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Synthesis and catalytic properties of polynuclear molybdenum silicon-containing carbene complexes

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The molybdenum silicon-containing carbene complexes $PhMe_2Si—CH=Mo(NAr)(OR)_2$ (**1**), $Ph_2Si[CH=Mo(NAr)(OR)_2]_2$ (**2**), and $(RO)_2(ArN)Mo=CH—(SiMe_2)_2—CH=Mo(NAr)(OR)_2$ ($Ar = 2,6\text{-}Pr^i_2C_6H_3$; $R = CMe_2CF_3$) were synthesized by the reaction of the $R´—CH=Mo(NAr)(OR)_2$ compounds ($R´ = Bu^t$ or $PhMe_2C$) with silicon-containing vinyl reagents. The structures of complexes **1** and **2** and the known $PhMe_2C—CH=Mo(NAr)(OCMe_2CF_3)_2$ compound were established by X-ray diffraction. The catalytic properties of the silicon-containing carbene complexes in homometathesis of hex-1-ene and metathesis polymerization of cyclooctene were studied. The catalytic activity of these complexes and the stereoregularity of the resulting polyoctenamers substantially depend on the nature of the substituent at the carbene carbon atom.

Key words: carbene complexes, molybdenum, silicon, synthesis, X-ray diffraction study, metathesis, polymerization.

The molybdenum carbene complexes $Alk—CH=Mo(NAr)(OR)_2$ ($Alk = Bu^t$ or $PhMe_2C$; $Ar = 2,6\text{-}Pr^i_2C_6H_3$; R = Alk or Ar) are active catalysts for olefin metathesis.[1—4] In spite of a large number of publications on the synthesis and the catalytic properties of these compounds, data on analogous complexes containing heteroorganic substituents instead of an alkyl or aryl group at the carbene carbon atom are scarce.[5—10]

Recently, we have described the synthesis and selected properties of the molybdenum silicon- and germanium-containing carbene complexes $Ph_3Si—CH=Mo(NAr)(OR)_2$ (see Ref. 11) and $R´_3Ge—CH=Mo(NAr)(OR)_2$ ($R = CMe_2CF_3$; $R´ = Me$ or Ph; $Ar = 2,6\text{-}Pr^i_2C_6H_3$).[12]

In the present study, we synthesized new di- and polynuclear molybdenum silicon-containing carbene complexes $PhMe_2Si—CH=Mo(NAr)(OR)_2$ (**1**), $Ph_2Si[—CH=Mo(NAr)(OR)_2]_2$ (**2**), and $(RO)_2(ArN)Mo=CH—(SiMe_2)_2—CH=Mo(NAr)(OR)_2$ (**3**) ($Ar = 2,6\text{-}Pr^i_2C_6H_3$; $R = CMe_2CF_3$) and investigated their catalytic properties.

Complexes **1—3** were synthesized by the reaction of the known $R´CH=Mo(NAr)(OR)_2$ compounds ($R = CMe_2CF_3$; $R´ = Bu^t$ (**4**)[5] or $PhMe_2C$ (**5**)[13]) with the corresponding vinylsilanes (Scheme 1).

The course of the reactions was monitored by ^1H NMR spectroscopy. It was found that the rate of complex formation substantially depends on the nature of organic substituents at the silicon atom in the starting vinyl reagent. The presence of Ph groups in the environment of the silicon atom leads to a substantial decrease in the reaction rate. Thus, complex **3** is formed in 20 h; complex **1**, in 2 weeks; complex **2**, in 2 months.

Scheme 1

$$\underset{\mathbf{5}}{R´CH=Mo(NAr)(OR)_2} + PhMe_2SiCH=CH_2 \xrightarrow{i} \underset{\mathbf{1}}{PhMe_2SiCH=Mo(NAr)(OR)_2} + CH_2=CHR´$$

$$2\,\underset{\mathbf{4}}{R´CH=Mo(NAr)(OR)_2} + Ph_2Si(CH=CH_2)_2 \xrightarrow{i} \underset{\mathbf{2}}{Ph_2Si[CH=Mo(NAr)(OR)_2]_2} + 2\,CH_2=CHR´$$

$$2\,\underset{\mathbf{5}}{R´CH=Mo(NAr)(OR)_2} + CH_2=CH(SiMe_2)_2CH=CH_2 \xrightarrow{i} \underset{\mathbf{3}}{(RO)_2(ArN)Mo=CH(SiMe_2)_2CH=Mo(NAr)(OR)_2} + 2\,CH_2=CHR´$$

i. PhH, 20 °C.

