

Synthesis, X-ray structure and reactivity of μ -(CF₃COO)₂-[Mo(N-2,6-*i*-Pr₂-C₆H₃)(CHCMe₂Ph)(OOCF₃)(Et₂O)]₂, the first Bis(trifluoroacetate) derivative of a Schrock catalyst

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Abstract

Reaction of Mo(N-2,6-*i*-Pr₂-C₆H₃)(CHCMe₂C₆H₅)(OSO₂CF₃)(DME) (DME = 1,2-dimethoxyethane) with 2 equiv. of CF₃COOK yields μ -(CF₃COO)₂-[Mo(N-2,6-*i*-Pr₂-C₆H₃)(CHCMe₂Ph)(OOCF₃)(Et₂O)]₂ (**1**). Compound **1** crystallizes in the orthorhombic space group Pna2₁ with $a = 17.2485(3)$, $b = 17.0336(3)$, $c = 25.4031(5)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 7463.5(2)$ Å³, $Z = 4$. 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*-Pr₂-C₆H₃)(CHCMe₂C₆H₅)(OOCF₃)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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1. Introduction

Metathesis has gone a long way [1,2] and quite recently the Chemistry Nobel Prize 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 RuX₂(NHC)(=CHR) (X=CF₃COO, CF₃CF₂COO, CF₃CF₂CF₂COO; NHC = 1,3-dimesityl-3,4-dihydroimidazolin-2-ylidene, 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene, R = 2-(2-PrO)-C₆H₄, 2,4,5-(CH₃O)₃C₆H₂, 2-(CH₃O)-5-NO₂-C₆H₃) 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*-Pr₂-C₆H₃)(CHCMe₂C₆H₅)(OSO₂CF₃)(DME) (DME = 1,2-dimethoxyethane) with 2 molequiv. of CF₃COOK 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 *Pna*2₁ with *a* = 17.2485(3), *b* = 17.0336(3), *c* = 25.4031(5) Å, $\alpha = \beta = \gamma = 90^\circ$, *V* = 7463.5(2) Å³, *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(trifluoromethanesulfonates) [17–19]. It is worth mentioning that ¹³C NMR data of **1** obtained in C₆D₆ 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 ¹H NMR shows only one signal at $\delta = 15.0$ ppm.

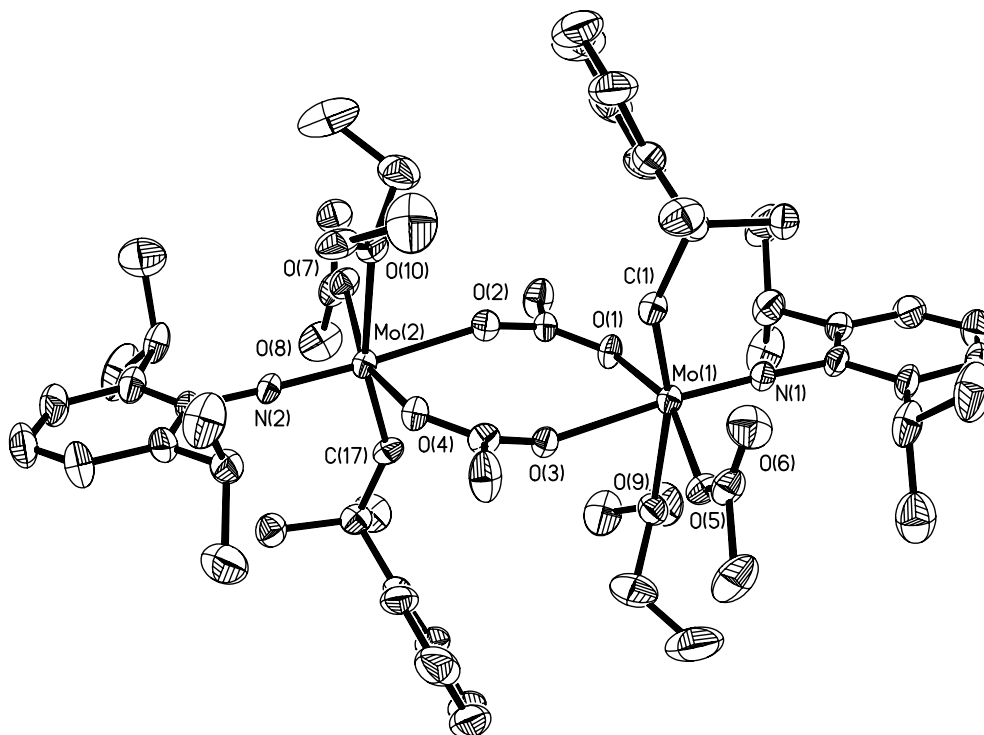


Fig. 1. Structure of **1** with 30% probability thermal ellipsoids. Hydrogen and fluorine atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Mo(1)–N(1) 1.730(4), Mo(1)–C(1) 1.902(6), Mo(1)–O(5) 2.074(4), Mo(1)–O(1) 2.124(3), Mo(1)–O(3) 2.250(5), Mo(1)–O(9) 2.324(5), Mo(2)–N(2) 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).

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