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Polymer-Supported Chiral Schrock Catalysts Immobilized *via* the Arylimido Ligand

Dongren Wang,[a] Roswitha Kröll,[a] Monika Mayr,[a] Klaus Wurst,[b] and Michael R. Buchmeiser[a, c,*]

[a] Leibniz Institut für Oberflächenmodifizierung e.V. (IOM), Permoserstr. 15, 04318 Leipzig, Germany
Fax: +49-341-235-2584; e-mail: dongren.wang@iom-leipzig.de
[b] Institut für Allgemeine, Anorganische und Theoretische Chemie, Universität Innsbruck, Innrain 52 a, 6020 Innsbruck, Austria
Fax: +43-512-507-2934
[c] Institut für Technische Chemie, Universität Leipzig, Linnéstr. 3, 04103 Leipzig, Germany
Fax: +49-341-235-2584; e-mail: buchmeiser@uni-leipzig.de

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Dedicated to Prof. Dr. Ing. Oskar Nuyken on the occasion of his retirement.

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Abstract: The immobilization of both chiral and non-chiral versions of the Schrock catalyst *via* the arylimido ligand was accomplished for the first time. For this purpose, four different 4-(6-halogenohexyl)-2,6-R_2-anilines, i.e., {4-[6-X-$(CH_2)_6$]-2,6-R_2-C_6H_2-NH_2} (**7**: R = Me, X = Br; **8**: R = Me, X = Cl, **9**: R = 2-Pr, X = Cl, **10**: R = 2-Pr, X = Br) were prepared and used for the synthesis of the corresponding Mo-bis(imido)dichloro complexes Mo{N-2,6-R_2-4-[6-X-$(CH_2)_6$]-C_6H_2}$_2$$Cl_2$·DME (**11**: R = Me, X = Br; **12**: R = Me, X = Cl; **13**: R = 2-Pr, X = Cl; **14**: R = 2-Pr, X = Br). Compounds **11**–**14** were transformed into the corresponding Mo-bis(imido)dialkyl complexes Mo{N-2,6-R_2-4-[6-X-$(CH_2)_6$]-C_6H_2}$_2$$(CH_2CMe_2Ph)_2$ (**15**: R = Me, X = Br; **16**: R = Me, X = Cl, **17**: R = 2-Pr, X = Cl; **18**: R = 2-Pr, X = Br). These were used for the synthesis of the Mo-imidoalkylidene triflates Mo{N-2,6-R_2-4-[6-X-$(CH_2)_6$]-C_6H_2}(CHCMe$_2$Ph)-$(OTf)_2$·DME (**19**: R = Me, X = Br; **20**: R = 2-Pr, X = Br, **21**: R = 2-Pr, X = Cl). Compounds **19**--**21** were used in the synthesis of the Schrock type catalysts Mo{N-2,6-Me_2-4-[6-Br-$(CH_2)_6$]-C_6H_2}(CHCMe$_2$Ph)[OC$(CH_3)(CF_3)_2$]$_2$ (**22**) and Mo{N-2,6-(2-Pr)$_2$-4-[6-Cl-$(CH_2)_6$]-C_6H_2}(CHCMe$_2$Ph)[OC-$(CH_3)(CF_3)_2$] (**23**), Mo{N-2,6-Me_2-4-[6-Br-$(CH_2)_6$]-C_6H_2}(CHCMe$_2$Ph)[(*R*)-BIPHEN] (**24**) and Mo{N-2,6-(2-Pr)$_2$-4-[6-Br-$(CH_2)_6$]-C_6H_2}(CHCMe$_2$Ph)[(*R*)-BIPHEN] (**25**). Compounds **22**, **24** and **25** were immobilized on Ag-perfluoroalkylsulfonate-modified PS- and PS-DVB materials to yield the corresponding immobilized catalysts Mo{N-2,6-Me_2-4-[PS-CH_2-O-CF_2-CF(CF_3)-SO_3-$(CH_2)_6$]-C_6H_2}(CHCMe$_2$Ph)-[OCMe$(CF_3)_2$]$_2$ (**26**), Mo{N-2,6-Me_2-4-[PS-DVB-CH_2-O-CF_2-CF(CF_3)-SO_3-$(CH_2)_6$]-C_6H_2}(CHCMe$_2$Ph)[(*R*)-BIPHEN] (**27**) Mo{N-2,6-(2-Pr)$_2$-4-[PS-DVB-CH_2-O-CF_2-CF(CF_3)-SO_3-$(CH_2)_6$]-C_6H_2}(CHCMe$_2$Ph)[(*R*)-BIPHEN] (**28**). These were used in a series of ring-closing metathesis (RCM), ring-opening cross metathesis, asymmetric RCM and desymmetrization reactions. The use of **27** and **28** resulted in values for enantiomeric excess (*ee*) virtually identical to those obtained with the corresponding homogeneous chiral catalysts.

Keywords: asymmetric catalysis; heterogeneous catalysis; immobilization; metathesis; molybdenum

Introduction

Together with palladium-catalyzed reactions such as the Heck, Suzuki and Sonohashira–Hagihara reactions,[1–3] metathesis reactions, particularly those that can be accomplished in an asymmetric way, belong nowadays to the most important C–C coupling reactions.[4–6] Due to the achievements made with catalysts necessary to accomplish these reactions,[7–9] an almost unprecedented progress has been made in this area of research; nevertheless, the demand for new catalytic systems is a continuous and growing one. In this context, particularly supported versions of metathesis catalysts are now in the center of interest. Ease

of catalyst removal, access to metal-free products, recyclability and access to combinatorial processes are major driving forces. In metathesis reactions, the latter is often restricted by the instability of intermediate transition metal methylidenes. While a comparably large number of supported ruthenium-based Grubbs- and Grubbs–Hoveyda-type metathesis catalysts are already available,[10–12] there exists still an only very limited number of supported Schrock-type catalysts.[6] In this context, surface-located transition metal carbenes have been reported to possess metathesis activity.[13,14] Alternatively, a silica-immobilized mimic of the Schrock catalyst, (≡SiO)Mo(=NH)(=CH-*t*-Bu)(CH_2-*t*-Bu), was recently reported.[15] Quite recently, Copéret, Basset, Emsley and Schrock reported in a joint paper on the immobilization of Mo[=N-2,6-(2-Pr)$_2$-C_6H_3](=CH-*t*-Bu)(CH_2-*t*-Bu)$_2$ on silica. The resulting supported Schrock-type catalyst (≡SiO)Mo[=N-2,6-(2-Pr)$_2$-C_6H_3](=CH-*t*-Bu)(CH_2-*t*-Bu) was subject to profound structural and catalytic characterization.[16] Immobilizations on other supports have been carried out, too,[17–20] however, the actual nature of the immobilized catalyst remained unknown. The first supported *chiral* version of a molybdenum-based Schrock catalyst was reported in 2002,[21] and consisted of a PS-DVB-bound version of Mo[N-2,6-(2-Pr)$_2$-C_6H_3](CHCMe$_2$Ph)[(*R*)-BIPHEN] (BIPHEN = 3,3′-di-*tert*-butyl-5,5′,6,6′-tetramethyl-2,2′-biphenolate). In course of ongoing projects we reported on a ring-opening metathesis polymerization (ROMP)-derived, supported version of the same catalyst[22] as well as on its immobilization on norborn-2-ene-based monolithic supports.[23] Additional chiral Schrock catalysts immobilized *via* biphenoxides and binaphthoxides were a short time later jointly reported by the Schrock and Hoveyda groups.[24] All supported catalysts prepared so far showed excellent results in terms of activity and enantioselectivity.

During the past years we were interested in the question whether immobilization of a Schrock catalyst might also be achieved *via* the *arylimido ligand*. Such an approach, if successful, would allow for a wider and, in fact, complementary variability in catalyst structure, the more, since both reactivity and selectivity of chiral Schrock-type catalysts are strongly governed by the nature of the alkoxides, (bi-)phenoxides and binaphtholates, respectively.[25] Thus, a supported version of a Schrock catalyst, where heterogenization is realized *via* the arylimido ligand, appeared highly favorable since it would allow for an ultimate variability in catalyst tuning. Here, we report on the successful realization of this task.

