1-C30 101.61(11), N1-Mo1-O4 153.17(9), C30-Mo1-O4 105.17(10), N1-Mo1-O1 96.08(9), C30-Mo1-O1 97.82(10), O4-Mo1-O1 78.86(7), N1-Mo1-C1 96.84(10), C30-Mo1-C1 103.36(11), O4-Mo1-C1 78.59(9), O1-Mo1-C1 152.35(9).

the Mo alkylidene in [Mo(NAr′)(CH-*t*Bu)(OTf)$_2$(DME)] (1.90/1.93 pm).[6] The distance Mo1−O1 with the triflate being *trans* to the NHC is somewhat longer than for the one that is *trans* to the imido ligand (Mo1−O4 213.52(18) vs. 211.45(18) pm). Clearly, the mesityl-containing NHC in **1** has a very unpronounced *trans*-effect on the triflate ligand, which is a direct consequence of the distorted geometry of the complex with a C1-Mo-O1 angle of only 152.35(9)°. In the solid state, the alkylidene adopts a *syn*-configuration, which also predominates in solution as evidenced by the $J_{\mathrm{C-H}}$ coupling constant of 118 Hz. Apart from the signal for the *syn*-alkylidene, **1** shows approximately 0.1 % of the *anti*-isomer at $\delta = 14.52$ ppm (see Figure S1 in the Supporting Information).

Compound **2** (Figure 2) crystallizes in the tetragonal system P42$_1$c, $a = 2449.86(11)$ pm, $b = 2449.86(11)$ pm, $c = 1093.68(7)$ pm, $\alpha = \beta = \gamma = 90°$, $Z = 8$. As in **1**, the complex is in its neutral form; the ligands adopt a distorted SP geometry with the Mo alkylidene unit in the apical position. Unlike in **1** and despite an unfavorable small angle O1-Mo1-C9 of 147.93(5)°, the triflate group located *trans* to the N-arylimido ligand experiences the most pronounced *trans*-effect, resulting in a weaker binding of this anionic ligand as suggested by the different bond lengths (Mo−O1 211.07(11) and Mo−O2 217.98(12) pm). Particularly the Mo−O2 distance is significantly larger than the distances found in "standard" bis(triflate) complexes of the general formula [Mo(NAr′)(CH-*t*Bu)(OTf)$_2$(DME)] (208.5 < Mo−O < 210.5 pm).[6] Notably, neither IMesH$_2$ nor I-*t*Bu, though strong bases, caused any (permanent) deprotonation of the α-hydrogen at the alkylidene ligand, a reaction that would result in the formation of Mo alkylidyne complexes.[7] This is because the NHCs used are more nucleophilic than basic[8] with I-*t*Bu being more nucleophilic than IMesH$_2$,[9] which can be explained by the Hückel aromaticity of [I-*t*Bu]$^+$. This order in nucleophilicity is also reflected by the chemical shifts for the corresponding alkylidene units. Thus, the chemical shift of the alkylidene in **2** ($\delta_{\mathrm{H}} = 14.60$ ppm) strongly suggests that the partial positive charge at the Mo is larger in **2** than in **1** ($\delta_{\mathrm{H}} = 12.76$ ppm). These data are also in line with the single-crystal X-ray data, which clearly show a more pronounced *trans*-effect on one triflate and thus charge separation in **2**.

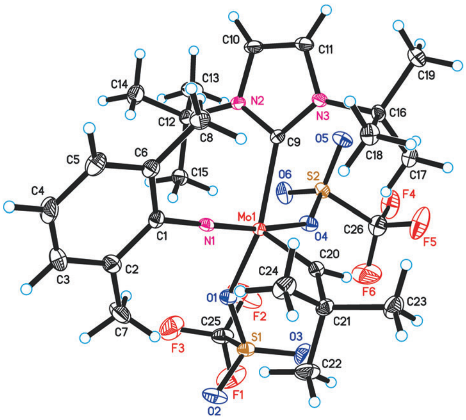


Figure 2. Single-crystal X-ray structure of **2**. Selected bond lengths [pm] and angles [°]: Mo1–C20 188.69(18); N1-Mo1-C20 97.03(8), N1-Mo1-O1 99.04(6), C20-Mo1-O1 98.13(6), N1-Mo1-O4 167.42(6), C20-Mo1-O4 95.48(7), O1-Mo1-O4 80.44(5), N1-Mo1-C9 93.43(6), C20-Mo1-C9 109.57(7), O1-Mo1-C9 147.93(5), O4-Mo1-C9 81.11(5).

