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Synthesis, X-ray structure and reactivity of μ-(CF$_3$COO)$_2$-[Mo(N-2,6-i-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OOCCF$_3$)(Et$_2$O)]$_2$, the first Bis(trifluoroacetate) derivative of a Schrock catalyst

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Abstract

Reaction of Mo(N-2,6-i-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$C$_6$H$_5$)(OSO$_2$CF$_3$)(DME) (DME = 1,2-dimethoxyethane) with 2 equiv. of CF$_3$COOK yields μ-(CF$_3$COO)$_2$-[Mo(N-2,6-i-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)(OOCCF$_3$)(Et$_2$O)]$_2$ (**1**). Compound **1** crystallizes in the orthorhombic space group Pna2$_1$ with $a = 17.2485(3)$, $b = 17.0336(3)$, $c = 25.4031(5)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 7463.5(2)$ Å^3, $Z = 4$. In contrast to alkoxide based Schrock type initiators, **1** is virtually inactive in numerous metathesis reactions including ring-closing metathesis (RCM) and homo metathesis reactions, the cyclopolymerization of 1,6-heptadiynes, and even ring-opening metathesis polymerization (ROMP) of norborn-2-ene. However, addition of quinuclidine results in the in situ formation of **1a** (Mo(N-2,6-i-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$C$_6$H$_5$)(OOCCF$_3$)$_2$(quinuclidine) which displays moderate activity in ROMP, cyclopolymerization of 1,6-heptadiynes and RCM. Theoretical investigations carried out on the B3LYP/LACVP* level provide substantial explanation for these findings.
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Keywords: Molybdenum; Schrock catalyst; Trifluroroacetate; Ring-opening metathesis polymerization; Cyclopolymerization; DFT quantum chemical calculations

1. Introduction

Metathesis has gone a long way [1,2] and quite recently the Chemistry Nobel Price 2005 was awarded to the protagonists of this research area for their major contributions [3,4]. Molybdenum based Schrock catalysts represent well-studied systems [5,6]. In general, the activity of these catalysts and catalyst precursors, respectively, increases when the Mo-core is substituted with electron withdrawing ligands [7]. This has been realized by the use hexafluoro-2-propoxides, 1,1,1,3,3,3-hexafluoro-t-butoxides and other ligands. In addition, Schrock and coworkers demonstrated that triphenylcarboxylate-containing systems may be used in the cyclopolymerization of 1,6-heptadiynes to produce polyenes exclusively consisting of poly(cyclohex-1-ene-3-methylidene)s. Our investigations on Ru-based Grubbs–Hoveyda type systems revealed that initiators of the general formula RuX$_2$(NHC)(=CHR) (X=CF$_3$COO, CF$_3$CF$_2$COO, CF$_3$CF$_2$CF$_2$COO; NHC = 1,3-dimesityl-3,4-dihydroimidazolin-2-ylidene, 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene, R = 2-(2-PrO)-C$_6$H$_4$, 2,4,5-(CH$_3$O)$_3$C$_6$H$_2$, 2-(CH$_3$O)-5-NO$_2$-C$_6$H$_3$) are excellent initiators for the cyclopolymerization of various 1,6-heptadiynes as well as highly reactive metathesis catalysts [8–16]. In view of these results we anticipated that the bis(trifluoroacetate) derivative of Schrock's catalyst

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would represent an interesting, highly active alternative to existing Schrock catalysts. In the following, our results on this topic are reported.

2. Results and discussion

2.1. Synthesis of 1 and structural characterization

Compound **1** was prepared via reaction of Mo(N-2,6-i-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$C$_6$H$_5$)(OSO$_2$CF$_3$)(DME) (DME = 1,2-dimethoxyethane) with 2 molequiv. of CF$_3$COOK in THF in 51% isolated yield. This compound is unstable and slowly decomposes even when stored inside a glove box at −36 °C. Compound **1** (Fig. 1) crystallizes in the orthorhombic space group $Pna2_1$ with $a = 17.2485(3)$, $b = 17.0336(3)$, $c = 25.4031(5)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 7463.5(2)$ Å^3, $Z = 4$. Relevant structural data are summarized in the experimental part. Only the (bis) *syn*-form of the catalyst is observed in the solid state.

