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Molybdenum Tin-containing π-Complexes $(R_3SnCH{=}CH_2)Mo(N\text{-}2,6\text{-}Pr^{i}_{2}\text{-}C_6H_3)(OCMe_2CF_3)_2$. Synthesis and Catalytic Properties

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Abstract—The tin-containing molybdenum π-complexes $(R_3SnCH{=}CH_2)Mo(N\text{-}2,6\text{-}Pr^{i}_{2}C_6H_3)(OCMe_2CF_3)_2$ (R = Me, Et, Ph) were synthesized by reaction of $PhMe_2CCH{=}Mo(N\text{-}2,6\text{-}Pr^{i}_{2}C_6H_3)(OCMe_2CF_3)_2$ with organotin vinyl reagents $R_3SnCH{=}CH_2$. The structure of compounds **I–III** was determined by NMR spectroscopy. Complexes **I–III** are active initiators of the norbornene metathesis polymerization.

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Reaction of the molybdenum alkylidene compounds $AlkylC(H){=}Mo(N\text{-}2,6\text{-}Pr^{i}_{2}C_6H_3)(OCMe_2CF_3)_2$ (Alkyl = *t*-Bu, $PhMe_2C$) with vinylsilanes $R_3SiCH{=}CH_2$ (R=Me, Et, Ph) is known to afford silicon-containing carbene complexes $R_3SiC(H){=}Mo(N\text{-}2,6\text{-}Pr^{i}_{2}C_6H_3)(OCMe_2CF_3)_2$ [1–3]. Similarly proceeds the interaction of the molybdenum alkylidene compounds with trimethylvinylgermane and triphenylvinylgermane [4]. Recently we found that the reaction of $PhMe_2CCH{=}Mo(N\text{-}2,6\text{-}Pr^{i}_{2}C_6H_3)(OCMe_2CF_3)_2$ with triethylvinylgermane proceeded in another direction and led to the formation of germanium-containing molybdenum π-complex $(Et_3GeCH{=}CH_2)\cdot Mo(N\text{-}2,6\text{-}Pr^{i}_{2}C_6H_3)(OCMe_2CF_3)_2$ [2]. In this study we found that the reaction of alkylidene compound $PhMe_2CC(H){=}Mo(N\text{-}2,6\text{-}Pr^{i}_{2}C_6H_3)(OCMe_2CF_3)_2$ with organotin vinyl reagents $R_3SnCH{=}CH_2$ (R=Me, Et, Ph) also led to the formation of molybdenum π-complexes.

Reaction of $PhMe_2CC(H){=}Mo(N\text{-}2,6\text{-}Pr^{i}_{2}C_6H_3)\cdot(OCMe_2CF_3)_2$ with triorganylvinylstannanes proceeds at room temperature over 5–10 min, and leads to the formation of π-complexes $(CF_3Me_2CO)_2(N\text{-}2,6\text{-}Pr^{i}_{2}C_6H_3)Mo(CH_2{=}CH\text{-}SnR_3)$ and asymmetric tin-containing olefin derivatives:

$$PhMe_2CCH{=}Mo(N\text{-}2,6\text{-}Pr^{i}_{2}\text{-}C_6H_3)(OCMe_2CF_3)_2 + 2\,R_3SnCH{=}CH_2$$

$$\xrightarrow{C_6D_6,\ 20°C} (CF_3Me_2CO)_2(C_6H_3\text{-}Pr^{i}_{2}\text{-}2,6\text{-}N)Mo(CH_2{=}CHSnR_3) + PhMe_2CCH{=}CHCH_2SnR_3,$$

R = Me (**I**), Et (**II**), Ph (**III**).

After the reaction completion, the ^1H NMR spectrum of the reaction mixture does not contain signals of the H^{α} atoms in the alkylidene region (8.0–20.0 ppm) of any carbene complexes, the only reaction products are compounds **I–III** and the tin-containing olefins. We failed to isolate individual π-complexes **I–III**. Therefore, these compounds were identified as components of a mixture with $PhMe_2CCH{=}CHCH_2SnR_3$ by ^1H and ^{13}C NMR spectroscopy using H–H and C–H correlations. Figures 1–3 show the regions of the signals of vinyl protons in the ^1H NMR spectra of the molybdenum π-complexes.