We subjected complexes **1** and **2** to various metathesis reactions. With diallyl diphenylsilane (Figure 3), **1** allows for turnover numbers of 480 in 1,2-dichloroethane at $T = 80\,°\mathrm{C}$ and thus clearly rivals other cationic Mo complexes.[2,3] With **1**, in the ROMP[10] of 5,6-bis((pentyloxy)methyl)bicyclo-[2.2.1]hept-2-ene (Figure 3), the corresponding polymer ($M_{\mathrm{n}} = 9000\ \mathrm{g\,mol^{-1}}$, PDI = 1.2), which was isolated in 90 % yield, contained 90 % *trans* double bonds (Figure S9). With catalyst **2**, the corresponding polymer had a lower *trans* content of 50 % (Figure S11).

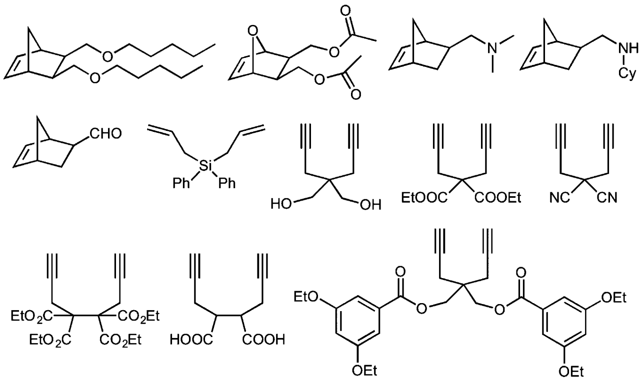


Figure 3. Substrates and monomers used in RCM, ROMP, and cyclopolymerization (Cy = cyclohexyl).

Similar results were found with poly(7-oxabicyclo-[2.2.1]hept-5-ene-2,3-diylbis(methylene) diacetate; Figure 3), which was obtained in quantitative yield by the action of **1** and also displayed a high *trans* content of 85 % ($M_{\mathrm{n}} = 13\,000\ \mathrm{g\,mol^{-1}}$, PDI = 1.7). With catalyst **2**, the *trans* content of this polymer was 33 %. To our knowledge, these are the first high-yield metathesis reactions reported for any Mo imidoalkylidene bis(triflate) complex.

The most striking feature of the novel catalysts, however, is related to the cyclopolymerization of 4,4-bis(hydroxymethyl)-1,6-heptadiyne (Figure 3), a monomer with two unprotected hydroxy groups. Unlike classic Schrock catalysts, which are very sensitive towards protic functionalities, this monomer is quantitatively polymerized within less than 5 min to yield the corresponding purple conjugated polymer (M_n (theor.) = 7700 g mol^{-1}, M_n = 6500 g mol^{-1}, PDI = 1.3, λ_{max} = 554, 593 nm). Unfortunately, no high-quality ^{13}C NMR spectra of this polyene could be obtained, probably a result of severe aggregation of the highly polar and protic polymer. Furthermore, a dinitrile compound, that is, dipropargylmalodinitrile was cyclopolymerized by the action of **1** and isolated in 60 % yield (M_n = 1100 g mol^{-1}, PDI = 1.15, M_n (theor.) = 1420 g mol^{-1}). The high functional-group tolerance also holds for ROMP: catalyst **1** polymerized norborn-5-ene-2,3-dimethanol, isolated in 80 % yield (M_n = 2800 g mol^{-1}, PDI = 1.12, M_n (theor.) = 1540 g mol^{-1}, σ_{trans} = 43 %). Similar results were obtained with 2-(*N*,*N*-dimethylaminomethyl)norborn-2-ene and 2-(*N*-cyclohexylaminomethyl)norborn-2-ene giving the corresponding polymers poly[2-(*N*,*N*-dimethylaminomethyl)-norborn-2-ene], M_n = 10 500 g mol^{-1}, PDI = 1.21 and poly[2-(*N*-cyclohexylaminomethyl)norborn-2-ene], M_n = 13 100 g mol^{-1}, PDI = 1.10, σ_{trans} = 35 %, isolated in 80 and 90 % yield. In view of these results and to gain information on the regioselectivity of insertion in cyclopolymerization, we subjected a less reactive 1,7-octadiyne, that is, 4,4,5,5-tetrakis(ethoxycarbonyl)-1,7-octadiyne (Figure 3) to cyclopolymerization, again using **1**. The corresponding polymer (M_n = 13 200 g mol^{-1}, PDI = 1.9, λ_{max} = 484 nm) was isolated in 81 % yield and formed with over 96 % α-insertion selectivity (Figure S21). NMR and UV/Vis spectroscopy data fit those of independently prepared samples.[11] Similar results were obtained for the cyclopolymerization of 4,4-bis[(3,5-diethoxybenzoyloxy)methyl]-1,6-heptadiyne. The corresponding polyene was isolated in 94 % yield and with 91 % α-selectivity.