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Complexes **1**—**3** were isolated in individual form in 56, 36, and 45% yields, respectively, as air-unstable crystalline yellow-orange compounds readily soluble in organic solvents. Compounds **1**—**3** were identified by elemental analysis and ^{1}H, ^{13}C, and ^{29}Si NMR spectroscopy. The structures of complexes **1** and **2** were established by X-ray diffraction. To compare the structural parameters, we also performed X-ray diffraction analysis for the known $PhMe_2C—CH=Mo(NAr)(OCMe_2CF_3)_2$ compound (**5**).[13]

The X-ray diffraction data show that complexes **1** and **5** are not isostructural (Fig. 1) in spite of the very similar compositions and structures. Unlike complex **1**, whose crystals were studied at 100 K, crystals of **5** cracked at this temperature. Because of this, the X-ray diffraction study of the latter compound was carried out at 250 K. The Mo atoms in compounds **1** and **5** have typical tetrahedral coordination. An analysis of the carbene fragments in the structures of **1** and **5** shows that the Mo(1)—C(1) distance is virtually equal to the Mo(1)—C(21) distance (1.877(1) and 1.880(3) Å, respectively), whereas the Mo—C—Si and Mo—C—C angles at the carbene carbon atom in molecules **1** (138.04(8)°) and **5** (144.3(2)°) are substantially different. The C(H)—C(Me$_2$Ph) distance in molecule **5** (1.514(4) Å) is indicative of the absence of electron density delocalization in the Mo=C(H)—C(Me$_2$Ph) fragment. The Si(1)—C(1) distance in molecule **1** is 1.856(2) Å and is comparable with the Si(1)—C(Me, Ph) single bond lengths (1.853(2)—1.875(2) Å). In the $Ph_3Si—CH=Mo(NAr)(OR)_2$ complex (**6**) (Ar = $2,6\text{-}Pr^{i}{}_2C_6H_3$; R = CMe_2CF_3) studied earlier,[11] the distances at the carbene carbon atom, Mo=C (1.883(3) Å) and C—Si (1.857(3) Å), are similar to the analogous distances in complex **1**, but the Mo—C—Si angle (144.8(2)°) is much more similar to the analogous angle in complex **5** rather than to that in complex **1**. In all complexes, the N—Mo=C(H)—Si(C) fragments are planar to within 0.002—0.013 Å. In complex **1**, the CF_3 groups of the CMe_2CF_3 ligands are in *cis* positions with respect to the O(1)Mo(1)O(2) fragment, whereas these groups in complex **5** are disordered over two positions, which is evidence for both the *cis* and *trans* arrangement with respect to the analogous fragment. The phenyl groups in dimethylphenylsilyl (**1**) and dimethylphenylmethyl (**5**) ligands point toward the Me groups of the CMe_2CF_3 substituents. Apparently, this arrangement of the Ph groups leads to a decrease in nonbonded repulsion between the dimethylphenylsilyl (**1**) and dimethylphenylmethyl (**5**) ligands, on the one hand, and the NAr group, on the other hand.