According to the data of NMR spectroscopy, compounds **I–III** exist in solution as isomers differing by the arrangement of R_3Sn groups relative to the ArN and OR ligands at the molybdenum atom. Keeping at room temperature for a week did not lead to noticeable changes in the NMR spectra of π-complexes, indicating a fairly high thermal stability of the compounds

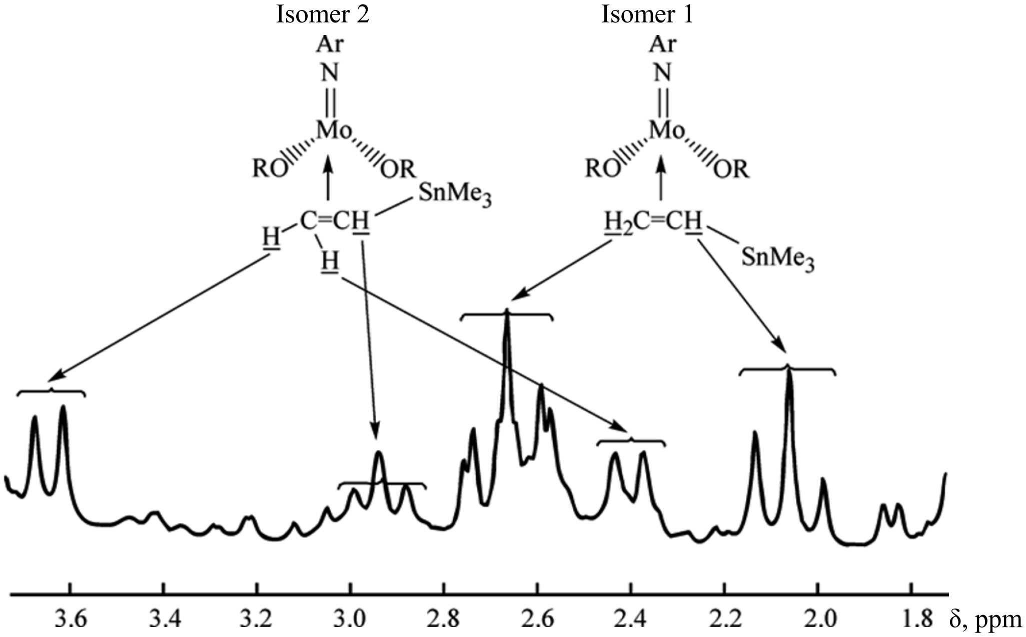


Fig. 1. ^{1}H NMR spectrum of π-complex **I** in the region of vinyl protons.

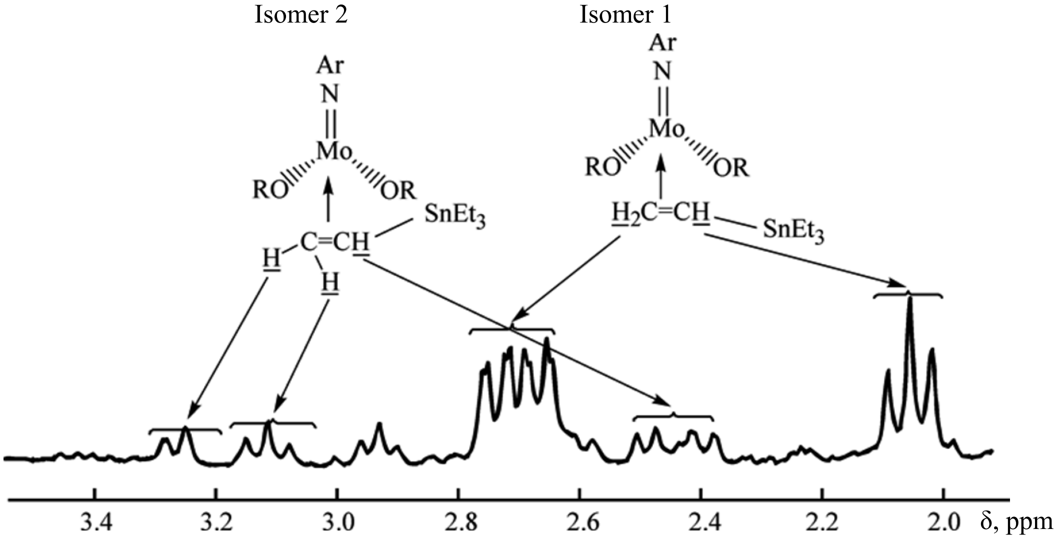
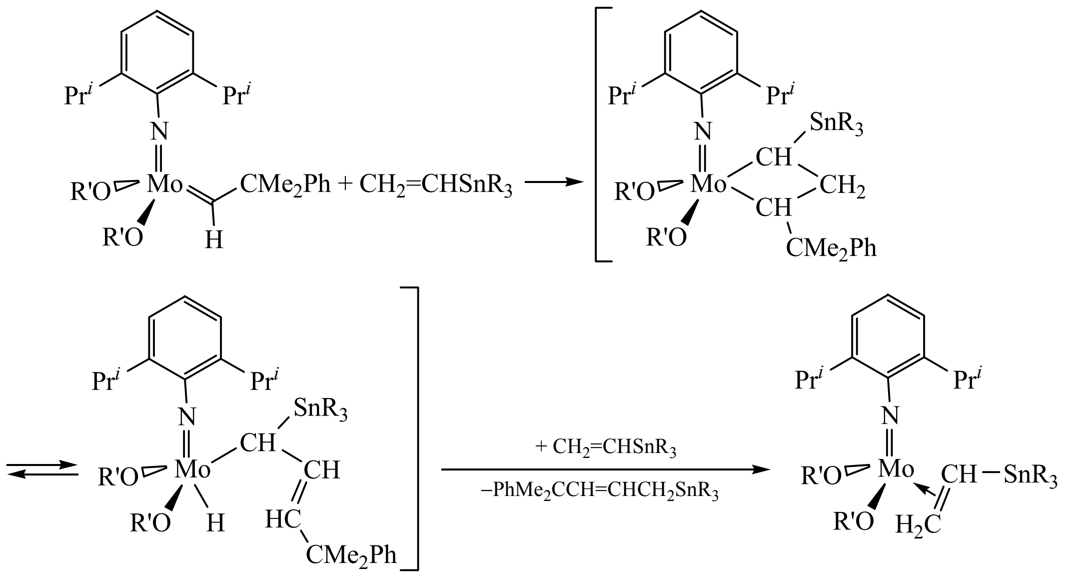