Due to the electron withdrawing character of the trifluoroacetate groups, the molybdenum center requires additional ligands for stabilization, e.g. diethyl ether. This and the bis(μ-carboxylato)-bridged dimeric structure results in a distorted octahedral coordination sphere for molybdenum. As can be deduced from Fig. 1, bond angles differ significantly from 90° and 180°, respectively. Instead, angles around 95–100° and 156–174° were found. There is no significant difference in terms of bond lengths and angles between the two bis(μ-carboxylato)-bridged Mo-alkylidenes. Moreover, the distances Mo(1)–N(1) and Mo(2)–N(2) (1.730(4) and 1.721(5) Å, respectively) in the six-coordinate complex **1** are comparable to those found in other 4-, 5- or 6-coordinate Mo-alkylidenes (1.717(2)–1.767(6) Å) [17–19]. The same applies to the distances Mo(1)–C(1) and Mo(2)–C(17) (1.902(6) and 1.934(6) Å, respectively), which are again comparable to those reported for other Mo-alkylidenes including Mo-bis(trifluoromethansulfonates) [17–19]. It is worth mentioning that ^{13}C NMR data of **1** obtained in C$_6$D$_6$ suggest a highly fluxional structure with all trifluoroacetate groups being equivalent. Thus, only one sharp set of signals for the trifluoromethyl group at $\delta = 115.8$ ppm and one broad signal for the carbonyl group at $\delta = 165.4$ ppm is observed. Similar, only a broad signal, unresolved for the alkylidene carbon at $\delta = 325.4$ ppm was observed. The ^{1}H NMR shows only one signal at $\delta = 15.0$ ppm.
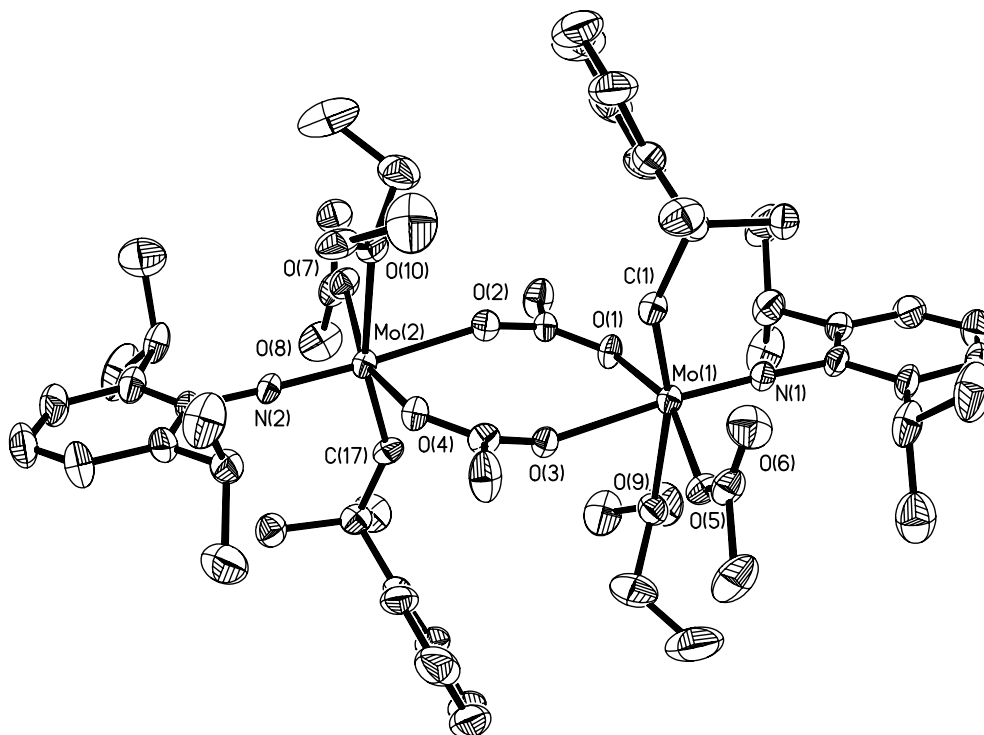