The high functional-group tolerance of both **1** and **2** is also reflected by the fact that the polymerization reactions cannot be terminated by the addition of an aldehyde, for example, ferrocene carbaldehyde. Instead, cross-metathesis with an olefin, for example, styrene is required to terminate the living polymer chain. Alternatively, termination can be accomplished by the addition of a HCl-containing methanol solution. This unreactivity towards aldehydes in turn allowed poly(norborn-5-ene-2-yl carbaldehyde) to be synthesized by the action of **1**, and be isolated in 55 % yield (M_n = 5000 g mol^{-1}, PDI = 2.1, M_n (theor.) = 6100 g mol^{-1}. Finally, and again absolutely unprecedented for molybdenum-based metathesis catalysts, a diyne containing two free carboxylic acids, that is, 1,7-octadiyne-4,5-dicarboxylic acid could be cyclopolymerized and the product isolated in 90 % yield by the action of **1** (M_n = 2600 g mol^{-1}, PDI = 1.3; M_n (theor.) = 2500 g mol^{-1}, λ_{max} = 432 nm).

In view of this remarkable metathesis activity and functional-group tolerance of a high oxidation state Mo alkylidene, we were interested in the nature of the active, that is, propagating species. At first glance the high reactivity in RCM, ROMP, and cyclopolymerization is very surprising, since all other Mo^{VI} bis(triflate) complexes of the general formula [Mo(NR′)(CHCMe$_2$R)(OTf)$_2$(DME)] (R = CH$_3$, C$_6$H$_5$) do not display any metathetical activity and have solely served as progenitors for the metathetically active alkoxide, phenoxide, and carboxylate complexes.[12] However, Schrock's Mo^{VI} bis(triflate)s are 18 electron complexes in which decoordination of DME does not occur. Both **1** and **2**, however, are 16 electron complexes with one triflate located nearly *trans* to the NHC and the imido ligand. Unlike the bipyridyl and phenantroyl adducts of Schrock's catalyst reported by Fürstner,[13] no dissociation of the NHC is required to activate the catalyst. Thus, NMR spectroscopy clearly shows that the NHC ligand remains bound to the metal center and no free NHC or imidazol(in)ium salt is observed. However, what does occur in the course of polymerization is the dissociation of one triflate ligand, presumably the one that experiences the strongest *trans*-effect (Scheme 1) once monomer has been added. The approach of the monomer must be expected to occur *trans* to the Mo alkylidene unit, thereby forming an octahedral 18-electron complex. In case this 18-electron complex is characterized by a more linear orientation of at least one triflate with respect to the NHC–Mo or arylimido–Mo bond, the *trans*-effect triggers the release of the corresponding triflate and a cationic, 16-electron complex forms (Scheme 1). This complex can either adopt a (distorted) SP or a trigonal bipyramidal (TBP) geometry. In view of the reactivity of Mo monoalkoxypyrrolide complexes[14] we postulate that either directly, or out of the SP geometry, a TBP complex forms by rearrangement. [2+2] Cycloaddition of the monomer to the alkylidene then starts ROMP. Formation of a polymer with a high *trans*-content should then start from the *anti*-isomer, which is in line with the chemistry of Schrock catalysts (Scheme 1). Clearly, the propensity to form a cationic complex strongly depends on both the nucleophilic character of the NHC and the ability to arrange at least one triflate almost perfectly *trans* to either the NHC or the arylimido ligand.