Fig. 2. ^{1}H NMR spectrum of π-complex **II** in the region of vinyl protons.

formed. The unsaturated derivatives $PhMe_2CCH=CHCH_2SnR_3$ (R = Me, Et) were isolated in individual state in 60–80% yield as colorless oils stable in air. Their structures were determined by IR, ^{1}H, ^{13}C NMR spectroscopy and elemental analysis.

The formation of the tin-containing molybdenum π-complexes and asymmetric olefin derivatives is probably a result of the following successive transformations (see the scheme bellow).

In accordance with commonly accepted mechanism for the olefin metathesis [5], at the initial stages of the reaction the intermediate molybdacyclobutane derivatives containing R_3Sn and $PhMe_2C$ substituents at the C^a atom of the metallacycle are formed. Then probably the β-hydride rearrangement of the molybdacyclobutane complex proceeds with the transformation into an intermediate alkyl hydride compound. In the final stage a second molecule of the vinylstannane reacts with the alkyl hydride compound, leading finally to the



R' = CMe_2CF_3.

formation of the tin-containing olefin $PhMe_2CCH{=}CHCH_2SnR_3$ and the molybdenum π-complex $(CF_3Me_2CO)_2(N\text{-}2,6\text{-}Pr^i_2C_6H_3)Mo(CH_2{=}CH\text{-}SnR_3)$. Similar processes of β-hydride rearrangements of molybdacyclobutane derivatives and the formation of π-complexes were observed earlier [6–8].

While studying the catalytic properties of synthesized π-complexes **I–III** we found that they are able to initiate the metathesis polymerization of norbornene without separation from the olefinic derivatives $PhMe_2CCH{=}CHCH_2SnR_3$. The reaction in benzene solu-tion is completed at room temperature in 2–3 min and leads to the formation of high-molecular weight poly-norbornenes with a predominant content of *cis*-units (see the table). The polymer yield after the repreci-pitation was 90–94%.

The high initiating ability of the molybdenum π-complexes can be probably attributed to the formation of carbene complexes in the reaction with cycloolefin, which are then involved in the stages of the chain growth.

Thus, we synthesized and characterized by NMR spectroscopy new tin-containing molybdenum π-complexes and asymmetric olefin derivatives. The obtained π-complexes actively initiate the metathesis