Fig. 1. Structure of **1** with 30% probability thermal ellipsoids. Hydrogen and fluorine atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Mo(1)–N(1) 1.730(4), Mo(1)–C(1) 1.902(6), Mo(1)–O(5) 2.074(4), Mo(1)–O(1) 2.124(3), Mo(1)–O(3) 2.250(5), Mo(1)–O(9) 2.324(5), Mo(2)–N(2) 1.721(5), Mo(2)–C(17) 1.934(6), Mo(2)–O(7) 2.052(4), Mo(2)–O(4) 2.124(4), Mo(2)–O(2) 2.226(5), Mo(2)–O(10) 2.318(4), N(1)–Mo(1)–C(1) 98.9(3), N(1)–Mo(1)–O(5) 98.43(19), C(1)–Mo(1)–O(5) 100.1(2), N(1)–Mo(1)–O(1) 95.79(18), C(1)–Mo(1)–O(1) 95.0(2), O(5)–Mo(1)–O(1) 157.38(17), N(1)–Mo(1)–O(3) 173.34(18), C(1)–Mo(1)–O(3) 87.6(2), O(5)–Mo(1)–O(3) 81.61(17), O(1)–Mo(1)–O(3) 82.25(15), N(1)–Mo(1)–O(9) 96.53(18), C(1)–Mo(1)–O(9) 164.2(2), O(5)–Mo(1)–O(9) 80.99(16), O(1)–Mo(1)–O(9) 79.98(16), O(3)–Mo(1)–O(9) 76.87(15), N(2)–Mo(2)–C(17) 97.5(3), N(2)–Mo(2)–O(7) 99.37(19), C(17)–Mo(2)–O(7) 101.0(2), N(2)–Mo(2)–O(4) 94.98(18), C(17)–Mo(2)–O(4) 95.3(2), O(7)–Mo(2)–O(4) 156.67(16), N(2)–Mo(2)–O(2) 173.77(18), C(17)–Mo(2)–O(2) 88.0(2), O(7)–Mo(2)–O(2) 82.31(18), O(4)–Mo(2)–O(2) 81.59(15), N(2)–Mo(2)–O(10) 97.79(18), C(17)–Mo(2)–O(10) 164.4(2), O(7)–Mo(2)–O(10) 79.32(16), O(4)–Mo(2)–O(10) 80.58(15), O(2)–Mo(2)–O(10) 76.56(15).

Based on the X-ray structure of **1** we ascribe this signal to the *syn*-isomer.

2.2. Reactivity of **1**

Compound **1** was used for various metathesis reactions including cross-metathesis of styrene, ring-closing metathesis of diethyl diallylmalonate (DEDAM), the cyclopolymerization of diethyl dipropargylmalonate (DEDPM), and the ring-opening metathesis polymerization (ROMP) of norborn-2-ene (NBE). In all cases, NO REACTION was observed. This is believed to be a consequence of the dimeric structure of **1** with an octahedral coordination of the Mo-core. In order to break down this dimeric structure, quinuclidine was added. In the ^{1}H NMR, a shift of the alkylidene signal from 15.00 ppm to 14.52 ppm was observed. In addition, the signal for the $N(CH_2)_3$-moiety of coordinated quinuclidine appeared at $\delta = 3.76$ ppm (all spectra recorded in C_6D_6). NMR data for in situ formed **1a** are in accordance with $Mo(N-2,6-i-Pr_2-C_6H_3)(CHC-Me_2C_6H_5)(OOCCF_3)$(quinuclidine), however, it still remains speculative whether the compound is purely monomeric, too (Scheme 1). Again, we tentatively ascribe a *syn* configuration to this compound.