Figure 4 shows the ^{19}F NMR spectra of the polymerization of 4,4-bis(hydroxymethyl)-1,6-heptadiyne by the action of **1**. As can be seen, the parent two signals for the two individual triflate ligands at δ = −74.65 and −76.7 ppm (integral ratio 1:1) vanish within less than 5 min and new signals are observed at δ = −76.45 and −79.1 ppm. While the signal at δ = −76.45 ppm can be assigned to a triflate bound to Mo, the signal at δ = −79.1 ppm corresponds to free triflate. Since the polymer with the initiator attached to it precipitates in the course of the reaction, the signal of the triflate bound to Mo appears weaker than the one for the fully soluble free triflate anion. An analogous release of one triflate is detected in the ^{19}F NMR spectra recorded during the polymerization of 5,6-bis[(pentyloxy)methyl]bicyclo[2.2.1]hept-2-ene, 7-oxabicyclo[2.2.1]hept-5-ene-2,3-diylbis(methylene) diacetate and tetrakis(ethoxycarbonyl)-1,7-octadiyne by the action of **1** (Figures S14 and 22). Again, the signals for the parent catalyst vanish, while the one of free triflate and those for different Mo triflates bound to the polymer (different initiation products) develop over time. These data clearly show that in the presence of monomer, but notably not in its

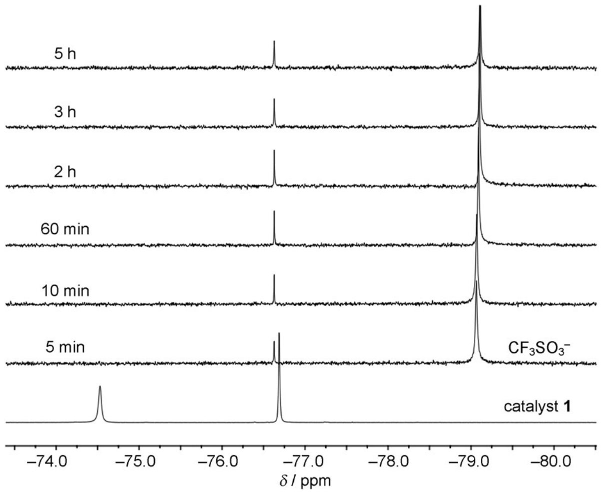


Figure 4. ^{19}F NMR spectra recorded at different time intervals for the polymerization of 4,4-bis(hydroxymethyl)-1,6-heptadiyne by catalyst **1**.

absence, **1** converts quickly into a cationic 16-electron species catalyst $[Mo(NAr')(IMesH_2)(monomer)_x(CH\text{-}t\text{Bu})(OTf)]^+$-$[OTf]^-$), which then initiates the corresponding metathesis reaction (Scheme 1).

In contrast, catalyst **2** is much more reluctant to release a triflate (Figure S24), a finding that corroborates with its lower metathesis activity and with the proposition that a cationic, 14-electron species is the active catalyst. Nonetheless, in view of the more pronounced nucleophilicity of I-*t*Bu, this is somewhat surprising, since the more nucleophilic NHC in **2** must stabilize the cationic charge better than the less nucleophilic one in **1**. On the other hand, the bulky character of I-*t*Bu might well impede the realization of a linear alignment of the NHC–Mo–OTf or arylimido–Mo–OTf bond that is a prerequisite for an effective release of the triflate. However, to comprehensively comment on that issue, the current data set, which is based on two complexes, is too small. Thus, the influence of the ring size and substituents at the NHC on the formation of the *syn*- and *anti*-isomers, their rates of interconversion and, finally, on the propensity of the corresponding catalyst to form cationic metal alkylidene complexes, needs to be investigated.

It is only possible to speculate about the reasons for the higher *trans*-content of polymers prepared by the action of **1**. It might be because this catalyst, in contrast to **2**, contains a small fraction of the *anti*-alkylidene. If these systems behave like the existing Schrock catalysts (Scheme 1), then an involvement of the *anti*-isomer in conjunction with a fast *syn*–*anti* interconversion should give rise to high *trans*-contents.[15] As outlined by Schrock et al.,[15a] a fast *syn*–*anti* interconversion requires the presence of electron-donating anionic ligands, for example, alkoxides. And in fact NHCs are strongly electron donating and thus fulfill this requirement. However, at this point, this explanation is only a reasonable hypothesis and the rates of interconversion need to be measured.

In summary, we have presented the first 16-electron NHC molybdenum imidoalkylidene Schrock-type catalysts that are active in various metathesis reactions including RCM, ROMP, and the cyclopolymerization of both 1,6-hepta- and 1,7-octadiynes. Unprecedented functional-group tolerance was observed. It is clear that substitution of one of the two chemically different triflate ligands by, for example, alkoxides, (chiral bi-) phenoxides, amides, offers access to a new family of cationic Mo alkylidenes that are chiral at the metal center and that hold great promise for various metathesis reactions. Our results on these issues will be reported in due course.