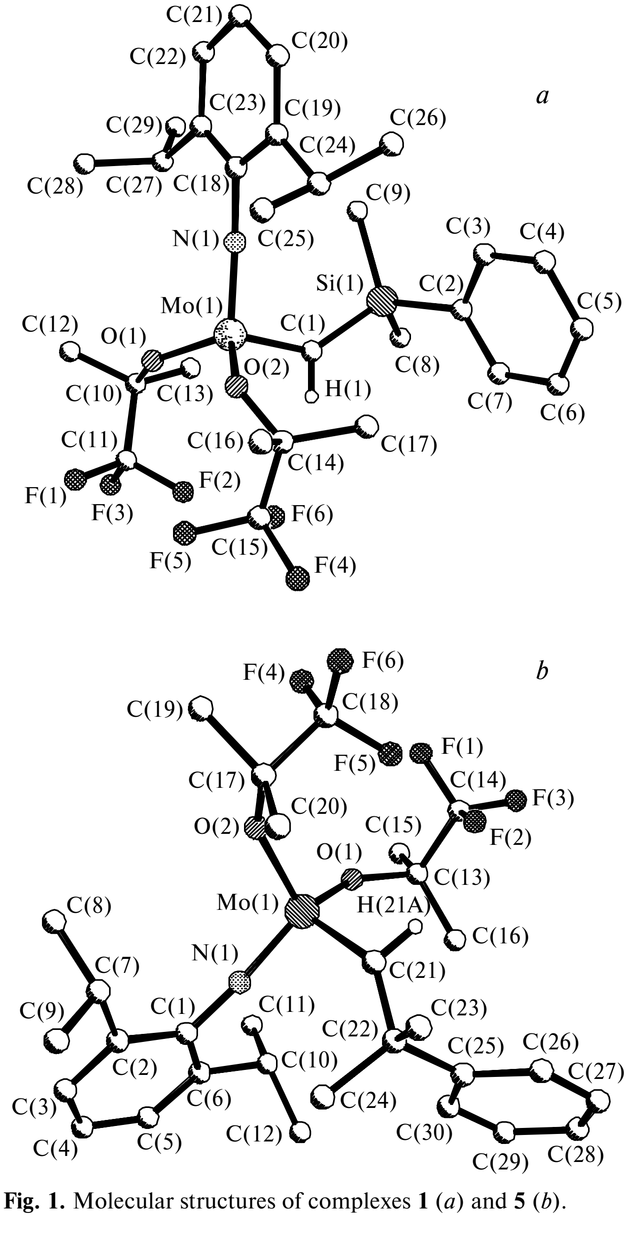

Fig. 1. Molecular structures of complexes **1** (*a*) and **5** (*b*).

In trinuclear complex **2** (Fig. 2), two $CH=Mo(NAr)(OR)_2$ fragments are linked to each other *via* the Ph_2Si group. The Mo—C(21) and Mo—C(34) distances in the carbene fragment are 1.891(2) and 1.887(2) Å, respectively, which are slightly larger than the analogous distances in molecules **1** and **5**. The Si(1)—C(21) (1.860(2) Å) and Si(1)—C(34) (1.857(2) Å) distances are also comparable with both the analogous distances in **1** and the Si—C(Ph) distances (1.869(2) and 1.875(2) Å) in **2**. Apparently, this is indicative of the absence of electron density delocalization in the Mo=C(H)—Si fragments. The Si(1)—C(21)—Mo(1) and Si(1)—C(34)—Mo(2) angles (146.0(1) and 137.4(1)°, respectively) are noticeably different. The carbene H atoms are in *cis* positions with respect to the Mo(1)C(21)Si(1)C(34)Mo(2) fragment and, consequently, are in *trans* positions with respect to the NAr groups, which corresponds to the *syn* conformation of the ligands about both molybdenum atoms. An analo-