Results and Discussion

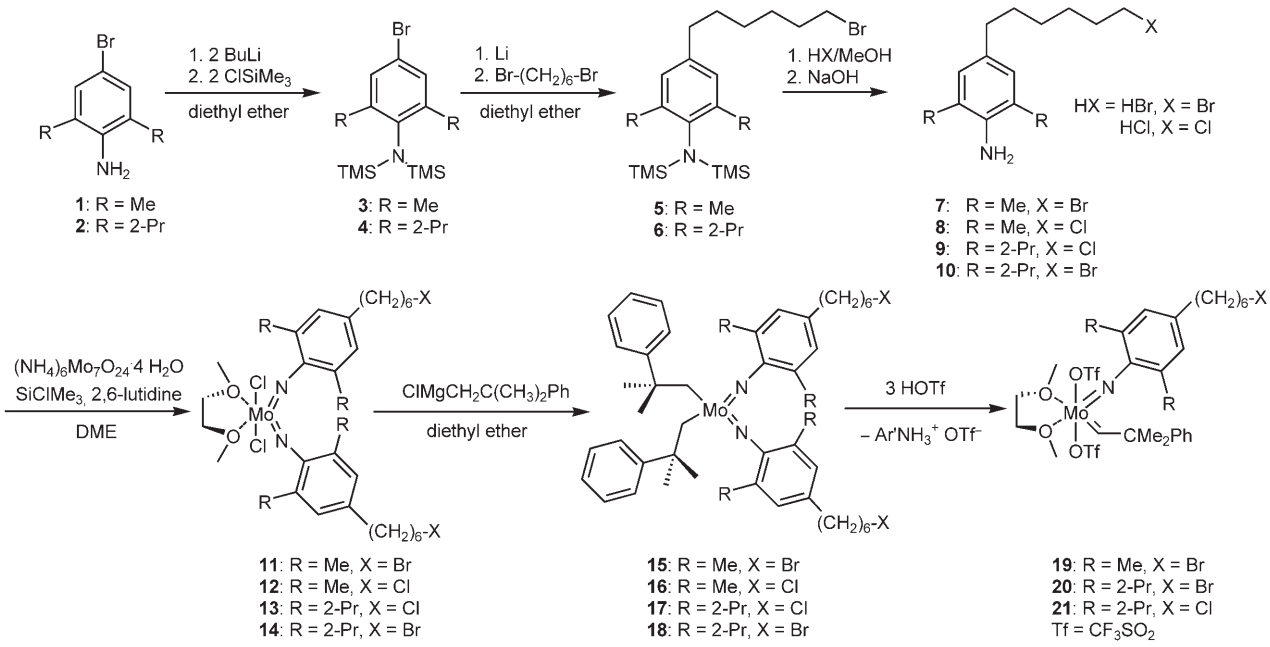
Synthesis of Ligands

The concept of immobilizing a Schrock catalyst *via* the arylimido ligand requires the synthesis of a suitable arylimido ligand. In principle, one might think of many different functional groups that can be attached to the arylimido ligand and that may be used for immobilization purposes later on. However, since both strongly nucleophilic and/or basic reagents, i.e., tertiary amines, Grignard reagents, alkoxides, phenoxides, and electrophilic reagents, i.e., triflic acid are used in the course of catalyst synthesis, only functional groups with low reactivity towards these reagents could be expected to survive catalyst synthesis. At this point it is worth mentioning that the existing protocol for a Schrock catalyst developed some 15 years ago[26] is, despite significant efforts,[27] the only broadly applicable one. For the given task, we identified ω-halogenoalkyl groups as suitable. A hexyl spacer was chosen for two reasons. First it was short enough to prevent interaction of the terminal halogen with the molybdenum center, second it was expected to be long enough to ensure sufficient spacing of the final catalyst from the support. We therefore prepared four different 4-(6-halogenohexyl)-2,6-R_2-anilines, i.e., {4-[6-X-$(CH_2)_6$]-2,6-R_2-C_6H_2-NH_2} (**7**: R = Me, X = Br; **8**: R = Me, X = Cl, **9**: R = 2-Pr, X = Cl; **10**: R = 2-Pr, X = Br) *via* the synthetic route shown in Scheme 1. Thus, the amino groups in the starting anilines, 2,6-dimethylaniline (**1**) and 2,6-di-2-propylaniline (**2**), were protected with trimethylsilyl moieties, which allowed replacement of the 4-bromo group by lithium. Subsequent reaction with the 1,6-dibromohexane yielded the desired protected 6-bromohexylanilines **5** and **6**.

Deprotection required the use of concentrated HBr/methanol. Interestingly, the 6-bromo group could be replaced by a chloro group by using concentrated HCl/methanol. In summary, we obtained the 4 different deprotected 6-halogeno-2,6-R_2-alkylanilines **7**–**10**.

Synthesis of Molybdenum Complexes

In order to be capable of using the thus modified anilines for catalysts synthesis (Scheme 1), special and subtle reaction conditions had to be elaborated in order to prevent the terminal alkyl halide from reacting with any of the various nucleophilic reagents used. Thus, triethylamine had to be substituted by a sterically hindered base, 2,6-lutidine, and reaction times and temperatures had to be adjusted in order to reduce salt formation between the base and the chloroalkyl group. Other bases, e.g., 2,6-di-*tert*-butylpyridine or dry $NaHCO_3$, K_2CO_3, Cs_2CO_3 were found



Scheme 1. Synthesis of halogenoalkyl-substituted anilines **7**–**10**, Mo-bis(imido) complexes **11**–**14**, Mo-bisimido-dialkyl complexes **15**–**18** and alkyl-substituted Mo-arylimido-neophylidene triflates **19**–**21**.

unsuitable. Following the modified standard protocol for Schrock catalyst synthesis, a series of Mo-bisamidodichloro complexes, i.e., Mo{N-2,6-R_2-4-[6-X-$(CH_2)_6$]-C_6H_2}$_2Cl_2$·DME (**11**: R = Me, X = Br; **12**: R = Me, X = Cl; **13**: R = 2-Pr, X = Cl; **14**: R = 2-Pr, X = Br), was prepared. Crystals suitable for X-ray analysis were obtained for **13**. Compound **13** crystallized in the monoclinic space group *C*2/*c* with $a = 2261.28(7)$ pm, $b = 1970.31(8)$ pm, $c = 1556.75(6)$ pm, $\alpha = \gamma = 90°$, $\beta = 132.566(2)°$, $Z = 4$ (Figure 1).

In a next step, compounds **11**–**14** were transformed into the corresponding Mo-bis(imido)dialkyl complexes Mo{N-2,6-R_2-4-[6-X-$(CH_2)_6$]-C_6H_2}$_2$(CH_2-CMe_2Ph)$_2$ (**15**: R = Me, X = Br; **16**: R = Me, X = Cl; **17**: R = 2-Pr, X = Cl; **18**: R = 2-Pr, X = Br). Crystals suitable for X-ray analysis were obtained for **15**. Compound **15** crystallized in the monoclinic space group $P2_1/n$ with $a = 1750.6(2)$ pm, $b = 845.5(2)$ pm, $c = 3206.6(2)$ pm, $\alpha = \gamma = 90°$, $\beta = 104.720(6)°$, $Z = 4$ (Figure 2).

