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Preparation and structure of the first *ansa*-molybdenocene and tungstenocene derivatives. Reaction of $[O(SiMe_2C_5H_4)_2]MoH_2$ with methyl methacrylate to probe the olefin attacking site

Takaya Mise [a], Mami Maeda [b], Takayuki Nakajima [c], Kimiko Kobayashi [a], Isao Shimizu [c], Yasuhiro Yamamoto [b] and Yasuo Wakatsuki [a]

[a] *The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01 (Japan)*
[b] *Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274 (Japan)*
[c] *Department of Applied Chemistry, School of Science and Engineering, Waseda University, 3-4-1 Ookubo, Shinjuku-ku, Tokyo 169 (Japan)*

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Abstract

Bridged-bis(cyclopentadienyl) molybdenum and tungsten dihydrides and their derivatives have been synthesized for the first time. [(1,1,3,3-Tetramethyldisiloxane-1,3-diyl)bis(η^5-cyclopentadienyl)]molybdenum dihydride (**1a**) and tungsten dihydride (**1b**) were prepared by sodium borohydride reduction of $[O(SiMe_2C_5H_4)_2]MCl_2$ (**2a**: M = Mo, **2b**: M = W) which was obtained by the reaction of disodium 1,1,3,3-tetramethyl-1,3-bis(cyclopentadienyl)disiloxane with $MCl_4(thf)_2$ (M = Mo, W). The dichlorides **2** reacted with $ZnMe_2$ and NaSEt to afford $[O(SiMe_2C_5H_4)_2]MMe_2$ (**3a**: M = Mo, **3b**: M = W) and $[O(SiMe_2C_5H_4)_2]M(SEt)_2$ (**4a**: M = Mo, **4b**: M = W), respectively. Photolysis of **1b** in benzene gave $[O(SiMe_2C_5H_4)_2]WH(C_6H_5)$ (**5b**). An X-ray crystal analysis of **3a** has proved that the bridging chain blocks one of the side positions of the complex, the siloxy unit being present at one side of the Me–Mo–Me bisector. Consistent with side position attack by olefins, the reaction rate of **1a** with methyl methacrylate was found to be nearly one half that of the parent Cp_2MoH_2 (**6a**).

Key words: Molybdenum; Tungsten; Metallocenes; Methyl methacrylate; Bridging ligand

1. Introduction

Bridging of two cyclopentadienyl ligands in titanocene, zirconocene and hafnocene dichloride has attracted considerable attention in relation to Kaminsky-type stereospecific polymerization of propylene [1,2]. However, *ansa*-metallocene derivatives of other early transition metals are represented by only a few examples, which have not been known for molybdenum and tungsten [3]. In general, introduction of substituents into the cyclopentadienyl ring in molybdenocene and tungstenocene derivatives seems to be difficult; ethyl- and pentamethyl-cyclopentadienyl derivatives have been successfully prepared only by metal-vapour synthesis [4]. Furthermore, the metal-vapour technique may not be applied for the reaction of bridged-bis(cyclopentadiene) because predominance of the intermolecular reaction is expected which leads to dinuclear or polynuclear metal compounds. Here, we report the first successful synthesis of bridged molybdenocene and tungstenocene type complexes, where the bridging group is $-Me_2Si-O-SiMe_2-$. The rates of reaction with an olefin of bridged and unbridged molybdenocene dihydrides are also compared to elucidate the mechanism of olefin attack by metallocene dihydrides in the olefin hydrogenation reaction.

2. Results and discussion

2.1. *Syntheses of disiloxane-bridged molybdenocene and tungstenocene derivatives*

Application of the conventional route for molybdenocene dihydride, *i.e.* the reaction *in situ* of $MoCl_5$ and $Na_2[O(SiMe_2C_5H_4)_2]$ followed by addition of $NaBH_4$ in refluxing THF, did not give any identifiable

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Correspondence to: Dr. T. Mise or Dr. Y. Wakatsuki.