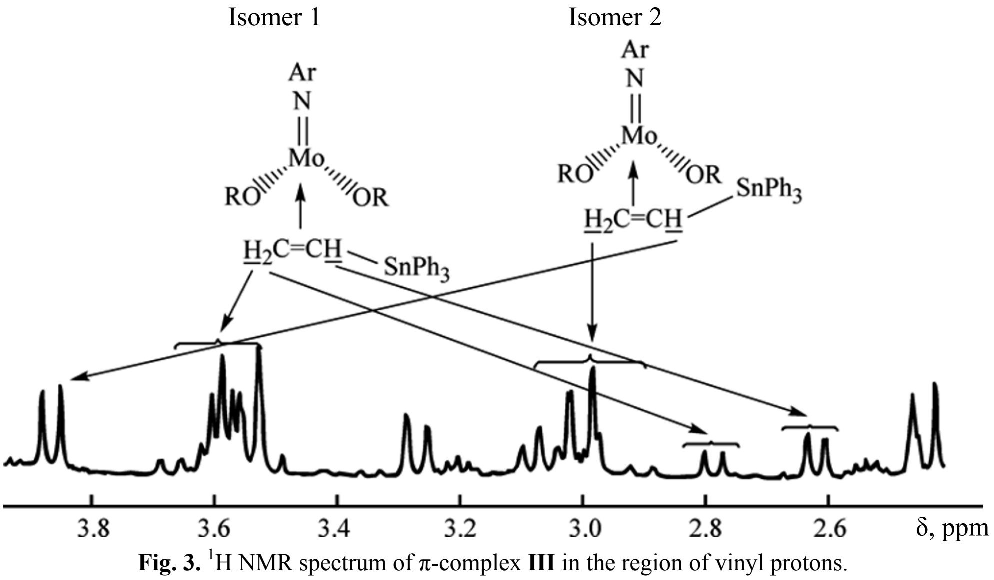
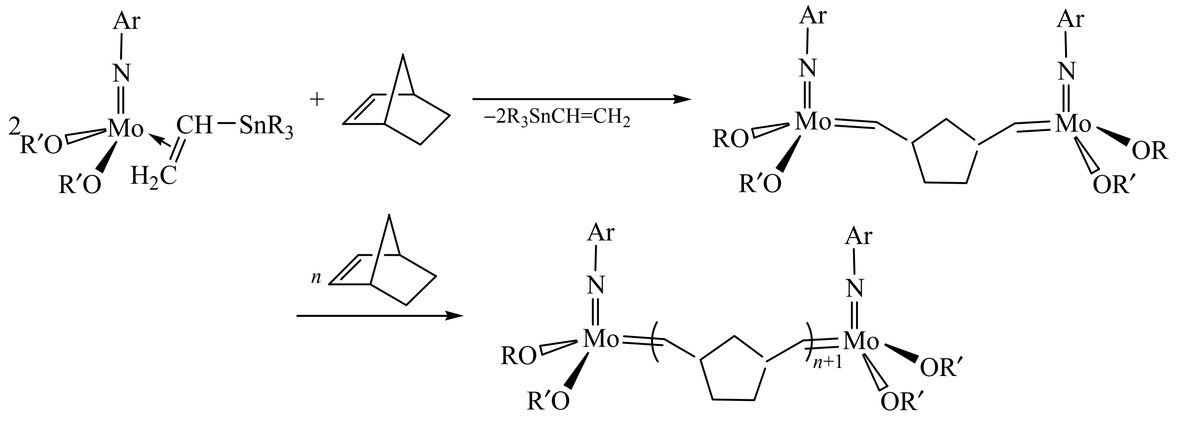


Fig. 3. ^1H NMR spectrum of π-complex **III** in the region of vinyl protons.


R = Me, Et, Ph, R' = CMe_2CF_3.

polymerization of norbornene in solution resulting in the formation of high-molecular weight polynorbornenes with a predominant content of *cis*-units.

EXPERIMENTAL

All operations were carried out in evacuated glass ampules using standard Schlenk technique. The solvents used were thoroughly purified and degassed. $PhMe_2CCH{=}Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3](OCMe_2CF_3)_2$ and $R_3SnCH{=}CH_2$ (R=Me, Et, Ph) were synthesized as described in the literature [9, 10]. Norbornene (Aldrich) was used without further purification.

NMR spectra of π-complexes **I–III** and the olefin derivatives $PhMe_2CCH{=}CHCH_2SnR_3$ were obtained on a Bruker Avance III-400 spectrometer (^1H NMR 400 MHz, ^{13}C NMR 100 MHz, ^{119}Sn NMR 149.5 MHz) in deuterobenzene, the assignment of signals was carried out using gradient 2D-spectroscopy: proton-proton correlation (GE-COSY) and proton-carbon correlation (GE-HSQC). The NMR spectra of polymer samples in deuterochloroform were obtained on a Bruker DPX-200 spectrometer (^1H NMR 200 MHz, ^{13}C NMR 50 MHz). Chemical shifts are given in ppm relative to tetramethylsilane as internal reference.

The IR spectra of compounds $PhMe_2CCH{=}CHCH_2SnR_3$ (R = Et, Me) were recorded on a FTIR spectrometer FSM 1201 from the liquid films between the KBr and CaF_2 plates.

Characteristics of the synthesized polynorbornenes (the ratio of monomer: initiator = 50:1)

Initiator	*trans*:*cis*	M_W	M_N	M_W/M_N
I	29:71	286363	225340	1.27
II	23:77	1107500	557700	1.98
III	27:73	1390000	955000	1.46

Molecular weight distribution of polymers was determined by gel permeation chromatography (GPC) on a Knauer chromatograph with a Smartline RID 2300 differential refractometer as a detector, using a set of two Phenomenex columns with the Phenogel sorbent, pore size of 10^4 and 10^5 Å (eluent THF, 2 ml min^{-1}, 40°C). Columns were calibrated with 13 polystyrene standards. Ratio of *cis*- and *trans*-units in the polynorbornene was determined by ^{13}C NMR spectroscopy using the known technique [11].