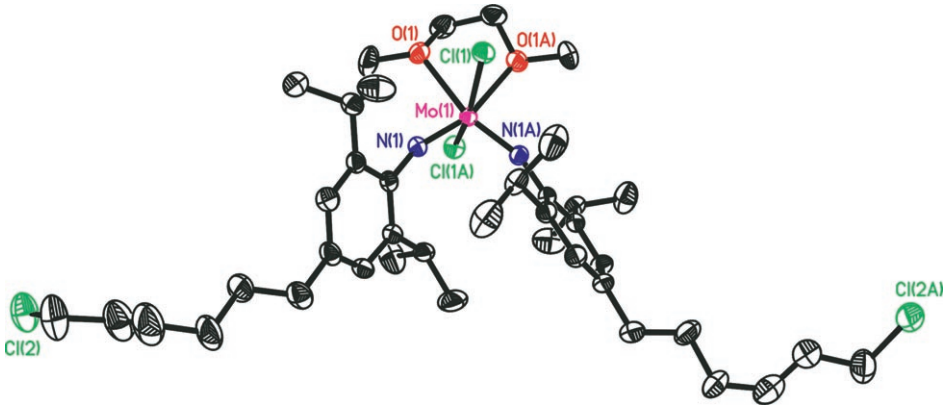


Figure 1. Mo[N-2,6-(2-Pr)$_2$-C_6H_2-4-$(CH_2)_6$-Cl]Cl_2 (DME) (**13**). Selected bond distances (pm) and angles (°): Mo(1)–N(1) 174.2(3), Mo(1)–N(1)#1 174.2(3), Mo(1)–O(1)#1 237.4(3), Mo(1)–O(1) 237.4(3), Mo(1)–Cl(1) 239.75(12), Mo(1)–Cl(1)#1 239.75(12), N(1)–Mo(1)–N(1)#1 103.6(2), N(1)–Mo(1)–O(1)#1 162.97(13), N(1)#1–Mo(1)–O(1)#1 93.45(13), N(1)–Mo(1)–O(1) 93.45(13), N(1)#1–Mo(1)–O(1) 162.97(14), O(1)#1–Mo(1)–O(1) 69.54(15), N(1)–Mo(1)–Cl(1) 97.28(12), N(1)#1–Mo(1)–Cl(1) 97.11(12), O(1)#1–Mo(1)–Cl(1) 79.79(9), O(1)–Mo(1)–Cl(1) 81.06(9), N(1)–Mo(1)–Cl(1)#1 97.11(12), N(1)#1–Mo(1)–Cl(1)#1 97.28(12), O(1)#1–Mo(1)–Cl(1)#1 81.06(9), O(1)–Mo(1)–Cl(1)#1 79.79(9), Cl(1)–Mo(1)–Cl(1)#1 156.63(7).

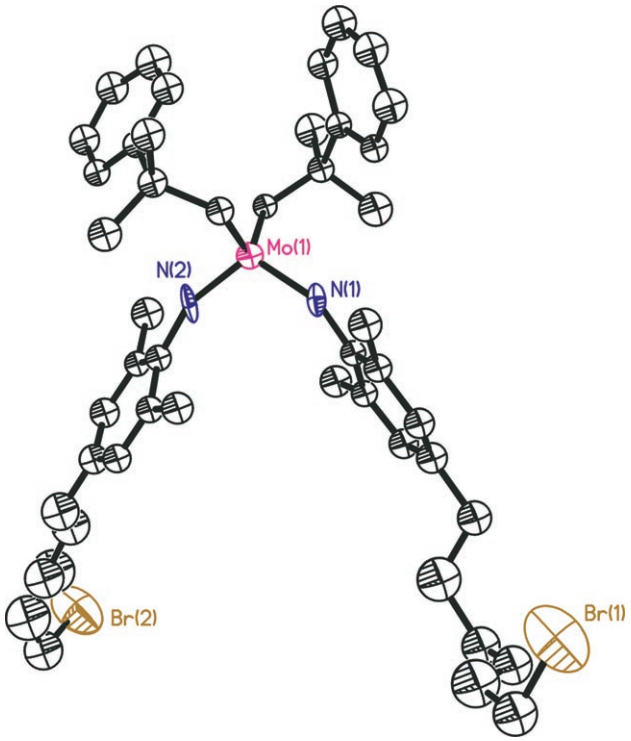


Figure 2. Mo[N-2,6-$(CH_3)_2$-C_6H_2-4-$(CH_2)_6$-Br][$CH_2C(CH_3)_2C_6H_5]_2$ (**15**). Selected bond distances (pm) and angles (°): Mo(1)–N(2) 172(2), Mo(1)–N(1) 175(2), Mo(1)–C(11) 203(3), Mo(1)–C(1) 219(2), N(2)–Mo(1)–N(1) 110.6(10), N(2)–Mo(1)–C(11) 104.1(11), N(1)–Mo(1)–C(11) 107.2(9), N(2)–Mo(1)–C(1) 102.2(9), N(1)–Mo(1)–C(1) 110.0(9), C(11)–Mo(1)–C(1) 122.3(9).

While **15** and **16** are obtained in crystalline form quite easily, compound **17** was hard to crystallize, which in turn significantly reduces its yield to 60%. This is, in view of the large amount of non-polar groups attached to the molecule, not surprising at all, however, it does significantly aggravate purification. In this context it is worth mentioning that, in contrast to "classic" Schrock type catalyst precursors, compounds **15**–**18** are quite soluble in basically any solvent including *n*-pentane, which in turn aggravated purification. Following the standard Schrock catalyst protocol, they were used for the synthesis of the corresponding Mo-imidoalkylidene triflates Mo{N-2,6-R_2-4-[6-X-$(CH_2)_6$]-C_6H_2}(CHCMe$_2$Ph)$(OTf)_2$·DME (**19**: R = Me, X = Br; **20**: R = 2-Pr, X = Br, **21**: R = 2-Pr, X = Cl). A major drawback in the purification of these compounds was the fact that the corresponding anilinium triflates, which form as a by-product in the course of the synthesis in stoichiometric amounts, were hard to remove from the target compounds. Again, both the anilinium triflates and the Mo-triflates **19--21** were found to be extremely soluble even in non-polar solvents such as benzene, toluene, xylenes and diethyl ether. In due consequence, the only applicable purification protocol entailed the extensive extraction of compounds **19**–**21** from the crude reaction mixture with *n*-pentane. This finally allowed for the isolation of pure **19**–**21** in gram amounts. Having the Mo-imidoalkylidene triflates as progenitors for the final catalysts at hand, the advantages of the concept of immobilizing Schrock catalysts *via* the arylimido ligands become evident. So far, Schrock catalysts with a very limited number of different imido ligands=N-R [R = adamantyl, 2,6-Me_2-C_6H_3, 2,6-(2-Pr)$_2$-C_6H_3, 2,6-Cl_2-C_6H_3] yet with a vast number of (chiral) alkoxides are the "working horses" in metathesis based organic chemistry.[8,28–30] Thus, with a small set of Mo triflates in hand, one can now exchange the triflates by any alkoxide, phenolate, biphenolate, carboxylate, etc., of interest and gain simple access to almost all relevant Schrock-type catalysts. Of similar importance is the fact that the final (chiral) catalysts may be prepared, purified, and analyzed prior to a last *single* immobilization step, providing utmost information about the actual composition of the corresponding supported catalyst.