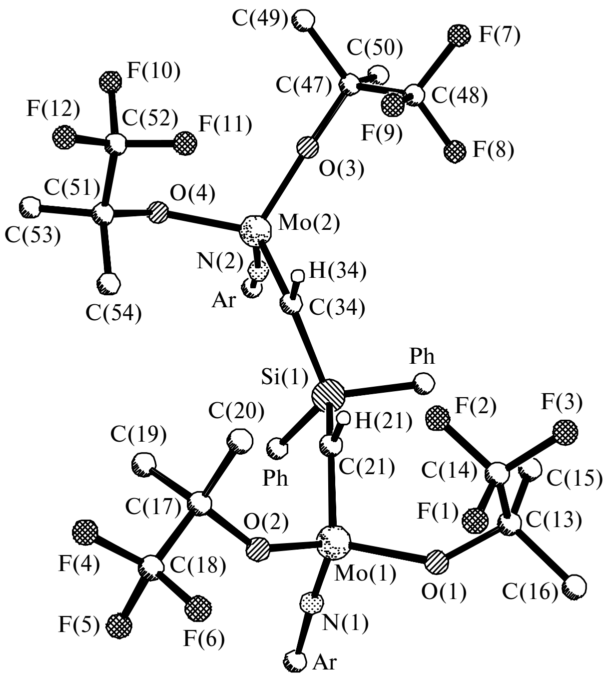

Fig. 2. Molecular structure of complex **2** (first carbon atoms of the 2,6-$\text{Pr}^{\text{i}}{}_2\text{C}_6\text{H}_3$ and Ph substituents are denoted as Ar and Ph, respectively).

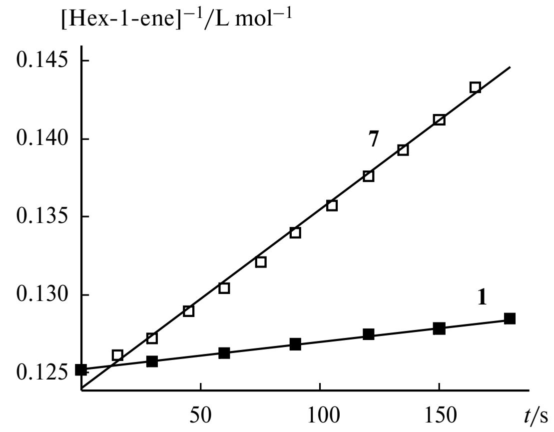

Fig. 3. Kinetic curves for metathesis of hex-1-ene in the presence of complexes **1** and **7** as catalysts ($[\text{hex-1-ene}]_0$ = 7.99 mol L^{-1}, [catalyst] = 0.027 mol L^{-1}). The kinetic curves obtained with the use of other catalysts have a similar shape characteristic of second-order reactions.

gous *syn* conformation is observed also in complexes **1**, **5**, and **6**.[11]

Catalytic activity of silicon-containing carbene complexes **1**, **3**, and **6**,[11] as well as of the known compounds $\text{Me}_3\text{Si—CH=Mo(NAr)(OCMe}_2\text{CF}_3)_2$ (**7**),[5] **4**, and **5**, was studied in homometathesis test reactions of hex-1-ene. A comparison of the rate constants (Table 1, Fig. 3) allows the conclusion that the nature of the substituent at the carbene carbon atom has a substantial effect on the catalyst activity. The compounds containing an organosilicon substituent are 4—19 times less active that their hydrocarbon analogs. In a series of silicon-containing carbene complexes, the catalytic activity depends on the nature of substituents at the silicon atom. The complexes containing Me substituents (**7** and **3**) are 4—8 times more active than the complexes containing Ph groups at the silicon atom (**1** and **6**). Earlier, we have demonstrated[11] that the catalytic activity of germanium-containing molybdenum complexes in metathesis of hex-1-ene depends similarly on the structure of the organogermanium substituent at the carbene carbon atom. An analogous change in activity is also observed in the complexes with hydrocarbon substituents (**4** and **5**), although to a lesser extent.

We found that the resulting molybdenum silicon-containing carbene complexes are active initiators of metathesis polymerization of cyclooctene. The stereoregularity of polyoctenamers prepared with the use of carbene molybdenum complexes and their hydrocarbon analogs substantially depend on the nature of the substituent at the carbene carbon atom. Selected characteristics of polyoctenamers prepared in the bulk with the use of various carbene molybdenum complexes as the catalysts are given in Table 2. We failed to determine the molecular-weight distribution by gel permeation chromatography for most polymers because of their poor solubility in THF, chloroform, and other organic solvents.

Table 1. Kinetics of metathesis of hex-1-ene with the use of molybdenum catalysts*

Catalyst	T/°C	Conversion (%)	$k \cdot 10^4$ /L mol^{-1} s^{-1}
1	19	2.37	0.17
3	19	7.83	0.61
4	22	40.55	4.77
5	22	30.17	3.22
6	20	2.25	0.15
7	20	13.98	1.14

* [Hex-1-ene]/[catalysts] = 300, under solvent-free conditions, the reaction time was 3 min.