(2,6-Diisopropylphenylimido)bis(1,1-dimethyl-2,2,2-trifluoroethanolato)(trimethylvinylstannane) molybdenum (I). To a solution of 0.1 g (0.15 mmol) of $PhMe_2CC(H){=}Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(OCMe_2CF_3)_2$ in 1.5 ml of deuterobenzene 0.06 g (0.3 mmol) of $Me_3SnCH{=}CH_2$ in 1 ml of C_6D_6 was added. According to the data of ^1H NMR spectroscopy the reaction completed within 5 min at room temperature. The solvent was removed by evaporation in vacuum. The dark-red oily residue was a mixture of **I** and 2-methyl-2-phenyl-5-(trimethylstannyl)pent-3-ene. The overall yield of compounds was 0.12 g (80%). The resulting π-complex $(Me_3SnCH{=}CH_2)Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)\cdot(OCMe_2CF_3)_2$, according to the data of NMR spectroscopy, was a mixture of two isomers with a ratio of 62:38%. **Isomer 1**, 62%. ^1H NMR spectrum (C_6D_6, δ, ppm, *J*, Hz): 6.97 br.s (3H, H_{arom}), 3.82 sept (2H, $C\underline{H}Me_2$, $^3J_{HH}$ 6.8), 2.67 m (2H, $C\underline{H_2}{=}CHSnMe_3$, $^2J_{HH}$ 3.5, $^3J_{HH}$ 14.5), 2.06 t (1H, $CH_2{=}C\mathit{H}SnMe_3$, $^3J_{HH}$ 14.5), 1.36 and 1.32 s (6H each, $OC\underline{Me_2}CF_3$), 1.26 d (12H, $CH\underline{Me_2}$), 0.07 s [9H, $Sn(CH_3)_3$]. ^{13}C NMR spectrum (C_6D_6, δ, ppm, *J*, Hz): 149.6 (C_{ipso}), 145.5 (C_o), 128.0 (C_p) 126.2 q ($OCMe_2\underline{C}F_3$, $^1J_{CF}$ 276.0), 124.9 (C_m) 79.8 q ($O\underline{C}Me_2CF_3$, $^2J_{CF}$ 28.9), 58.9 ($CH_2{=}\underline{C}HSnMe_3$), 56.7 ($\underline{C}H_2{=}CHSnMe_3$), 29.2 and 28.8 ($CH\underline{Me_2}$), 28.5 ($\underline{C}HMe_2$), 23.98 and 22.9 ($OC\underline{Me_2}CF_3$), –7.89 ($SnCH_3$). **Isomer 2** (38%), ^1H NMR spectrum (C_6D_6, δ, ppm, *J*, Hz): 6.97 br.s (3H, H_{arom}), 3.82 sept (2H, $C\underline{H}Me_2$, $^3J_{HH}$ 6.8), 3.62 d (1H, $C\underline{H_2}{=}CHSnMe_3$, $^3J_{HH}$ 12.05), 2.43 d (1H, $CH_2{=}C\underline{H}SnMe_3$, $^3J_{HH}$ 12.05), 1.36 and 1.32 s (6H each, $OC\underline{Me_2}CF_3$), 1.26 d (12H, $CH\underline{Me_2}$, $^2J_{HH}$ 6.8), 0.07 s [9H, $Sn(C\underline{H_3})_3$]. ^{13}C NMR spectrum (C_6D_6, δ, ppm, *J*, Hz): 149.6 (C_{ipso}), 145.5 (C_o), 128.0 (C_p) 126.2 q ($OCMe_2\underline{C}F_3$ $^1J_{CF}$ 276.0), 124.9 (C_m), 79.8 q ($O\underline{C}Me_2F_3$, $^2J_{CF}$ 28.9), 73.8 ($CH_2{=}\underline{C}HSnMe_3$), 68.9 ($\underline{C}H_2{=}CHSnMe_3$), 29.2 and 28.8 ($CH\underline{Me_2}$), 28.5 ($\underline{C}HMe_2$), 23.98 and 22.9 ($OC\underline{Me_2}CF_3$), –7.89 ($Sn\underline{C}H_3$).