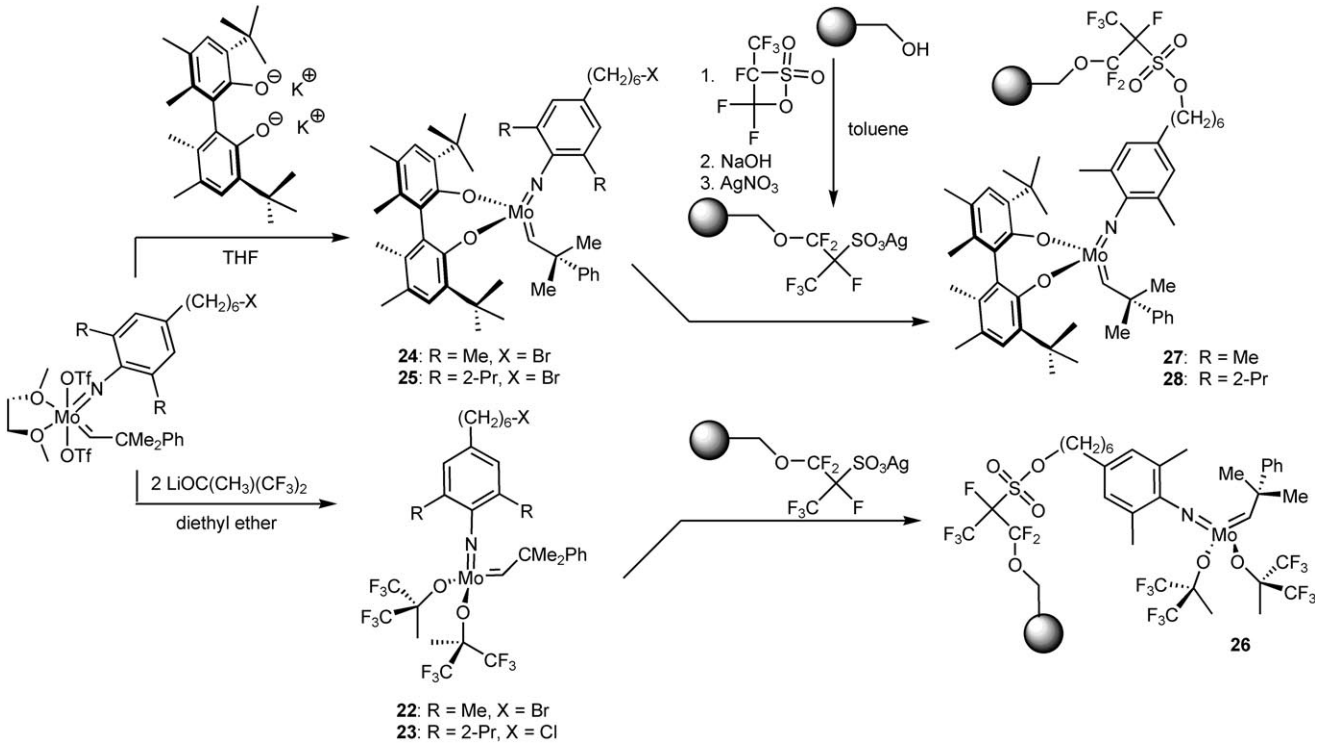
Synthesis of Catalysts

Compounds **19**–**21** were used in the synthesis of the Schrock-type catalysts. Thus, reaction of **19** and **20**, respectively, with 2 equivs. of Li-OCMe$(CF_3)_2$ yielded Mo{N-2,6-Me_2-4-[6-Br-$(CH_2)_6$]-C_6H_2}(CHCMe$_2$Ph)-[$OC(CH_3)(CF_3)_2]_2$ (**22**) and Mo{N-2,6-(2-Pr)$_2$-4-[6-Cl-$(CH_2)_6$]-C_6H_2}(CHCMe$_2$Ph)[$OC(CH_3)(CF_3)_2$] (**23**). Similarly, Mo{N-2,6-Me_2-4-[6-Br-$(CH_2)_6$]-C_6H_2}(CHCMe$_2$Ph)[(*R*)-BIPHEN] (**24**) and Mo{N-2,6-(2-Pr)$_2$-4-[6-Br-$(CH_2)_6$]-C_6H_2}(CHCMe$_2$Ph)[(*R*)-BIPHEN] (**25**) were prepared from **19** and **20** and 1 equiv. of the dipotassium salt of (*R*)-BIPHEN. An illustration is given in Scheme 2.

At this point, compounds **22**, **24** and **25** are perfect mimics of the parent Schrock catalysts. The halogenohexyl group might well be expected to have low – if any – impact on the geometry of the catalyst. Unfortunately, we were not able to obtain any X-ray data on the final catalysts so far to provide experimental evidence for this statement.

Immobilization of Catalysts

Generally, immobilization of compounds **22**–**25** had to be accomplished in the *absence* of any (even weak) nucleophile, since this would rather lead to the replacement of the alkoxide ligands by the nucleophile than to any reaction with the 6-halogenoalkyl group. For this purposes, the reaction of a polymer-bound silver perfluoroalkanesulfonate with the terminal bromo or, respectively, chloro group appeared suitable. The principal applicability of this reaction was



Scheme 2. Synthesis of catalysts **22**–**24** and immobilization procedure for the synthesis of the supported catalysts **26**–**28**.

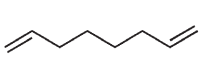
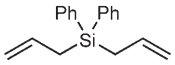
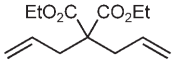
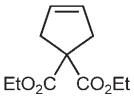
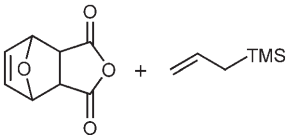
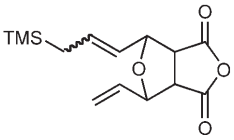
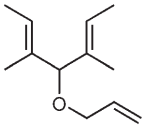
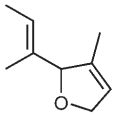
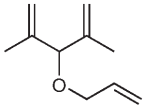
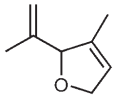
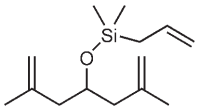
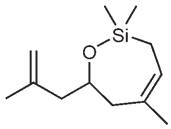
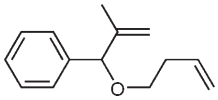
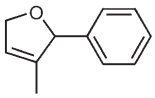
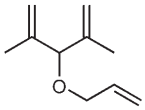
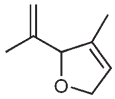
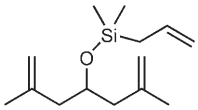
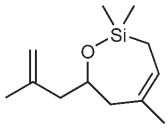
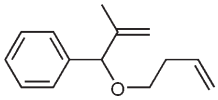
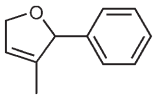
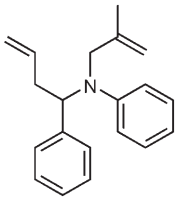
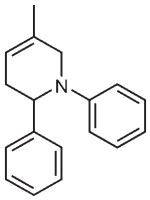
demonstrated by reacting 1-bromooctane with silver trifluoromethanesulfonate in tetrahydrofuran. ^{1}H NMR clearly showed the formation of the corresponding ester ($\delta = 3.50$ ppm, OCH_2) after 8 h at room temperature.

We first investigated the utility of Nafion®, a perfluorosulfonated resin for our purposes. These fluorosulfonated resins have been used as solid super acid catalysts and in many other variations as catalytic supports,[31–37] nevertheless, in all cases metal immobilization was accomplished by an ion-exchange procedure, i.e., exchange of H^+ by the metal of interest. Here, immobilization of compounds **22**–**25** was attempted by formation of an *alkanesulfonate* according to the above-mentioned reaction. Disappointingly, reaction with polymer-bound silver trifluoromethanesulfonate groups as provided by various different Nafion® resins – whether soluble or insoluble – did not result in systems with *any* catalytic activity. We tentatively attribute this finding to both the high perfluorosulfonic acid capacity of these resins as well as to inappropriate swelling characteristics. Both factors together are believed to result in a significant number of free perfluoroalkanesulfonic acid groups, which in turn destroy the catalytic species. In search of an alternative we prepared linear poly(styrene) (PS) *via* free radical polymerization ($M_n = 10{,}000\ g\,mol^{-1}$, PDI = 1.50). This PS was hydroxymethylated and reacted with 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethanesulfonic acid sultone (Scheme 2).[38] The resulting free perfluoroalkanesulfonic acid was finally converted into the corresponding silver salt. Using this support, an immobilized version of **22**, Mo{N-2,6-Me_2-4-[PS-CH_2-O-CF_2-CF(CF_3)-SO_3-$(CH_2)_6$]-C_6H_2)} ($CHCMe_2Ph$){[$O(CH_3)(CF_3)_2]_2$} (**26**, 11.4 μmol Mo/g), was prepared by reaction of the support (Ag form) with **22**. To the best of our knowledge this is the first time such a reaction of a halogenoalkylgroup and a polymer-supported silver perfluoroalkanesulfonate has been described. Using **26**, standard RCM reactions such as the conversion of 1,7-octadiene, diallyldiphenylsilane and diethyldiallyl malonate could be accomplished in high yields (Table 1). The same accounts for a ring-opening cross metathesis reaction between 7-oxanorborn-5-ene-2,3-dicarboxylic anhydride and allyltrimethylsilane.

Asymmetric RCM/Desymmetrization Reactions With Supported Catalysts 24 and 25

Encouraged by these findings compounds **24** and **25** were immobilized on Ag-perfluoroalkanesulfonate-modified PS-DVB materials to yield the corresponding immobilized catalysts Mo{N-2,6-$(2\text{-Pr})_2$-4-[PS-DVB-CH_2-O-CF_2-CF(CF_3)-SO_3-$(CH_2)_6$]-C_6H_2} ($CHCMe_2Ph$)[(*R*)-BIPHEN] (**27**) Mo{N-2,6-$(2\text{-Pr})_2$-4-[PS-DVB-CH_2-O-CF_2-CF(CF_3)-SO_3-$(CH_2)_6$]-C_6H_2} ($CHCMe_2Ph$)[(*R*)-BIPHEN] (**28**). Since enhanced reactivity had to be expected from the 6-bromoalkyl de-

Table 1. Results for (asymmetric) RCM and ring-opening cross reactions carried out with catalysts **26**–**28**.