An argument for a monomeric structure of **1a** is the fact that upon addition of norborn-2-ene, poly-NBE is formed. The polymerization appears to be rather uncontrolled, resulting in high M_n, high PDI poly-NBE. As observed for other Schrock catalysts containing fluorinated alkoxides, a high *cis*-content of 65% was observed. This suggests that, similar to fluorinated alkoxides, *syn-anti* conversion is slow [20]. Addition of diethyl diallylmalonate (DEDAM, 10 and 100 molequiv, respectively) to in situ formed **1a** gave 4% conversion to 1,1-bis(ethoxycarbonyl)cyclopent-3-ene.

Upon addition of diethyl dipropargylmalonate (DEDPM) to intermediary formed **1a**, a color change to purple was observed and a polymer formed in low yields (11%). This low reactivity is in accordance with findings for complexes of the general formula $Mo(N-2,6-R_2-C_6H_3)(CHCMe_2R')$-$(OOCCPh_3)_2$ (R = Me, 2-Pr, R' = Me, Ph), which were reported to display similar low reactivity [21]. The ^{13}C NMR spectrum of poly-DEDPM produced by the action

of **1a** shows two (broad) signals a $\delta = 171.8$ and 170.3 ppm and numerous signals around 140–120 ppm, indicative for the formation of both 5- and 6-membered rings, i.e. poly(cyclopent-1-ene-2-vinylene)s and poly-(cyclohex-1-ene-3-methylidene)s. These findings are important for three reasons. First, they again proof the concept of "large carboxylates", which has been proposed by Schrock et al. to be necessary for the formation of polyenes from DEDPM solely based on poly(cyclohex-1-ene-3-methylidene)s [21,22]. Second, they show that the use of carboxylates does not *per se* lead to the formation of pure poly(cyclohex-1-ene-3-methylidene)s. Third, these experiments demonstrate that (small) electron-withdrawing carboxylates basically behave similar to (small) electron-withdrawing alkoxides [23–26]. Thus, both types of ligands lead to a (approx. 1:1) mixture of poly(cyclopent-1-ene-2-vinylene)s and poly(cyclohex-1-ene-3-methylidene)s.

2.3. Theoretical considerations

DFT quantum chemical calculations were performed at the B3LYP/LACVP* level. In order to check for the applicability of this method for the calculation of relevant parameters of **1a**, we first performed calculations on $Mo(N-2-t-Bu-C_6H_4)(CH-t-Bu)(OOCCPh_3)_2$, since crystallographic data have been reported for this compound [21]. Excellent agreement between the calculated and measured values was observed (see Supplementary Information). The geometrical and quantum chemical parameters (total energy, Mulliken atomic charges and electron distribution) of **1a** and its reactivity versus styrene are summarized in Scheme 2. Selected data are shown in Table 1. As can be deduced there from, the structural parameters of **1a** and $Mo(N-2-t-Bu-C_6H_4)(CH-t-Bu)(OOCCPh_3)_2$ are quite similar.