Experimental Section

1: $[Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CH\text{-}t\text{Bu})(OTf)_2(DME)]$ (0.300 g, 0.445 mmol) was dissolved in benzene (8 mL) and stirred for 15 min. Then a solution of 1,3-bis(2,4,6-trimethylphenyl)-2-imidazolinylidene (0.136 g, 0.445 mmol) in benzene (5 mL) was added. Immediately, a color change from yellow to deep red was observed and a precipitate formed. The mixture was stirred for a further 3 h, the benzene was decanted and the precipitate was washed with benzene to obtain a yellow colored solid (0.32 g, 81 %). The compound was dissolved in a minimum amount of CH_2Cl_2 and the solution was stored at −30 °C for 24 h to afford a yellow crystalline material in 73 % yield. ^{1}H NMR (CD_2Cl_2): (*syn*-isomer, 99.9 %) $\delta = 12.76$ (s, 1, C*H*CMe$_3$, $J_{CH} = 118$ Hz), 7.06–6.61 (7 H, Ar*H*), 3.98 (4 H, C*H*$_2$NC), 2.69–1.71 (24 H, Me), 0.93 ppm (s, 9 H, CH$_2$C*Me*$_3$); ^{19}F NMR (CD_2Cl_2): $\delta = -74.65$ (SO_3CF_3), −76.7 ppm (SO_3CF_3). ^{13}C NMR (CD_2Cl_2): $\delta = 320.9$ (*C*H-*t*Bu), 208.7 (*C*N$_{carbene}$), 154.6 (C$_{ipso}$), 140.4 (C$_{ortho}$), 137.1 (C$_{aryl}$), 136.8 (C$_{aryl}$), 135.7 (C$_{aryl}$), 131.1 (*C*H$_{aryl}$), 130.5 (*C*H$_{aryl}$), 130.1 (*C*H$_{aryl}$), 128.2(*C*$_{aryl}$), 120.2 (q, CF$_3$, $J = 319$ Hz), 119.8 (q, CF$_3$, $J = 320$ Hz), 53.1 (*C*Me$_3$), 50.7 (*C*H$_{2\text{-imidazolylene}}$), 30.5 (C*Me*$_3$), 21.3 (*C*H$_3$), 19.0 (*C*H$_3$), 18.9 ppm (*C*H$_3$); elemental analysis calcd (%) for $C_{36}H_{45}F_6MoN_3O_6S_2{\cdot}CH_2Cl_2$: C 45.54, H 4.96, N 4.31; found: C 45.52, H 4.75, N 4.37.

2: $[Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CH\text{-}t\text{Bu})(OTf)_2(DME)]$ (0.100 g, 0.148 mmol) was dissolved in benzene (3 mL). Then a benzene solution (1 mL) of 1,3-di-*tert*-butylimidazol-2-ylidene (0.027 g, 0.15 mmol) was added under stirring. Immediately, a color change from yellow to deep red was observed and a precipitate formed. The mixture was stirred for a further 3 h; then, the benzene was decanted and the precipitate was washed with benzene to obtain a yellow colored solid (0.060 g, 65 %). The yellow solid was dissolved in a minimum amount of CH_2Cl_2 and stored at −30 °C for 24 h to afford a yellow crystalline material in 60 % yield. ^{1}H NMR (CD_2Cl_2): $\delta = 14.60$ (s, 1 H, C*H*CMe$_3$, $J_{CH} = 121$ Hz, *syn*-isomer), 7.12–6.95 (3 H, Ar*H*), 2.60 (2 H, C*H*NC), 1.80–1.67 (24 H, Me), 1.32 (s, 9 H, CH$_2$C*Me*$_3$); ^{19}F NMR (CD_2Cl_2): $\delta = -77.68$, −77.69, −77.70, −77.71 (CF_3SO_3), −78.06, −78.07, −78.08, −78.09 ppm (CF_3SO_3); ^{13}C NMR (CD_2Cl_2): $\delta = 329.6$ (*C*H-*t*Bu), 175.4 (*C*N$_{carbene}$), 154.3 (C$_{ipso}$), 142.2 (C$_{aryl}$), 136.9 (*C*$_{aryl}$), 129.7 (*C*H$_{aryl}$), 129.6 (*C*H$_{aryl}$), 128.9 (*C*H$_{aryl}$), 121.7 (*C*$_{C=C}$), 120.6 (*C*$_{C=C}$), 119.8 (q, *C*F$_3$, $J = 318$ Hz), 119.7 (q, *C*F$_3$, $J = 319$ Hz), 61.7 (N*C*Me$_3$), 61.3 (*C*Me$_3$), 32.8 (C*Me*$_3$), 30.5 (C*Me*$_3$), 30.1 (C*Me*$_3$), 21.1 (*C*H$_3$), 18.4 ppm (*C*H$_3$). Elemental analysis calcd (%) for $C_{26}H_{39}F_6MoN_3O_6S_2$: C 40.84, H 5.27, N 5.50; found: C 40.88, H 5.20, N 5.56.