Cat [mol%]	Substrate	Product	*t* [h]	conversion [%] (conversion [%])[a]	*ee* [%] (*ee* [%])[a]
26 (0.1)			2	64[c]	-
26 (1)			1	100[c]	-
26 (0.3)			2	98[c]	-
26 (1)			2	86[b,e]	-
26 (1)			4	77 (95)[d],[41]	95 (99)[41]
27 (5)			2	91 (93)[d],[41]	79 (93)[41]
27 (5)			1	99 (-)[d]	86 (-)
27 (5)			1	99 (>99)[d]	6 (4)[39]
28 (5)			3	>98 (97)[d]	87 (89)[20]
28 (5)			2	91 (86)[d],[42]	94 (89)[42]
28 (5)			2	43 (56)[d],[41]	30 (-)[41]
28 (5)			2	20 (35)[d],[38]	k_{rel}=2.1 (3)[38]

Reactions were run at room temperature.
[a] Analogous homogeneous or heterogeneous catalysts.
[b] Polymer formed.
[c] In CH_2Cl_2.
[d] In benzene.
[e] In $CDCl_3$.

rivatives of the Mo-imidoalkylidene triflates, we rather focused on these derivatives than on the corresponding 6-chloroalkyl compounds so far. Both supported chiral Schrock catalysts **27** and **28** were subject to various enantioselective ring-closing metathesis (RCM) reactions. The results obtained were compared to those obtained with the parent, unsupported catalysts, i.e., Mo(N-2,6-Me_2-C_6H_3)($CHCMe_2Ph$)[(*R*)-BIPHEN] and Mo[N-2,6-(2-Pr)$_2$-C_6H_3]($CHCMe_2Ph$)[(*R*)-BIPHEN], respectively, as well as with other supported systems. A summary is given in Table 1.

With one exception, conversions were $>90\,\%$ using 5 mol% of supported catalyst. Only 3,5-dimethyl-4-allyloxy-hepta-2,5-diene gave 77% yield, however, the observed enantiomeric excess (*ee*, 95%) was basically identical to the reported one (99%). Very similar enantioselectivity was also observed with both supported systems **27** and **28** compared to the parent catalysts. These data strongly suggest that the supported systems are perfect mimics of the parent chiral catalysts and any interference of the support with the catalyst, which ever, may be excluded. Compound **28** was further used in a desymmetrization reaction. Thus, 20% conversion of enantiomeric *N*-(1-*p*henyl-4-buten-1-yl)-*N*-(2-methyl-2-propen-1-yl)aniline revealed a value for k_{rel} of 2.1, compared to 3 (@ 30% conversion) with the parent system.[39] This might be indicative for a non-optimized accessibility of the catalytic sites which may require additional optimization of the polymeric support. However, the principle attractiveness and competitiveness of the concept is illustrated by the fact that 4 different catalysts precursors, i.e., **22**, **23**, **24**, **25**, have been prepared from only 2 progenitor triflates **19** and **20**, resulting in three different immobilized catalysts. The supported systems prepared are only exemplary illustrations and the range of immobilized catalysts may be well expected to be easily expanded to other (chiral) versions as well as to other supports. All supported versions may easily be removed from the reaction mixture by simple filtration. The average molybdenum leaching was 5.5% as measured by ICP-OES, which translates into an average Mo contamination of the products of less than 0.14%. This is comparable to or, respectively less, than Mo contaminations observed with systems immobilized *via* the biphenolate.[21,40] In view of the inherent instability of intermediate molybdenum methylidenes, no attempts to recycle any of the supported catalysts have been undertaken, the more since these are the final species at conversions $>99\,\%$. Finally, it is worth noting that the ester linkage between the support and the catalyst provides sufficient stability for immobilization as evidenced by the use of basic substrates such as *N*-(1-*p*henyl-4-buten-1-yl)-*N*-(2-methyl-2-propen-1-yl)aniline. This is not surprising since even the traces of water that would be necessary to cleave the ester must be kept away from the reaction mixture due to the inherent instability of the catalyst itself.

Conclusions

An entirely novel approach for the synthesis of immobilized (chiral) Schrock catalysts has been elaborated. The concept entails the manufacture of Schrock catalysts with ω-halogenoalkyl groups in the 4-position of the aryl imido ligand. Immobilization is achieved *via* reaction with polymer-bound perfluoroalkanesulfonate groups and formation of an ester linkage. This concept offers a broader variability in catalyst structure compared to existing immobilization routes that proceed *via* polymer-bound alkoxides (biphenolates). Future investigations will focus on the identification of more suitable supports, e.g., monolithic ones that might well improve recyclability of the catalysts and offer access to high-throughput screening techniques.

Experimental Section

General Remarks

NMR data were recorded at 300.13 MHz for proton and at 75.74 MHz for carbon in the indicated solvent at 25 °C on a Bruker Spectrospin 300 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants *J* are listed in Hz. IR spectra were recorded on a Bruker Vector 22 using ATR technology. GC-MS investigations were carried out on a Shimadzu GCMS-QP5050, using a SPB-5 fused silica column (30 m × 0.25 mm × 25 mm film thickness). GC separation of enantiomers was accomplished on a Supelco, Beta DexTM-120, 30 m × 0.25 mm × 0.25 μm film thickness), separation of enantiomeric amines was accomplished by chiral HPLC using a Chiralpak AD (4.6 mm × 250 mm) in comparison to authentic racemic material. Elemental analyses were carried out at the Microanalytical Laboratory, Anorganisch-Chemisches Institut, TU München, Lichtenbergstr. 4, 85747 Garching, Germany. A Jobin Yvon JY 38 plus was used for ICP-OES measurements, a MLS 1200 mega for microwave experiments. Syntheses of the ligands and catalysts were performed under an argon atmosphere by standard Schlenk techniques or in an N_2-mediated dry-box (MBraun, Germany) unless stated otherwise. Reagent grade diethyl ether, pentane, tetrahydrofuran (THF), dimethoxyethane (DME) and toluene were distilled from sodium benzophenone ketyl under argon. Reagent grade dichloromethane was distilled from calcium hydride under argon. Other solvents and reagents were used as purchased. Silica G60 (220–440 mesh, Fluka, Germany) was used for chromatography. Deionized, degassed water was used throughout. A molybdenum standard containing 1000 ppm of molybdenum was purchased from Alfa Aesar/Johnson Matthey (Karlsruhe, Germany). Mass spectra were recorded on a Finnigan MAT 95S using FAB ionization (Cs-

gun: 20 kV, 3 μA, matrix: *m*-nitrobenzylic alcohol). (*R*)-H_2-[Biphen] was purchased from Strem (USA), 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethanesulfonic acid sultone (95%) was purchased from ABCR (Germany). A microwave system (MWS, Germany) was used for dissolving the samples. Hydroxymethylated polystyrene (55763 Fluka, ~0.6 mmol OH/g, 200–400 mesh, 1% cross-linked with DVB) was used. 4-Bromo-2,6-dimethylaniline (**1**) was purchased from Aldrich Chem. Co. IR, ^{1}H NMR, ^{13}C NMR, and MS data as well data of elemental analyses for compounds **2**–**25** may be found in the Supporting Information.

4-Bromo-2,6-di-2-propylaniline (2)

Bromine (16.082 g, 100.64 mmol) was dissolved in small portions in 30 mL of cooled (−10 °C) pyridine. The red solution was added drop wise to a cooled (−10 °C) mixture of 2,6-di-2-propylaniline (16.99 g, 95.84 mmol) in 20 mL of pyridine. The reaction mixture was stirred for 30 min at 0 °C and for a further 1.5 h at room temperature. Next, it was treated with an excess of sodium carbonate in water and extracted with diethyl ether. All volatiles were evaporated. vacuum distillation afforded of the product (bp 110 °C/0.14 Torr), which was crystallized from *n*-pentane; yield: 17.01 g (66.40 mmol, 69%).