Table 2. Characteristics of polyoctenamers obtained in the bulk with the use of molybdenum catalysts[a]

Catalyst	Conversion (%)[b]	Ratio *trans* : *cis*	[η] /dL g^{-1}	T_{m}/°C
1	82	64 : 36	5.97	48.0±0.5
3	88	74 : 26	3.81	55.0±0.5
4	87	83 : 17	—	59.0±0.8
5	70	30 : 70	4.23	−27.0±0.9
7[c]	73	40 : 60	3.55	51.0±0.3

[a] [Monomer]/[catalyst] = 300, the reaction time was 10—50 min.
[b] Determined by the gravimetric method.
[c] M_{n} = 267000, M_{w} = 569600, $M_{\text{w}}/M_{\text{n}}$ = 2.13.

To summarize, we synthesized new di- and polynuclear molybdenum silicon-containing carbene complexes. The resulting compounds were demonstrated to be active catalysts for homometathesis of hex-1-ene and metathesis polymerization of cyclooctene. It was found that catalytic activity of the complexes substantially depends on the nature of the substituent bound to the carbene carbon atom. The stereoregularity of polyoctenamers prepared with the use of molybdenum initiators also substantially depends on the nature of the substituent at the carbene carbon atom.

Experimental

All operations were carried out in evacuated sealed tubes using the standard Schlenk technique. The solvents were thoroughly dried and degassed before use. The starting reagents Alk—CH=Mo(NAr)($OCMe_2CF_3$)$_2$ (Alk = Bu^t,[5] $PhMe_2C$ [13]), $PhMe_2SiCH=CH_2$,[14] $Ph_2Si(CH=CH_2)_2$,[15] and $CH_2=CH-(SiMe_2)_2-CH=CH_2$ [15] were synthesized according to known procedures. Hex-1-ene and cyclooctene (both from Aldrich) were degassed and stored over sodium mirror before use. The necessary amounts were withdrawn by condensation in vacuum. The ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker DPX-200 spectrometer in C_6D_6 and $CDCl_3$ with Me_4Si as the internal standard.

The experimental intensities were measured on an automated Smart APEX diffractometer (graphite monochromator, Mo-Kα radiation, φ—ω-scanning technique, λ = 0.71073 Å). The structures were solved by direct methods and refined by the least-squares method against F^2_{hkl} with anisotropic displacement parameters for all nonhydrogen atoms using the SHELXTL program package.[16] The H atoms in complexes **1** and **2** were located in difference Fourier maps and refined isotropically. The hydrogen atoms in complex **5** were positioned geometrically and refined using a riding model. Absorption corrections were applied using the SADABS program.[17] Principal crystallographic characteristics and the X-ray data collection and refinement statistics are given in Table 3. Selected bond lengths and bond angles are listed in Table 4.

Kinetic experiments were performed and the rate constants of homometathesis of hex-1-ene were determined according to known procedures.[18,19] Polymerization reactions were carried out under solvent-free conditions. The resulting polyoctenamer was purified by multiple reprecipitation from chloroform with methanol. The polymer samples were dried to constant weight in vacuum at ~20 °C. The ratios of the monomer units in *trans* and *cis* conformations in the polymers were evaluated by

Table 3. Crystallographic data and the structure refinement statistics for complexes **1**, **2**, and **5**