Received: April 24, 2014

Keywords: alkylidenes · cyclopolymerization · molybdenum · N-heterocyclic carbenes · ring-opening metathesis polymerization

---

[1] a) A. S. Gamble, J. M. Boncella, *Organometallics* **1993**, *12*, 2814–2819; b) L. L. Blosch, A. S. Gamble, K. Abboud, J. M. Boncella, *Organometallics* **1992**, *11*, 2342–2344; c) G. A. Miller, N. J. Cooper, *J. Am. Chem. Soc.* **1985**, *107*, 709–711.

[2] Z. J. Tonzetich, A. J. Jiang, R. R. Schrock, P. Müller, *Organometallics* **2006**, *25*, 4725–4727.

[3] A. J. Jiang, R. R. Schrock, P. Müller, *Organometallics* **2008**, *27*, 4428–4438.

[4] a) B. Autenrieth, F. Willig, D. Pursley, S. Naumann, M. R. Buchmeiser, *ChemCatChem* **2013**, *5*, 3033–3040; b) B. Autenrieth, W. Frey, M. R. Buchmeiser, *Chem. Eur. J.* **2012**, *18*, 14069–14078; c) B. Autenrieth, E. B. Anderson, D. Wang, M. R. Buchmeiser, *Macromol. Chem. Phys.* **2013**, *214*, 33–40.

[5] W. Zhang, K. Nomura, *Organometallics* **2008**, *27*, 6400–6402.

[6] R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare, M. O'Regan, *J. Am. Chem. Soc.* **1990**, *112*, 3875–3886.

[7] a) Z. J. Tonzetich, R. R. Schrock, P. Müller, *Organometallics* **2006**, *25*, 4301–4306; b) L. J. Guggenberger, R. R. Schrock, *J. Am. Chem. Soc.* **1975**, *97*, 2935; c) S. M. Rocklage, R. R. Schrock, M. R. Churchill, H. J. Wasserman, *Organometallics* **1982**, *1*, 1332–1338.

[8] S. Naumann, F.-G. Schmidt, R. Schowner, W. Frey, M. R. Buchmeiser, *Polym. Chem.* **2013**, *4*, 2731–2740.

[9] E. M. Higgins, J. A. Sherwood, A. G. Lindsay, J. Armstrong, R. S. Massey, R. W. Alder, A. C. O'Donoghue, *Chem. Commun.* **2011**, 1559–1561.

[10] M. R. Buchmeiser, *Chem. Rev.* **2000**, *100*, 1565–1604.

[11] J. Unold, D. Wang, W. Frey, M. R. Buchmeiser, *Polym. Chem.* **2013**, *4*, 4219–4233.

[12] J. H. Oskam, H. H. Fox, K. B. Yap, D. H. McConville, R. O'Dell, B. J. Lichtenstein, R. R. Schrock, *J. Organomet. Chem.* **1993**, *459*, 185–197.

[13] J. Heppekausen, A. Fürstner, *Angew. Chem.* **2011**, *123*, 7975–7978; *Angew. Chem. Int. Ed.* **2011**, *50*, 7829–7832.

[14] a) A. J. Jiang, J. H. Simpson, P. Müller, R. Schrock, *J. Am. Chem. Soc.* **2009**, *131*, 7770–7780; b) H. Jeong, D. J. Kozera, R. R. Schrock, S. J. Smith, J. Zhang, N. Ren, M. A. Hillmyer, *Organometallics* **2013**, *32*, 4843–4850; c) S. C. Marinescu, R. Singh, A. S. Hock, K. M. Wampler, R. R. Schrock, P. Müller, *Organometallics* **2008**, *27*, 6570–6578.

[15] a) J. H. Oskam, R. R. Schrock, *J. Am. Chem. Soc.* **1992**, *114*, 7588–7590; b) R. R. Schrock, J.-K. Lee, R. O'Dell, J. H. Oskam, *Macromolecules* **1995**, *28*, 5933–5940; c) R. R. Schrock, W. E. Crowe, G. C. Bazan, M. DiMare, M. B. O'Regan, M. H. Schofield, *Organometallics* **1991**, *10*, 1832–1843.