4-Bromo-2,6-dimethyl-*N,N*-bis-trimethylsilylaniline (3)

Compound **1** (17.47 g, 87.29 mmol) was dissolved in 200 mL of diethyl ether and chilled to −50 °C, *n*-butyllithium (2.2 equivs., 96.02 mL, 192.05 mmol) was added. The mixture was stirred for 1 h at room temperature. Afterwards, the solution was re-chilled to −50 °C and trimethylsilyl chloride (27.60 mL, 218.2 mmol) was added in small portions over a period of 10 min. After 2 h of further stirring at room temperature the diethyl ether was removed under vacuum, the resulting solid was extracted with *n*-pentane and filtered through a bed of silica G60. The solution was concentrated and the crude product was collected as a white solid. For further purification the solid was crystallized from *n*-pentane; yield: 29.49 g (85.62 mmol, 98%, white crystals).

4-Bromo-2,6-di-2-propyl-*N,N*-bis-trimethylsilylaniline (4)

Compound **2** (10.94 g, 42.70 mmol) was dissolved in 200 mL of diethyl ether and chilled to −50 °C. *n*-Butyllithium (2.2 equivs., 47.97 mL, 93.94 mmol) was added. The mixture was stirred for 1 h at room temperature. Afterwards, the solution was re-chilled to −50 °C and trimethylsilyl chloride (12.96 mL, 102.5 mmol) was added in small portions over a period of 10 min. After 2 h of further stirring at room temperature the diethyl ether was removed under vacuum, the resulting solid was extracted with *n*-pentane and filtered through a bed of silica G60. The solution was concentrated and the crude product was collected as yellowish crystals. For further purification the solid was crystallized from *n*-pentane and white crystals were isolated; yield: 13.59 g (33.93 mmol, 80%).

4-(6-Bromohexyl)-2,6-dimethyl-*N,N*-bis-trimethylsilylaniline (5)

To an ethereal solution of **3** (16.78 g, 57.45 mmol) was added lithium (3 equivs., 1.20 g, 172.3 mmol) and the mixture was refluxed for 4 h. Excess lithium was filtered off and the light yellow solution was chilled to −40 °C. 1,6-Dibromohexane (26.26 mL, 172.34 mmol) was added and the mixture was stirred overnight at room temperature. Next, the solvent was removed and the product was extracted with *n*-pentane. Then, the solution was filtered through a bed of silica G60, all volatiles were evaporated and the product was extracted with *n*-pentane. For further purification the product was subject to chromatography over silica G60 (column dimensions 2.5 × 30 cm) using hexane as eluent; Yield: 12.32 g (28.73 mmol, 50%).

4-(6-Bromohexyl)-2,6-di-2-propyl-*N,N*-bis-trimethylsilylaniline (6)

To an ethereal solution of **4** (8.11 g, 57.45 mmol) was added lithium (3 equivs., 1.20 g, 172.3 mmol) and the mixture was refluxed for 4 h. Excess lithium was filtered off and the light yellow solution was chilled to −40 °C. 1,6-Dibromohexane (26.26 mL, 172.34 mmol) was added and the mixture was stirred overnight at room temperature. Next, the solvent was removed and the product was extracted with *n*-pentane. Then, the solution was filtered through a bed of silica G60, all volatiles were evaporated and the product was extracted with *n*-pentane. For further purification the product was subject to chromatography over silica G60 (column dimensions 2.5 × 30 cm) using hexane as eluent; yield: 13.88 g (28.73 mmol, 50%).

4-(6-Bromohexyl)-2,6-dimethylaniline (7)

Compound **5** (12.3 g, 28.71 mmol) was mixed with 20 mL of concentrated hydrobromic acid and stirred at 60 °C for 5 h. The resulting precipitate was filtered off and washed with *n*-pentane. The solid was stirred with an aqueous sodium hydroxide solution (2 N) and finally the product was extracted with *n*-pentane; yield: 7.26 g (25.55 mmol, 89%, colorless oil).

4-(6-Chlorohexyl)-2,6-dimethylaniline (8)

Compound **5** was suspended in methanolic hydrochloric acid (150 mL) and stirred overnight at 100 °C. All volatiles were evaporated and the residue was collected and washed thoroughly with *n*-pentane. The slightly brown salt was treated with an excess of sodium hydroxide and the product was extracted with *n*-pentane. The pentane solution was dried over

Na_2SO_4 and finally all solvent was evaporated to afford a brownish oil; yield: 6.39 g (26.7 mmol, 90%).

4-(6-Chlorohexyl)-2,6-di-2-propylaniline (9)

Compound **6** was suspended in methanolic hydrochloric acid (150 mL) and stirred overnight at 100 °C. All volatile solvents were evaporated and the precipitate was collected and washed thoroughly with *n*-pentane. The slightly brown colored salt was treated with an excess of NaOH and the product was extracted with *n*-pentane. The organic layer was dried over Na_2SO_4 and finally the solvent was evaporated; yield of pure product: 4.58 g (15.5 mmol, 73%).

4-(6-Bromohexyl)-2,6-di-2-propylaniline (10)

Compound **6** (12.3 g, 25.4 mmol) was mixed with 20 mL of hydrobromic acid and stirred at 60 °C for 5 h. The resulting precipitate was filtered off and washed with *n*-pentane. The solid was stirred with an aqueous sodium hydroxide solution (2 N) and finally the product was extracted with *n*-pentane; yield: 6.82 g (20.10 mmol, 79%, colorless oil).

$Mo\{N[2,6\text{-}Me_2\text{-}4(6\text{-}BrC_6H_{12})]C_6H_2\}_2Cl_2(DME)$ (11)

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (2.69 g, 2.18 mmol) was suspended in DME (200 mL). 2,6-Lutidine (6.53 g, 60.9 mmol) and trimethylsilyl chloride (14.06 g, 129.5 mmol) were added and the solution was stirred for 5 min at room temperature. Next, **7** (8.66 g, 30.6 mmol) was added and the solution was stirred at 50 °C oil-bath temperature for 3 h. During this time the solution turned deep red. The reaction mixture was cooled to room temperature, filtered through celite and all volatile compounds were evaporated. Finally, the product was extracted with ether/*n*-pentane and stored at −38 °C for crystallization. A red solid was obtained; yield: 5.6 g (4.0 mmol, 45%).

$Mo\{N[2,6\text{-}Me_2\text{-}4(6\text{-}ClC_6H_{12})]C_6H_2\}_2Cl_2(DME)$ (12)

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.713 g, 0.577 mmol) was suspended in DME (60 mL) at room temperature. 2,6-Lutidine (1.88 mL, 16.2 mmol) and trimethylsilyl chloride (5.37 mL, 42.4 mmol) were added and the solution was stirred for 10 min. Next, **8** (2.297 g, 9.580 mmol) was added and the solution was stirred at 65 °C for 3.5 h. The solution turned orange, becoming dark red over time and a white precipitate formed. The mixture was allowed to cool to room temperature and was filtered through celite. The solid was rinsed with DME until the washings ran through colorless. The volatiles were removed under vacuum to yield a dark red solid. The product was extracted with diethyl ether and crystallized from diethyl ether with a few drops of *n*-pentane. Red crystals were obtained; yield:1.054 g (1.439 mmol, 36%).

$Mo\{N[2,6\text{-}(2\text{-}Pr)_2\text{-}4(6\text{-}Cl\text{-}C_6H_{12})]C_6H_2\}_2Cl_2(DME)$ (13)

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.737 g, 0.596 mmol) was suspended in DME (40 mL) at room temperature. 2,6-Lutidine (1.94 mL, 16.7 mmol) and trimethylsilyl chloride (5.54 mL, 43.8 mmol) were added and the solution was stirred for 10 min. Next, **9** (2.840 g, 9.598 mmol) was added and the solution was stirred at 65 °C for 6 h. The solution turned orange, becoming dark red over time and a white precipitate formed. The mixture was allowed to cool to room temperature and was filtered through celite. The solid was rinsed with DME until the washings ran through colorless. The volatile components were removed under vacuum to yield a dark red solid. The product was extracted with diethyl ether and crystallized from diethyl ether with a few drops of *n*-pentane (for further purification). Red crystals were isolated; yield: 2.97 g (3.51 mmol, 84%).