Parameter	**1**	**2**	**5**
Molecular formula	$C_{29}H_{41}F_6NO_2SiMo$	$C_{54}H_{70}F_{12}N_2O_4SiMo_2$	$C_{30}H_{41}F_6NO_2Mo$
Molecular weight	673.66	1259.09	657.58
Crystal dimensions/mm	0.25×0.23×0.11	0.22×0.21×0.20	0.35×0.32×0.10
T/K	100	100	250
Space group	$P2(1)/c$	$P\bar{1}$	$P2(1)/c$
a/Å	16.6708(9)	10.8598(8)	9.6809(4)
b/Å	17.1192(9)	13.5647(10)	18.7142(8)
c/Å	11.1076(6)	20.6881(15)	17.8017(8)
α/deg	—	77.279(2)	—
β/deg	91.710(1)	77.666(1)	90.553(1)
γ/deg	—	76.600(1)	—
V/Å^3	3168.6(3)	2849.1(4)	3225.0(2)
Z	4	2	4
d_{calc}/g cm^{-3}	1.412	1.468	1.354
μ/mm^{-1}	0.513	0.545	0.467
T_{min}/T_{max}	0.9457/0.8825	0.8988/0.8895	0.9548/0.8536
F(000)	1392	1292	1360
θ_{max}/deg	27.54	27.00	24.00
Number of measured/independent reflections (R_{int})	29693/7276 (0.040)	18169/12281 (0.0242)	22883/5045 (0.0248)
GOF	1.036	0.975	1.047
R_1/wR_2 ($I > 2\sigma(I)$)	0.0278/0.0642	0.0425/0.1012	0.0490/0.1471
R_1/wR_2 (based on all measured reflections)	0.0393/0.0686	0.0606/0.1071	0.0613/0.1575
Data^a/restraints^b/parameters^c	7276/6/525	12281/19/956	5045/113/455
Residual electron density (max/min)/e Å^{-3}	0.660/–0.451	1.679/–0.802	0.811/–0.448

[a] The number of reflections used in the final refinement.

[b] The number of fixed parameters.

[c] The number of parameters in the refinement.

Table 4. Selected bond lengths (*d*) and bond angles (ω) in complexes **1**, **2**, and **5**

Parameter	**1**	**2**	**5**
Bond		*d*/Å	
Mo(1)—N(1)	1.725(1)	1.729(2)	1.722(3)
Mo(1)—O(1)	1.901(1)	1.899(1)	1.901(2)
Mo(1)—O(2)	1.906(1)	1.895(2)	1.903(2)
Mo(1)—C(1)	1.877(1)	—	—
Mo(1)—C(21)	—	1.891(2)	1.880(3)
Mo(2)—N(2)	—	1.732(2)	—
Mo(2)—O(3)	—	1.864(2)	—
Mo(2)—O(4)	—	1.895(1)	—
Mo(2)—C(34)	—	1.887(2)	—
Si(1)—C(1)	1.856(2)	—	—
Si(1)—C(21)	—	1.860(2)	—
Si(1)—C(34)	—	1.857(2)	—
C(21)—C(22)	—	—	1.514(4)
Angle		ω/deg	
Mo(1)—C(1)—Si(1)	138.04(8)	—	—
Mo(1)—C(21)—Si(1)	—	146.0(1)	—
Mo(1)—C(21)—C(22)	—	—	144.3(2)
Mo(2)—C(34)—Si(1)	—	137.4(1)	—

^{13}C NMR spectroscopy according to a known procedure.[20] The intrinsic viscosity (η) was determined in chloroform at 25 °C. The molecular-weight distribution of the polyoctenamer prepared with the use of complex **7** as initiator was determined by gel permeation chromatography. A set of styrogel columns with pore diameters of $1 \cdot 10^5$, $3 \cdot 10^4$ $1 \cdot 10^4$, $1 \cdot 10^3$, and 250 Å (Waters) was used. An R-403 differential refractometer (Waters) was used as a detector; THF, as the solvent. Calibration was performed with a set of polystyrene standards. The melting point (T_m) was determined by DSC on a NETSCH DSC 204 F1 instrument in the temperature range 10—80 °C at a heating rate of 10 °C min^{-1}. For each sample, several series of experiments were carried out.