As can be deduced from Scheme 2, dissociation of quinuclidine from **1a** requires a dissociation energy E_{diss} of about 26 kcal mol^{-1}. Calculations reveal that the base-free, 12-electron complex **2** either rebinds quinuclidine or immediately undergoes intramolecular stabilization in that it is stabilized via coordination of all 4 oxygens of the two carboxylates to the Mo-center to form the distorted octahedrally coordinated complex **3**. Similar has already been
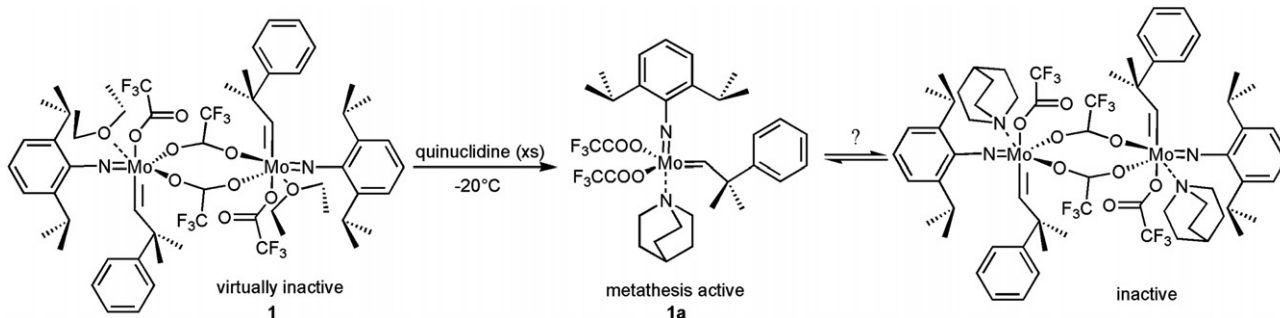
Scheme 1. Synthesis and proposed structure of **1a**.
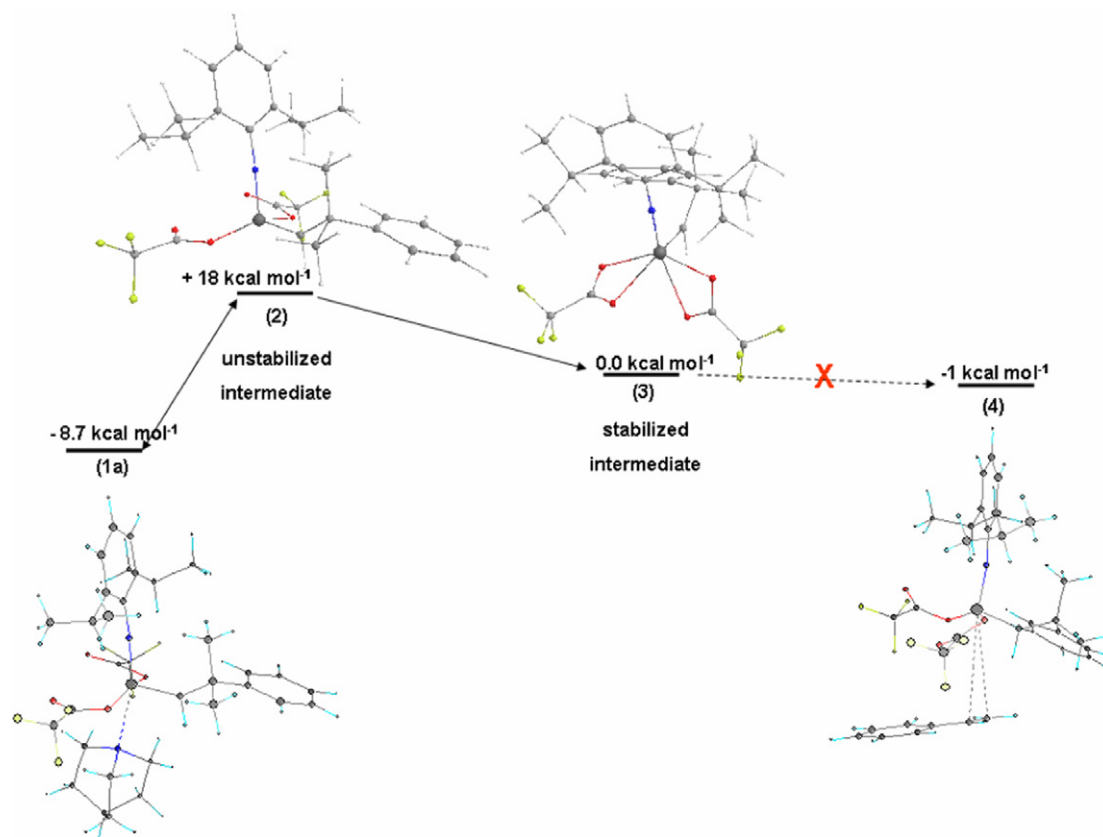
Scheme 2. Reaction pathway and energy diagram for the dissociation of quinuclidine from **1a** to form **2**, intramolecular stabilization of **3** via the carboxylates and reduced reactivity vs. styrene.