2-Methyl-2-phenyl-5-(trimethylstannyl)pent-3-ene. After fractionation of the reaction mixture in vacuum (10^{-2} mm Hg) at 100–110°C the olefin derivative $PhMe_2CCH{=}CHCH_2SnMe_3$ was isolated as air stable colorless oil. Yield 0.05 g (62%). IR spectrum, ν, cm^{-1}: 3083 w, 3060 w (C_{arom}–H), 2966 s, 2914 s, 2869 m (C–H, CH_3), 1646 w (C=C), 1600 w, 1492 m (C_{arom}–C_{arom}, Ph), 1462 m (C–H, CH_3), 1446 m (CH, CH_2Sn), 1383 w (C–H, CH_3), 1186 w (C–H, CH_3), 1100 m, 1030 m (CH, $SnMe_3$), 698 m, 763 m (C_{arom}–H), 527 m, 512 [Sn–C, $Sn(CH_3)_3$]. Signals in the ^1H and ^{13}C NMR spectra of the isolated compounds correspond to the signals of $PhMe_2CCH{=}CHCH_2SnMe_3$ in the reaction mixture prior to frac-tionation. ^1H NMR spectrum (C_6D_6, δ, ppm, *J*, Hz): 7.35 d (2H, H_{arom}, $^2J_{HH}$ 7.8), 7.30 t (2H, H_{arom}, $^2J_{HH}$ 7.4), 7.18 t (1H, H_{arom}, $^2J_{HH}$ 7.2), 5.48 m (2H, $C\underline{H}{=}C\underline{H}$, $^2J_{HH}$ 7.8, $^3J_{HH}$ 15.4), 1.76 d (2H, $C\underline{H_2}Sn$, J_{HSn} 64.4), 1.38 s (6H, $C\underline{Me_2}Ph$), 0.09 s (9H, $SnC\underline{H_3}$, J_{HSn} 51.9). ^{13}C NMR spectrum (C_6D_6, δ, ppm): 149.91 (C_{ipso}, Ph), 136.03 ($CH{=}\underline{C}H$), 127.92 (C_m, Ph), 126.23 (C_o, Ph), 125.48 (C_p, Ph), 125.06 ($\underline{C}H{=}CH$), 40.35 ($\underline{C}Me_2Ph$), 29.34 ($C\underline{Me_2}Ph$), 16.11 ($\underline{C}H_2Sn$), –10.13 ($Sn\underline{C}H_3$). ^{119}Sn NMR spectrum (C_6D_6, δ, ppm): –2.9. Found, %: C 56.19, H 7.71. $C_{15}H_{24}Sn$. Calculated, %: C 55.8, H 7.44.

(2,6-Diisopropylphenylimido)bis(1,1-dimethyl-2,2,2-trifluoroethanolato)(triethylvinylstannane)molybdenum (II). To a solution of $PhMe_2CC(H){=}Mo(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(OCMe_2CF_3)_2$ 0.11 g (0.16 mmol) in 1.5 ml of deuterobenzene 0.07 g (0.3 mmol) of $Et_3SnCH{=}CH_2$ was added at room temperature. According to the ^1H NMR spectroscopy, the reaction was completed at room temperature within 5 min. The solvent was removed by evaporation in vacuum at room temperature. The red-brown oily residue was a mixture of (2,6-diisopropylphenylimido)bis(1,1-di-methyl-2,2,2-triftoretanolato)(trimethylvinylstannane)molybdenum **II** and 2-methyl-2-phenyl-5-(triethyl-stannyl)pent-3-ene. The overall yield of compounds was 0.17 g (94%). The resulting π-complex $(Et_3SnCH{=}CH_2)Mo\cdot(N\text{-}2,6\text{-}Pr^i_2C_6H_3)(OCMe_2CF_3)_2$ was a mixture of two isomers with a ratio of 74:26%. **Isomer 1** (74%). ^1H NMR spectrum (δ, ppm, *J*, Hz): 6.97 br.s (3H, H_{arom}), 3.85 sept (2H, $C\underline{H}Me_2$, $^3J_{HH}$ 6.8), 2.70 m (2H, $C\underline{H_2}{=}CHSnEt_3$ $^3J_{HH}$ 14.5), 2.05 t (1H, $CH_2{=}C\underline{H}SnEt_3$, $^3J_{HH}$ 14.5), 1.38 and 1.35 s (6H each, $OC\underline{Me_2}CF_3$), 1.24 d (12H, $CH\underline{Me_2}$, $^2J_{HH}$ 6.5), 1.17 t (9H, $SnCH_2C\underline{H_3}$, $^2J_{HH}$ 7.9), 0.85 q (6H, $SnC\underline{H_2}CH_3$, $^2J_{HH}$ 7.8). ^{13}C NMR spectrum (C_6D_6, δ, ppm, *J*, Hz): 150.0 (C_{ipso}), 145.8 (C_o), 128.0 (C_p) 127.5 q ($OCMe_2\underline{C}F_3$, $^1J_{CF}$ 286.0), 123.3 (C_m), 79.3 q ($O\underline{C}Me_2CF_3$, $^2J_{CF}$ 28.5), 58.0 ($CH_2{=}\underline{C}HSnEt_3$), 57.9 ($\underline{C}H_2{=}CHSnEt_3$), 29.9 and 29.5 ($CH\underline{Me_2}$) , 28.6 ($\underline{C}HMe_2$), 24.1 and 23.3 ($OC\underline{Me_2}$ CF_3), 2.4 ($Sn\underline{C}H_2CH_3$), 1.02 ($SnCH_2\underline{C}H_3$). ^{119}Sn NMR spectrum (C_6D_6, δ, ppm): 36.2. **Isomer 2** (26%), ^1H NMR spectrum (C_6D_6, δ, ppm, *J*, Hz): 6.97 br.s (3H, H_{arom}), 3.85 sept (2H, $C\underline{H}Me_2$ $^3J_{HH}$ 6.8), 3.26 d.d (1H, $C\underline{H_2}{=}CHSnEt_3$ $^2J_{HH}$ 2.2, $^3J_{HH}$ 14.0), 3.11 t (1H, $CH_2{=}C\underline{H}SnEt_3$, $^3J_{HH}$ 14.0), 2.39 d.d (1H, $C\underline{H_2}{=}CHSnEt_2$ $^2J_{HH}$ 2.5, $^3J_{HH}$ 14.0), 1.38 and 1.35 s (6H each, $OC\underline{Me_2}CF_3$), 1.24 d (12H, $CH\underline{Me_2}$, $^2J_{HH}$ 6.5), 1.17 t (9H, $SnCH_2C\underline{H_3}$, $^2J_{HH}$ 7.9), 0.85 q (6H, $SnC\underline{H_2}CH_3$, $^2J_{HH}$ 7.8). ^{13}C NMR spectrum (C_6D_6, δ, ppm, *J*, Hz): 150.0 (C_{ipso}), 145.8 (C_o), 128.0 (C_p), 127.5 q ($OCMe_2\underline{C}F_3$, $^1J_{CF}$ 286.0), 123.3 (C_m), 79.3 q ($O\underline{C}Me_2CF_3$, $^2J_{CF}$ 28.5), 70.6 ($CH_2{=}\underline{C}HSnEt_3$), 66.0 ($\underline{C}H_2{=}CHSnEt_3$), 29.9 and 29.5 ($CH\underline{Me_2}$), 28.6 ($\underline{C}HMe_2$), 24.11 and 23.3 ($OC\underline{Me_2}CF_3$), 2.41 ($Sn\underline{C}H_2CH_3$), 1.02 ($SnCH_2\underline{C}H_3$). ^{119}Sn NMR spectrum (C_6D_6, δ, ppm): 91.1.