$Mo\{N[2,6\text{-}(2\text{-}Pr)_2\text{-}4(6\text{-}Br\text{-}C_6H_{12})]C_6H_2\}_2Cl_2(DME)$ (14)

$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.737 g, 0.596 mmol) was suspended in DME (40 mL) at room temperature. 2,6-Lutidine (1.94 mL, 16.7 mmol) and trimethylsilyl chloride (5.54 mL, 43.8 mmol) were added and the solution was stirred for 10 min. Next, **10** (2.829 g, 8.344 mmol) was added and the solution was stirred at 65 °C for 6 h. The solution turned orange, becoming dark red over time and a white precipitate formed. The mixture was allowed to cool to room temperature and was filtered through celite. The solid was rinsed with DME until the washings ran through colorless. The volatile components were removed under vacuum to yield a dark red solid. The product was extracted with diethyl ether and crystallized from diethyl ether with a few drops of *n*-pentane (for further purification). Red crystals were isolated; yield: 1.91 g (2.01 mmol, 50%).

$Mo\{N[2,6\text{-}Me_2\text{-}4(6\text{-}BrC_6H_{12})]C_6H_2\}_2(CH_2CMe_2C_6H_5)_2$ (15)

Compound **11** (0.50 g, 0.61 mmol) was dissolved in 50 mL of diethyl ether. The solution was cooled to −40 °C and 2 equivs. of neophylmagnesium chloride (2.42 mL, 1.22 mmol, 0.503 M in diethyl ether) were added dropwise. The solution turned orange and a precipitate formed. After 3 h of stirring at room temperature the solvent was removed under vacuum. The resulting solid was extracted with *n*-pentane, filtered through celite and concentrated for crystallization; yield: 0.449 g (0.485 mmol, 80%, orange crystals).

$Mo\{N[2,6\text{-}Me_2\text{-}4(6\text{-}ClC_6H_{12})]C_6H_2\}_2(CH_2CMe_2C_6H_5)_2$ (16)

Compound **12** (0.740 g, 1.01 mmol) was dissolved in 100 mL of diethyl ether. The solution was cooled to −38 °C and 2

equivs. of neophylmagnesium chloride (2.84 mL, 2.02 mmol, 0.71 M in diethyl ether) were added over a period of 10 min. The solution turned orange and a precipitate formed. After 14 h of stirring at room temperature the solvent was removed under vacuum. The resulting solid was extracted with *n*-pentane. Next, the solution was filtered through celite and concentrated for crystallization. Yellow-orange crystals were obtained; yield: 0.679 g (0.810 mmol, 80%).

Mo{N[2,6-(2-Pr)$_2$-4-(6-Cl-C$_6$H$_{12}$)]C$_6$H$_2$}$_2$-(CH$_2$CMe$_2$C$_6$H$_5$)$_2$ (17)

Compound **13** (1.377 g, 1.630 mmol) was dissolved in 50 mL of diethyl ether. The solution was cooled to −40 °C and 2 equivs. of neophylmagnesium chloride (4.59 mL, 3.26 mmol; 0.71 M in diethyl ether) was added dropwise. The solution turned orange and a precipitate formed. After 16 h stirring at room temperature the solvent was removed under vacuum. The resulting solid was extracted with *n*-pentane, filtered through celite and then concentrated for crystallization; yield: 0.945 g (0.994 mmol, 61%).

Mo{N[2,6-(2-Pr)$_2$-4(6-Br-C$_6$H$_{12}$)]C$_6$H$_2$}$_2$-(CH$_2$CMe$_2$C$_6$H$_5$)$_2$ (18)

Compound **14** (1.52 g, 1.63 mmol) was dissolved in 50 mL of diethyl ether. The solution was cooled to −38 °C and 2 equivs. of neophylmagnesium chloride (4.59 mL, 3.26 mmol, 0.71 M in diethyl ether) were added over a period of 10 min. The solution turned orange and a precipitate formed. After 16 h of stirring at room temperature the solvent was removed under vacuum. The resulting solid was extracted with *n*-pentane. Next, the solution was filtered through celite and concentrated for crystallization. An orange oil was isolated; yield: 1.354 g (1.3 mmol, 80%).

Mo{N[2,6-Me$_2$-4(6-BrC$_6$H$_{12}$)]C$_6$H$_2$}(CHCMe$_2$C$_6$H$_5$)-(OTf)$_2$(DME) (19)

Compound **15** (0.972 g, 1.049 mmol) was dissolved in 100 mL of dimethoxyethane (DME) and the solution was cooled to −38 °C. Triflic acid (0.472 g, 3.15 mmol) diluted in 10 mL of DME and chilled to −38 °C was added and the mixture was stirred for 12 h. The volatile components were removed under vacuum and the solid was re-dissolved in diethyl ether and filtered. All volatiles were removed; the residue was extracted with *n*-pentane. The solution was filtered through celite and all volatile compounds were evaporated; yield: 0.802 g (0.891 mmol, 85%, yellow-brownish oil).

Mo{N[2,6-(2-Pr)$_2$-4-(6-Br-C$_6$H$_{12}$)]C$_6$H$_2$}$_2$-(CHCMe$_2$C$_6$H$_5$)(OTf)$_2$(DME) (20)

Compound **18** (511.8 mg, 0.49 mmol) was dissolved in 30 mL of DME and cooled to −40 °C. Triflic acid (221.8 mg, 1.47 mmol) diluted in 5 mL of DME and chilled to −40 °C was added. The mixture was stirred 4 h at room temperature; the solvent was removed under vacuum. The solid was re-dissolved in cooled diethyl ether and filtered. Finally, all volatiles were removed under vacuum to afford a yellow-brownish oil; yield: 374 mg (0.392 mmol, 80%). For further purification, the oil was extracted with *n*-pentane.

Mo{N[2,6-(2-Pr)$_2$-4(6-ClC$_6$H$_{12}$)]C$_6$H$_2$}(CHCMe$_2$C$_6$H$_5$)-(OTf)$_2$(DME) (21)

Compound **17** (0.380 g, 0.399 mmol) was dissolved in 30 mL of DME and the solution was cooled to −38 °C. Triflic acid (0.168 g, 1.12 mmol) diluted in 10 mL of DME and chilled to −38 °C was added and the mixture was stirred for 2 h. The volatiles were removed under vacuum and the solid was extracted with *n*-pentane. The brownish solution was filtered through celite and dried under vacuum, affording a yellow-brownish oil; yield: 0.218 g (0.239 mmol, 60%).

Mo{N[2,6-Me$_2$-4(6-BrC$_6$H$_{12}$)]C$_6$H$_2$}(CHCMe$_2$C$_6$H$_5$)-[OC(CF$_3$)$_2$Me]$_2$ (22)

Compound **19** (246 mg, 0.185 mmol) was dissolved in diethyl ether and cooled to −38 °C. LiOC(CF$_3$)$_2$CH$_3$ (108 mg, 0.572 mmol) was added and the solution was stirred for 30 min at room temperature. The solvents were removed under vacuum and the resulting solid was extracted with *n*-pentane. The brown organic layer was filtered through celite. Finally, all volatile compounds were removed under vacuum. A yellow-brownish oil was obtained; yield: 121 mg (0.139 mmol, 75%).

Mo{N[2,6-(2-Pr)$_2$-4(6-ClC$_6$H$_{12}$)]C$_6$H$_2$}-(CHCMe$_2$C$_6$H$_5$)[OC(CF$_3$)$_2$Me]$_2$ (23)

Compound **21** (57.0 mg, 0.063 mmol) was dissolved in diethyl ether and cooled to −38 °C. LiOC(CF$_3$)$_2$CH$_3$ (24.0 mg, 0.126 mmol) was added and the solution was stirred for 30 min at room temperature. The solvents were removed under vacuum and the resulting solid was extracted with *n*-pentane. The organic layer was filtered through celite. Finally, all volatile compounds were removed under vacuum, affording a brown oil; yield: 41 mg (0.047 mmol, 74%).

Mo{N[2,6-Me_2-4-(6-Br-C_6H_{12})]C_6H_2}$_2$-($CHCMe_2C_6H_5$)[(*R*)-BIPHEN] (24)

Potassium hydride (3 equivs., 68.73 mg, 1.71 mmol) was added in portions to a stirred THF (20 mL) solution of (*R*)-H_2[Biphen] (202.5 mg, 0.57 mmol). After 18 h, a THF solution of **19** (513.3 mg, 0.57 mmol) was added. The red solution was stirred for 3 h at room temperature and then concentrated under vacuum. The residue was extracted with benzene. The suspension was filtered through Celite and washed with benzene until the washings were colorless. The benzene was removed under vacuum to furnish a red solid product; yield: 160 mg (0.185 mmol, 33%).