(2,6-Diisopropylphenylimido)bis(1,1-dimethyl-2,2,2-trifluoroethanolato)(dimethylphenylsilylmethylidene)molybdenum (1). A solution of $PhMe_2SiCH=CH_2$ (0.1115 g, 0.69 mmol) in benzene (5 mL) was added to a dark-yellow solution of $PhMe_2C—CH=Mo(NAr)(OCMe_2CF_3)_2$ (0.4455 g, 0.68 mmol) in benzene (10 mL) at ~20 °C. The reaction mixture was kept at ~20 °C for 2 weeks. The solvent and volatile products were removed by vacuum evaporation. Recrystallization of the residue from a minimum amount of pentane afforded compound **1** as yellow crystals in a yield of 0.26 g (56%). Found (%): C, 51.78; H, 6.20. $C_{29}H_{41}F_6MoNO_2Si$. Calculated (%): C, 51.70; H, 6.15. ^{1}H NMR (C_6D_6), δ: 0.41 (s, 6 H, $CHSi\underline{Me}_2Ph$); 1.19 (d, 12 H, $CH\underline{Me}_2$); 1.21 and 1.29 (both s, 6 H each, $OC\underline{Me}_2CF_3$); 3.69 (sept, 2 H, $C\underline{H}Me_2$, $^3J_{H,H}$ = 6.8 Hz); 7.01 (s, 3 H, $2,6\text{-}Pr^i{}_2C_6\underline{H}_3$); 7.13—7.19 (m, 3 H, H(2), H(4), H(6) from $CHSiMe_2\underline{Ph}$); 7.40—7.47 (m, 2 H, H(3), H(5) from $CHSiMe_2\underline{Ph}$); 13.33 (s, 1 H, $Mo=C\underline{H}SiMe_2Ph$). ^{13}C NMR ($C_6D_6$), δ: 0.49 ($Mo=CHSi\underline{Me}_2Ph$); 23.8 ($CH\underline{Me}_2$); 24.3, 24.4 ($OC\underline{Me}_2CF_3$); 28.5 ($\underline{C}HMe_2$); 79.0 (q, $O\underline{C}Me_2CF_3$, $^2J_{C,F}$ = 28.9 Hz); 123.2 (C(3), $2,6\text{-}Pr^i{}_2\underline{C}_6H_3$); 127.2 (q, $OCMe_2\underline{C}F_3$, $^1J_{C,F}$ = 286 Hz); 128.1 (C(3), $CHSiMe_2\underline{Ph}$); 128.3 (C(4), $2,6\text{-}Pr^i{}_2\underline{C}_6H_3$); 129.4 (C(4), $CHSiMe_2\underline{Ph}$); 133.8 (C(2), $CHSiMe_2\underline{Ph}$); 139.6 (C(1), $CHSiMe_2\underline{Ph}$); 145.9 (C(2), $2,6\text{-}Pr^i{}_2\underline{C}_6H_3$); 154.3 (C(1), $2,6\text{-}Pr^i{}_2\underline{C}_6H_3$); 270.9 (d, $Mo=\underline{C}HSiMe_2Ph$, $J_{C,H}$ = 116 Hz). ^{29}Si NMR (C_6D_6), δ: −5.0.

The synthesis and isolation of complex **1** from $Bu^t—CH=Mo(NAr)(OCMe_2CF_3)_2$ and $PhMe_2SiCH=CH_2$ were carried out analogously. The yield was 52%.

(μ$_2$-Diphenylsilane-1,1´-dienylidene)bis(2,6-diisopropylphenylimido)tetrakis(1,1-dimethyl-2,2,2-trifluoroethanolato)dimolybdenum (2). The synthesis and isolation of complex **2** were performed as described above starting from $Bu^t—CH=Mo(NAr)(OCMe_2CF_3)_2$ (0.5250 g, 0.88 mmol) and $Ph_2Si(CH=CH_2)_2$ (0.1045 g, 0.44 mmol). The reaction mixture was kept at ~20 °C for 2 months. Recrystallization from a minimum amount of pentane afforded compound **2** as yellow-orange crystals in a yield of 0.20 g (36%). Found (%): C, 51.81; H, 5.75. $C_{54}H_{70}F_{12}Mo_2N_2O_4Si$. Calculated (%): C, 51.51; H, 5.62. ^{1}H NMR (C_6D_6), δ: 1.04 (d, 24 H, $CH\underline{Me}_2$, J = 7.0 Hz); 1.29 and 1.39 (both s, 12 H each, $OC\underline{Me}_2CF_3$); 3.42 (sept, 4 H, $C\underline{H}Me_2$, $^3J_{H,H}$ = 6.8 Hz); 6.78—6.99 (m, 12 H, $2,6\text{-}Pr^i{}_2C_6\underline{H}_3$, H(3), H(4), H(5) from $Si\underline{Ph}_2$); 7.63—7.75 (m, 4 H, H(2), H(6) from $Si\underline{Ph}_2$); 13.18 (s, 2 H, $(Mo=C\underline{H})_2SiPh$). ^{13}C NMR ($C_6D_6$), δ: 23.6 ($CH\underline{Me}_2$); 24.5, 24.7 ($OC\underline{Me}_2CF_3$); 28.5 ($\underline{C}HMe_2$); 79.5 (q, $O\underline{C}Me_2CF_3$, $^2J_{C,F}$ = 28.8 Hz); 122.7, 124.3 (C_{Ar}); 127.2 (q, $OCMe_2\underline{C}F_3$, $^1J_{C,F}$ = 286 Hz); 129.6, 130.0, 136.2, 136.3, 145.5, 153.9 (C_{Ar}); 262.9 ($(Mo=\underline{C}H)_2SiPh$).