2-Methyl-2-phenyl-5-(triethylstannyl)pent-3-ene. The olefin derivative $PhMe_2CCH{=}CHCH_2SnEt_3$ was isolated by fractionation of the reaction mixture in a vacuum (10^{-2} mm Hg) at 100–110°C as air stable, colorless oil. Yield 0.04 g (80%). IR spectrum (ν, cm^{-1}: 3083 w, 3060 w, 3022 w (C_{arom}–H), 2955 m, 2943 s, 2900 s, 2865 (C–H, CH_3, CH_2), 1645 w (C=C), 1600 w, 1490 w (C_{arom}–C_{arom}, Ph), 1460 m, 1420 m (C–H, CH_3, CH_2), 1380 w, 1360 w (C–H, CH_3), 1258 w (C–H, CH_3, $C(CH_3)_2Ph$), 1232 w, 1186 w (C–H, CH_3), 1096 m, 1017 m. (C_{arom}–H, Ph), 969 m, 807 m (HC=CH), 761 m (C_{arom}–H), 742 (C–H, CH_2–Sn) 506 m (Sn–C, $SnEt_3$). ^1H NMR spectrum (C_6D_6, δ, ppm, *J*, Hz): 7.38 d (2H, H_{arom}, $^2J_{HH}$ 7.5), 7.24 t (2H, H_{arom}, $^2J_{HH}$ 7.2), 7.14 t (1H, H_{arom}, $^2J_{HH}$ 6.9), 5.57 m (2H, C$\underline{H}$=C$\underline{H}$), 1.80 d [2H, C$\underline{H}_2$Sn, J(H–^{119}Sn) 57.8], 1.39 s (6H, C$\underline{Me}_2$Ph), 1.20 m (9H, SnCH$_2$C$\underline{H}_3$, $^2J_{HH}$ 7.6.), 0.86 q (6H, SnC$\underline{H}_2$CH$_3$, $^2J_{HH}$ 8.0). ^{13}C NMR spectrum (C_6D_6, δ, ppm): 149.71 (C$_{ipso}$), 136.02 (CH=$\underline{C}$H), 128.0 (C$_m$), 126.3 (C$_o$), 125.6 (C$_p$) 125.4 ($\underline{C}$H=CH), 40.2 ($\underline{C}$Me$_2$Ph), 29.2 (C$\underline{Me}_2$Ph), 13.02 ($\underline{C}$H$_2$Sn), 10.9 (SnCH$_2\underline{C}$H$_3$), 0.37 (Sn$\underline{C}$H$_2$CH$_3$). ^{119}Sn NMR spectrum (C_6D_6, δ, ppm): –4.9. Found, %: C 59.42, H 8.29. $C_{18}H_{30}Sn$. Calculated, %: C 59.23, H 8.23.