Mo{N[2,6-(2-Pr)$_2$-4-(6-Br-C_6H_{12})]C_6H_2}$_2$-($CHCMe_2C_6H_5$)[(*R*)-BIPHEN] (25)

Potassium hydride (3 equivs. 19.0 mg, 0.48 mmol) was added in portions to a stirred THF (10 mL) solution of (*R*)-H_2-[Biphen] (57.0 mg, 0.16 mmol). After 18 h, a THF solution of **20** (153 mg, 0.16 mmol) was added. The red solution was stirred for 3 h at room temperature, and then concentrated under vacuum. The residue was extracted with benzene. The suspension was filtered through celite and washed with benzene until the washings were colorless. The benzene was removed under vacuum to furnish the red solid product; yield: 105 mg (71%).

Synthesis of Poly(styrene)

Styrene (5.20 g, 50.0 mmol) and perbenzoic anhydride (0.120 g, 0.5 mmol) were dissolved in 10 mL of absolute toluene. The solution was stirred at 60°C for 4 h. After addition of acidic methanol with HCl, a white solid precipitated, it was filtered off, washed with methanol and finally dried under vacuum; yield: 3.00 g (60%) (M_n: 10,000 g mol^{-1}, PDI: 1.5).

Chloromethylation of Poly(styrene) and Hydrolysis[41]

Trioxane (0.90 g, 10.0 mmol) and chlorotrimethylsilane (3.8 mL, 30.0 mmol) were dissolved in 10 mL of absolute chloroform. Poly(styrene) (1.00 g) and $SnCl_4$ (0.5 mL, 4.30 mmol) were added at 0°C. The mixture was stirred at 0°C for 30 min and for another 2 h at room temperature. After addition of methanolic water, the polymer was filtered and washed with methanol and water and finally dried under vacuum overnight; anal. found: C 81.35, H 7.13, Cl 9.43.

The polymer was then suspended in an aqueous solution of NaOH (100 mL, 0.01 N) and 10 mL of THF, and then the mixture was stirred for 12 h at room temperature. The polymer was filtered and washed with water until the washings were neutral, and dried at 100°C overnight. (~0.2 mmol OH/g).

Reaction of Hydroxymethylpoly(styrene) with 1,2,2-Trifluoro-2-hydroxy-1-trifluoromethylethanesulfonic Acid Sultone,[38] Conversion into the Ag Salt

Hydroxymethylpoly(styrene-*co*-divinylbenzene) (1.0 g, 0.60 mmol OH) was added to a solution of 1,2,2-trifluoro-2-hydroxy-1-trifluoromethylethanesulfonic acid sultone (2.5 equivs., 345 mg, 1.50 mmol) in 50 mL of dry toluene. The mixture was refluxed for 8 h, the solid was filtered and washed thoroughly with toluene and finally dried at°C overnight. It was then suspended in an aqueous solution of KOH (25 mL, 0.1 N), mixed with 10 mL of THF and the mixture was stirred for 12 h. The solid was filtered off and washed with water until the washings were neutral. Finally, the solid was suspended in an aqueous solution of $AgNO_3$ (25 mL, 0.1 M) with 10 mL THF and stirred for 4 h at room temperature. The solid was filtered and washed with water until the washings were free of silver, as checked with aqueous sodium iodide solution, Finally, the solid was washed with dry THF. The brown solid was dried at 100°C overnight.

Reaction of Ag Trifluoromethanesulfonate with 1-Bromooctane

1-Bromooctane (19.1 mg, 0.099 mmol) and silver trifluoromethanesulfonate (22.7 mg, 0.089 mmol) were dissolved in dimethyl sulfoxide-d_6. The mixture was stirred for 8 h and then subject to ^{1}H NMR [$\delta = 3.50$ (m, 2H, OCH_2)]. *Circa* 30% conversion of the parent 1-bromooctane into the ester was observed. No vinyl compounds (1-octene), resulting from elimination reactions, were observed.

Synthesis of Poly(styrene)-Supported (F_6) Mo Complex (26)

A suspension of the silver salt of trifuoromethansulfonated PS (200 mg, 0.04 mmol) and the molybdenum complex **22** (36 mg, 0.04 mmol g^{-1}) in C_6H_6 (50 mL) was stirred at room temperature for 24 h. The resulting product was filtered, washed with C_6H_6 (3×15 mL, only slightly yellow washings) and pentane (4×5 mL) and dried under vacuum to afford 180 mg of a grey powder. Catalyst-loadings as determined by measurement of Mo by means of ICP-OES: **26**: 0.01 mmol g.$^{-1}$

Synthesis of Poly(styrene-*co*-divinylbenzene)-Supported (Chiral) Mo Complexes 27 and 28 (Representative Example)

A suspension of the silver salt of trifuoromethansulfonated poly(styrene-*co*-DVB) (200 mg, 0.120 mmol) and the corre-

sponding molybdenum complexes **24** (100 mg, 0.12 mmol g^{-1}) and **25** (112 mg, 0.12 mmol g^{-1}) in C_6H_6 (50 mL) was stirred at room temperature for 24 h. The resulting product was filtered, washed with C_6H_6 (3×15 mL, only slightly yellow washings) and pentane (4×5 mL) and dried under vacuum to afford 180 mg of a dark-grey powder. Catalyst-loadings as determined by measurement of Mo by means of ICP-OES: **27**: 0.08 mmol g^{-1}; **28**: 0.13 mmol g^{-1}.

Representative RCM with Supported (Chiral) Complexes

A vial was charged with monomer (8×10^{-3} mmol) and the supported catalyst (4×10^{-4} mmol Mo) in the indicated solvent. The reaction mixture was stirred at room temperature for the time indicated in Table 1 and conversion was checked by GC-MS. The mixture was filtered and washed with pentane. The crude material was concentrated under vacuum and analyzed by chiral GC-MS for *ee*. Desymmetrization reactions were checked for *ee* by means of chiral HPLC. Separation conditions were identical to those reported in the literature.[39,42,43] Finally, the sample was dissolved in aqua regia (5 mL) and analyzed by means of ICP-OES for the residual metal content (5.5% average leaching).

X-Ray Measurement and Structure Determination of 13 and 15

Single crystals of **13** and **15** suitable for X-ray analysis were obtained by slow crystallization from dichloromethane/pentane. Data collection was performed on a Nonius Kappa CCD equipped with graphite-monochromatized *Mo-K*$_\alpha$-radiation ($\lambda=0.71073$ Å) and a nominal crystal to area detector distance of 36 mm. Compound **13**: monoclinic space group *C*2/*c* (No.15), $a=2261.28(7)$ pm, $b=1970.31(8)$ pm, $c=1556.75(6)$ pm, $\beta=132.566(2)°$, $V=5.1083(3)$ nm^3, $Z=4$, $\varsigma_{calcd.}=1.209$ g cm^{-3}, $T=233.2$ K, $\mu=0.708$ mm^{-1}, red prism, 2513 reflections $>2\sigma(I)$. The structure was solved and refined using SHELXS83 and SHELXL97 to $R_1=0.0477$ and $\omega R^2=0.11738$. Compound **15**: monoclinic space group $C2_1/n$ (No.14), $a=1750.6(2)$ pm, $b=845.5(2)$ pm, $c=3206.6(2)$ pm, $\beta=104.720(6)°$, $V=4.5904(12)$ nm^3, $Z=4$, $\varsigma_{calcd.}=1.341$ g cm^{-3}, $T=233.2$ K, $\mu=2.050$ mm^{-1}, yellow plates, 2673 reflections $>2\sigma(I)$. The structure was solved and refined using SHELXS83 and SHELXL97 to $R_1=0.1604$ and $\omega R^2=1.136$.

Intensities were integrated using DENZO and scaled with SCALEPACK.[44] Several scans in$\phi$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.[45] The function minimized was $\Sigma[w(F_o^2-F_c^2)^2]$ with the weight defined as $w^{-1}=[\sigma^2(F_o^2)+(xP)^2+P]$ and $P=(F_o^2+2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 602508 and 602509. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44(1223)336–033; E-mail: deposit@ccdc.cam.ac.uk].

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