Table 1
Comparison of structural and geometrical parameters (Å) of complex **3** and Mo(N-2-*t*-Bu-C$_6$H$_4$)(CH-*t*-Bu)(OOCCPh$_3$)$_2$ (X-ray data)

	3	Mo(N-2-*t*-Bu-C$_6$H$_4$)(CH-*t*-Bu)(OOCCPh$_3$)$_2$ (X-ray data)
Mo–N	1.733	1.710
Mo–C	1.901	1.884
Mo–O1	2.133	2.090
Mo–O2	2.155	2.136
Mo–O3	2.468	2.336
Mo–O4	2.394	2.261

observed in the X-ray structure of Mo(N-2-*t*-Bu-C$_6$H$_4$)(CH-*t*-Bu)(OOCCPh$_3$)$_2$ and underlines the high stability of these complexes [21]. In addition, these findings appear to be a general explanation of the low reactivity of Mo-carboxylates [21] and the high reactivity of Mo-alkoxides [4], since the latter are NOT capable of this kind of intramolecular stabilization. Calculations clearly explain the low reactivity of **1a** vs styrene. Dissociation of quinuclidine from **1a** is required to form **2**, however, **3** is formed immediately therefrom. Addition of styrene to **3** is energetically not favored. The more electron rich DEDAM is apparently capable of coordinating to intermediary **2** to some minor extent, which explains the low conversion (4%) of this compound. The electron rich and strained norborn-2-ene apparently forms stable alkene-complexes,

which then transform into metallacyclobutanes and give rise to the formation of poly-NBE. The same accounts for DEDPM, however, again to a minor extent.

3. Summary

The first example of a Schrock catalyst containing fluorinated carboxylates has been prepared and characterized. It is a dimeric complex with virtually no metathesis activity. Addition of a base (i.e. quinuclidine) results in a Schrock catalyst with low reactivity, comparable with other Mo-imido-alkylidene carboxylates. In polymerizations, the novel Schrock catalyst behaves like a Mo-imidoalkylidene bisalkoxide in that is produces ROMP-derived polymers with a high *cis*-content and DEDPM-based cyclopolymerization-derived polyenes consisting of a roughly 1:1 mixture of poly(cyclopent-1-ene-2-vinylene) and poly(cyclohex-1-ene-3-methylidene) units.

4. Experimental

All manipulations were performed under a nitrogen atmosphere in a glove box (MBraun LabMaster 130) or by standard Schlenk techniques. Purchased starting materials were used without any further purification. Tetrahydrofuran (THF) and dichloroethane were distilled from sodium benzophenone ketyl and calcium hydride under

nitrogen, respectively. Pentane, diethyl ether, toluene and methylene chloride were dried by an MBraun SPS solvent drying system. NMR data were obtained at 250.13 MHz for proton and 62.90 MHz for carbon in the indicated solvent at 25 °C on a Bruker Spectrospin 250 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in Hz. IR spectra were recorded on a Bruker Vector 22 using ATR technology. Molecular weights and polydispersity indices (PDIs) of the polymers were determined by GPC at 30 °C on Polymer laboratories columns (PLgel 10 μm MIXED-B, 7.5×300 mm) in THF at 25 °C using a Waters Autosampler, a Waters 484 UV spectrometer detector (254 nm), an Optilab Rex refractive index detector (Wyatt) and a MiniDawn light scattering detector (Wyatt). Synthesis of Mo(N-2,6-i-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$C$_6$H$_5$)(OSO$_2$CF$_3$)-(DME) (DME = 1,2-dimethoxyethane) is reported elsewhere [7]. Styrene and DEDAM were distilled from CaH$_2$, DEDPM was prepared as reported earlier [23]. All compounds were checked for purity by NMR.

4.1. Computational methods

Density Functional Theory (DFT) calculations were carried out using Becke's three-parameter functional (B3) [27,28] in combination with the Lee, Yang, and Parr (LYP) correlation functional [29] using a LACVP* basis set (Jaguar, version 6.5 program [30,31]). The LACVP* basis set uses the standard 6-31G* basis set for light elements and the LAC pseudo potential [32] for Mo atom. The molecular geometries and energies of all calculated structures were obtained at the same B3LYP/LACVP* level of theory. The stability of the different structures was calculated as a balance of the total energies of intermediary Mo(CHCH$_2$Ph)(N-2,6-i-Pr$_2$C$_6$H$_3$)(OOCCF$_3$)$_2$.