(2,6-Diisopropylphenylimido)bis(1,1-dimethyl-2,2,2-trifluoroethanolato)(triphenylvinylstannane)molybdenum (III). To a solution of 0.14 g (0.21 mmol) of PhMe$_2$CC(H)=Mo(N-2,6-Pr$^i_2$C$_6$H$_3$)(OCMe$_2$CF$_3$)$_2$ in 1.5 ml of deuterobenzene a solution of 0.12 g (0.31 mmol) of Ph$_3$SnCH=CH$_2$ in 1 ml of C_6D_6 was added at room temperature. According to the ^{1}H NMR spectroscopy the reaction at room temperature completed within 10 min. The solvent was removed by evaporation in vacuum at room temperature. The red-brown oily residue was a mixture of (2,6-diisopropylphenylimido)bis(1,1-dimethyl-2,2,2-trifluoroetanolato)(triphenylvinylstannane)molybdenum (**III**) and 2-methyl-2-phenyl-5-(triphenylstannyl)pent-3-ene. The overall yield 0.26 g (96%). NMR study showed that π-complex (Ph$_3$SnCH=CH$_2$)Mo(N-2,6-Pr$^i_2$C$_6$H$_3$)(OCMe$_2$CF$_3$)$_2$ in C_6D_6 consisted of two isomers with a ratio of 50: 50%. **Isomer 1**. ^{1}H NMR spectrum (C_6D_6, δ, ppm, J, Hz): 7.23–6.90 m (15H, Sn$\underline{Ph}_3$), 7.03 br.s [3H, 2,6-(Pr-i)$_2$C$_6\underline{H}_3$], 3.99 sept (2H, C$\underline{H}$Me$_2$, $^3J_{HH}$ 6.8), 3.56 m (1H, C$\underline{H}_2$=CHSnPh$_3$), 2.78 d (1H, C$\underline{H}_2$=CHSnPh$_3$), 2.60 d (1H, CH$_2$=C$\underline{H}$SnPh$_3$), 1.38 and 1.35 s (6H each, OC$\underline{Me}_2$CF$_3$), 1.25 d (12H, CH$\underline{Me}_2$, $^2J_{HH}$ 6.5). ^{13}C NMR spectrum (C_6D_6, δ, ppm): 152.8, 145.2, 136.8, 137.2, 128.9, 128.4 (C$_{arom}$), 127.5 (OCMe$_2\underline{C}$F$_3$), 122.6 (C$_{arom}$), 79.8 (O$\underline{C}$Me$_2$CF$_3$), 57.6 ($\underline{C}$H$_2$=CHSnPh$_3$), 54.9 (CH$_2$= $\underline{C}$HSnPh$_3$), 29.9 and 29.5 (CH$\underline{Me}_2$), 28.6 ($\underline{C}$HMe$_2$), 24.1 and 23.3 (OC$\underline{Me}_2$CF$_3$). **Isomer 2.** ^{1}H NMR spectrum (C_6D_6, δ, ppm, J, Hz): 6.90–7.23m (15H, SnPh$_3$), 7.03 br.s [3H, 2,6-(Pr-i)$_2$C$_6\underline{H}_3$], 3.99 sept (2H, C$\underline{H}$Me$_2$, $^3J_{HH}$ 6.8), 3.88 d (1H, CH$_2$=C$\underline{H}$SnPh$_3$, $^3J_{HH}$ 12.04), 3.08 d (2H, C$\underline{H}_2$=CHSnPh$_3$, $^3J_{HH}$ 12.04), 1.38 and 1.35 s (6H each, OC$\underline{Me}_2$CF$_3$), 1.25 d (12H, CH$\underline{Me}_2$, $^2J_{HH}$ 6.5). ^{13}C NMR spectrum (C_6D_6, δ, ppm): 152.8, 145.2, 136.8, 137.2, 128.9, 128.4 (C$_{arom}$) 126.2 q (OCMe$_2\underline{C}$F$_3$), 122.6 (C$_{arom}$), 79.8 (O$\underline{C}$Me$_2$CF$_3$), 79.6 (CH$_2$=$\underline{C}$HSnPh$_3$), 68.2 ($\underline{C}$H$_2$=CHSnPh$_3$), 29.9 and 28.8 (CH$\underline{Me}_2$), 28.6 ($\underline{C}$HMe$_2$), 24.1 and 23.3 (OC$\underline{Me}_2$CF$_3$).

The norbornene metathesis polymerization. Into an ampule containing 0.03 g (0.04 mmol) of π-complex **I** (equimolar mixture with PhMe$_2$C–CH=CHCH$_2$SnMe$_3$) in 1 ml of benzene 0.60 g (6.38 mmol) of norbornene in 1 ml of benzene was charged at room temperature. After 3 min the reaction mixture became viscous. The resulting polymer was dissolved in THF and benzaldehyde was added for the decomposition of the catalyst. Then polymer precipitated with methanol, purified by reprecipitation three times with methanol from THF and dried in vacuum at room temperature until the weight was unchanged. The polymer yield 0.57 g (96%). Experiments on the polymerization of norbornene with the initiators **II** and **III** were carried our similarly.

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