(μ$_2$-Tetramethyldisilane-1,1´-dienylidene)bis(2,6-diisopropylphenylimido)tetrakis(1,1-dimethyl-2,2,2-trifluoroethanolato)dimolybdenum (3). The synthesis and isolation of complex **3** were performed as described above. The reaction time was 20 h. Compound **3** was obtained as small yellow crystals in a yield of 0.25 g (45%) from $PhMe_2C—CH=Mo(NAr)(OCMe_2CF_3)_2$ (0.6103 g, 0.93 mmol) and $(Me_2SiCH=CH_2)_2$ (0.0791 g, 0.46 mmol). Found (%): C, 46.37; H, 6.16. $C_{46}H_{72}F_{12}Mo_2N_2O_4Si_2$. Calculated (%): C, 46.30; H, 6.09. ^{1}H NMR (C_6D_6), δ: 0.29 (s, 12 H, $Si\underline{Me}_2$); 1.21 (d, 24 H, $CH\underline{Me}_2$, J = 7.0 Hz); 1.31 and 1.39 (both s, 12 H each, $OC\underline{Me}_2CF_3$); 3.69 (sept, 4 H, $C\underline{H}Me_2$); 6.81—7.07 (m, 6 H, $2,6\text{-}Pr^i{}_2C_6\underline{H}_3$); 13.23 (s, 2 H, $Mo=C\underline{H}SiMe_2$). ^{13}C NMR (C_6D_6), δ: −0.4 ($Si\underline{Me}_2$); 23.8 ($CH\underline{Me}_2$); 24.4, 24.6 ($OC\underline{Me}_2CF_3$); 28.5 ($\underline{C}HMe_2$); 78.9 (q, $OCMe_2\underline{C}F_3$, $^2J_{C,F}$ = 29.4 Hz); 123.2 (C(3), $2,6\text{-}Pr^i{}_2\underline{C}_6H_3$); 127.33 (q, $OCMe_2\underline{C}F_3$, $^1J_{C,F}$ = 286 Hz); 128.2 (C(4), $2,6\text{-}Pr^i{}_2\underline{C}_6H_3$); 145.8 (C(2), $2,6\text{-}Pr^i{}_2\underline{C}_6H_3$); 154.7 (C(1), $2,6\text{-}Pr^i{}_2\underline{C}_6H_3$); 270.6 ($Mo=\underline{C}HSiMe_2$). ^{29}Si NMR ($C_6D_6$), δ: −11.8.

Metathesis of hex-1-ene. The reaction was performed under solvent-free conditions at ~20 °C. Hex-1-ene (0.6187 g, 7.348 mmol) was added under argon into a tube, which was connected to a gas burette and contained complex **1** (16 mg, 0.024 mmol). The reaction mixture was stirred. The amount of released ethylene was determined volumetrically. The reaction was terminated by adding Al_2O_3 to the reaction mixture. The metathesis reactions of hex-1-ene with the use of other catalysts were performed analogously.

Metathesis polymerization of cyclooctene. Cyclooctene (1.227 g, 11.135 mmol) was added into an evacuated tube containing complex **1** (25 mg, 0.037 mmol). The reaction mixture was magnetically stirred at ~20 °C. A solid transparent block was formed within 40 min. Metathesis polymerization of cyclooctene with the use of other catalysts was performed analogously.

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