4.2. μ-(CF$_3$COO)$_2$-[Mo(N-2,6-i-Pr$_2$-C$_6$H$_3$)-(CHCMe$_2$Ph)(OOCCF$_3$)(Et$_2$O)]$_2$ (1)

Mo[N-2,6-i-Pr$_2$-C$_6$H$_3$]$_2$(CHCMe$_2$C$_6$H$_5$)(OTf)$_2$(DME) (500 mg, 0.63 mmol) was dissolved in 5 mL of THF, then the solution was cooled to −40 °C. Potassium trifluroacetate (191.8 mg 1.26 mmol), dissolved in 20 mL abs. THF and chilled to −40 °C was added and the mixture was stirred for 2 h. The volatiles were removed *in vacuo* and the solid was extracted with diethyl ether. The brownish solution was filtered through celite and dried *in vacuo*, yielding 224 mg (51%) of a yellow solid. Orange crystals suitable for X-ray were obtained by layering pentane over the diethyl ether solution of it at −40 °C. ^{1}H NMR (C$_6$D$_6$): δ 15.0 (s, 1H), 7.12–7.09 (m, 4H), 6.96 (t, $^3J = 7.18$ Hz, 1H), 6.83 (bs, 3H), 3.71 (m, 2H, CH), 3.28 (q, $^3J = 6.95$ Hz, 2H, CH$_2$O), 1.65 (s, 6H), 1.20 (d, $^1J = 6.75$ Hz, 12H), 1.12 (t, $^1J = 7.09$ Hz, 3H, CH$_3$CH$_2$O); ^{13}C NMR (C$_6$D$_6$): δ 325.4 (broad), 165.4 (CO), 152.9, 150.6, 148.5, 130.1, 126.7, 126.0, 123.8, 115.8 (J (C,F) = 287.3 Hz), 69.6, 65.9, 58.6, 30.3, 28.7, 25.4, 23.6, 15.5.

4.3. [Mo(N-2,6-i-Pr$_2$-C$_6$H$_3$)(CHCMe$_2$Ph)-(OOCCF$_3$)$_2$(quinuclidine)] (1a)

This compound was prepared *in situ* by adding 1.05 molequiv. of quinuclidine to a solution of **1** in C$_6$D$_6$. ^{1}H NMR (C$_6$D$_6$): δ 14.52 (s, 1H), 7.5–6.65 (m, 8H), 4.00 (m, 2H, CH), 3.76 (t, $^3J = 7.5$ Hz, 2H, CH$_2$O), 1.70 (bs, 7H), 1.36 (m, 18H).

4.4. Polymerization of NBE

Compound **1** (20 mg, 14 μmol) and quinuclidine (3.1 mg, 14 μmol, 1 molequiv. with respect to **1**) were dissolved in 0.5 mL of CH$_2$Cl$_2$. The solution was chilled to −38 °C and a solution of NBE (14 mg, 0.14 mmol) in 1 mL of CH$_2$Cl$_2$ was added. The mixture was stirred for 2 h at room temperature, then ferrocene carbaldehyde (2 molequiv. with respect to **1**) were added and stirring was continued for another 30 min. The mixture was poured into methanol, the polymer was filtered off. Yield: 85%. **Poly-NBE**: $M_n = 339,000$, PDI = 2.11, $dn/dc = 0.162$; ^{1}H NMR (CDCl$_3$) δ: 5.34 (b, HC=CH$_{trans}$), 5.21 (d, HC=CH$_{cis}$, $J = 2.5$ Hz), 2.79 (b), 2.44 (b), 1.81 (b), 1.36 (b), 1.01 (b). A *cis*-content of 65% was derived there from. ^{13}C NMR (CDCl$_3$) δ 133.8 (C=C), 133.02 (C=C), 132.9 (C=C), 43.4, 43.1, 42.7, 41.4, 38.6, 38.4, 33.11, 32.9, 32.3, 32.2.

4.5. Polymerization of DEDPM

Compound **1** (20 mg, 14 μmol) and quinuclidine (3.1 mg, 14 μmol, 1 molequiv. with respect to **1**) were dissolved in 0.5 mL of CH$_2$Cl$_2$. The solution was chilled to −38 °C and a solution of DEDPM (290 mg, 1.4 mmol) in 1 mL of CH$_2$Cl$_2$ was added. The mixture was stirred for 2 h at room temperature, then ferrocene carbaldehyde (10 molequiv. with respect to **1**) were added and stirring was continued for another 30 min. The mixture was poured into methanol, the polymer was filtered off. Yield: 11%. **Poly-DEDPM**: $M_n = 7100$, PDI = 2.94 (bimodal), $dn/dc = 0.463$; ^{13}C NMR (CDCl$_3$) δ 171.8 ($\underline{C}$O$_{5-membered\ ring}$), 170.7 ($\underline{C}$O$_{6-membered\ ring}$), 140–120 (unresolved, $\underline{C}$=C), 61.7 ($\underline{C}$H$_2$-O), 56.9 (C$_{ipso,5-membered\ ring}$), 54.2 (C$_{ipso,6-membered\ ring}$), 46.5, 41.5, 40.1 (CH$_{2,5-membered\ ring}$), 23.05 ($\underline{C}$H$_2$), 19.9, 14.0 ($\underline{C}$H$_3$). UV(CHCl$_3$): 530 nm.

4.6. Typical RCM and CM experiments

Compound **1** (20 mg, 14 μmol) was dissolved in 0.5 mL of C$_6$D$_6$. The solution was chilled to 4 °C and a solution of either styrene or diethyldipropargyl malonate (DEDPM) (285 μmol) dissolved in 1 mL of C$_6$D$_6$ was added. The corresponding mixture was stirred for 2 h at room temperature, then conversion was checked by GC–MS. No product formation was observed. Experiments were repeated in the presence of quinuclidine (3.1 mg, 14 μmol, 1 molequiv. with respect to **1**). 4% conversion was observed.

4.7. X-ray measurement and structure determination of *1*

Data collection was performed on a Nonius Kappa CCD equipped with graphite-monochromatized Mo K_{α}-radiation ($\lambda = 0.71073$ Å) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK [33]. Several scans in ϕ and ω direction were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces in a good approximation an empirical absorption correction. The structures were solved with direct methods SHELXS86 and refined against F^2 SHELX97 [34]. The function minimized was $\sum[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. Positions of hydrogen atoms were calculated except for those at C(1) and C(17), which were refined isotropically.

4.8. Crystal data for *1*

$C_{60}H_{78}F_{12}Mo_2N_2O_{10}$, $M_r = 1407.12$ g/mol; red plates, size: $0.25 \times 0.12 \times 0.08$ mm^3, unstable under air or at room temperature, orthorhombic, $Pna2_1$ (no.33), $a = 17.2485$ (3) Å, $\alpha = 90°$, $b = 17.0336(3)$ Å, $\beta = 90°$, $c = 25.4031(5)$ Å, $\gamma = 90°$, $V = 7463.5(2)$ Å^3, $T = 233(2)$ K, $Z = 4$, density(calculated) $= 1.252$ g/cm^3, absorption coefficient $= 0.414$ mm^{-1}, theta range for data collection: 1.86–25.00°. index ranges: $-20 <= h <= 20$, $-20 <= k <= 18$, $-27 <= l <= 30$, reflections collected: 37219, independent reflections: 12833 $[R(\text{int}) = 0.0452]$, reflections $[I > 2\sigma(I)]$: 10289, absorption correction: none, refinement method: full-matrix least-squares on F^2; goodness-of-fit on F^2: 1.056, final R indices $[I > 2\sigma(I)]$: $R_1 = 0.0508$, $wR^2 = 0.1369$, R indices (all data): $R_1 = 0.0688$, $wR^2 = 0.1466$.

Appendix A. Supplementary data

The crystallographic data for *1* have been deposited with the CCDC-No. 613070 on the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). In addition, structure and geometrical parameters of complex (*3*) and Mo(N-2-*t*-Bu-C$_6$H$_4$)(CH-*t*-Bu)(OOCCPh$_3$)$_2$ are available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.08.087.

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