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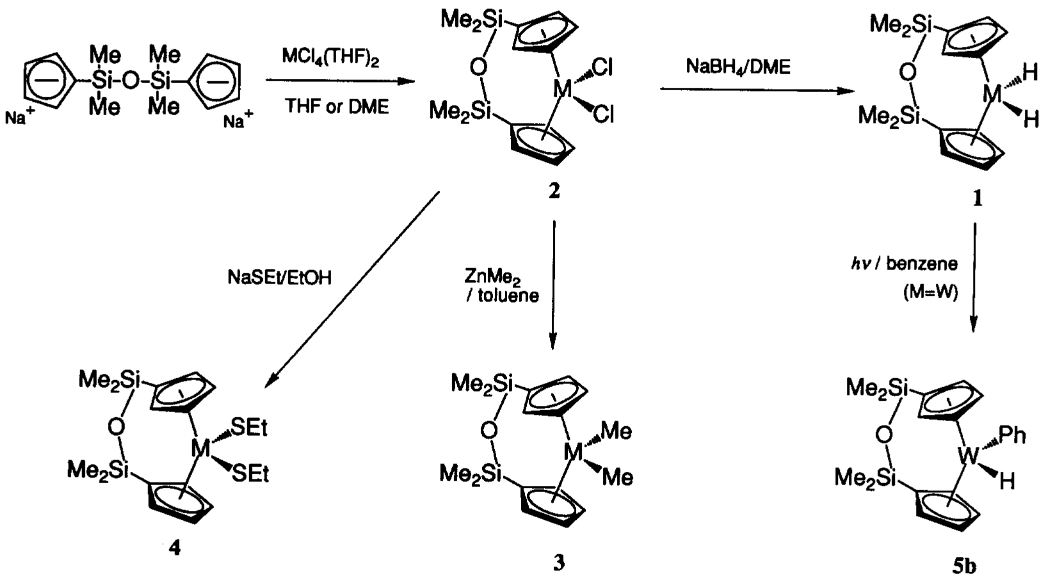
Mo complex. As a starting complex to synthesize the present molybdenum system, a bridged molybdenocene dichloride was found to be most appropriate: dichloro[(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(η^5-cyclopentadienyl)]-molybdenum (**2a**) could be prepared in 59% crude yield by the reaction of 1,3-bis(cyclopentadienyl)disiloxane with NaH in THF and subsequent treatment with $MoCl_4(THF)_2$. Since dichloride **2a** is sparingly soluble in organic solvents, as is Cp_2MoCl_2 ($Cp = \eta^5 - C_5H_5$), it could not be well characterized. However, successful transformation of **2a** into several derivatives described below shows that **2a** is thus obtained in moderate purity.

Reduction of **2a** with $NaBH_4$ in refluxing THF did not give the desired $[O(SiMe_2C_5H_4)_2]MoH_2$ (**1a**). At elevated reaction temperature, *i.e.* in refluxing DME, **1a** was found to be formed in only a trace amount. The major difficulty in this reaction seems to arise from very low solubility of **2a**: once isolated as solid, it does not dissolve at all in refluxing THF or DME. We concluded that the best way is to prepare **2a** in DME, in which some of the **2a** dissolves as is indicated by its colour though most precipitates at the bottom of the flask, and immediately to add excess $NaBH_4$ and then to reflux for several hours. This procedure afforded **1a** in 18% overall yield. The dihydride **1a** forms pale-yellow crystals which are unstable in air and decompose to a dark-brown solid.

The dimethyl derivative of ansa-molybdenocene, $[O(SiMe_2C_5H_4)_2]MoMe_2$ (**3a**), could not be obtained by the reaction of **2a** with MeLi or MeMgBr in THF. Instead, moderately air-stable orange crystals of **3a** were successfully isolated by the reaction of **2a** with $ZnMe_2$ in toluene at room temperature in 85% yield. The mass spectrum of **3a** shows the molecular ion (m/z 388 (^{98}Mo)) and two peaks corresponding to a stepwise loss of the methyl ligands. Reaction of **3a** with H_2 (140 kg/cm^2) in toluene at 105°C for 17 h gave a 1:1 mixture of dihydride **1a** and unreacted **3a**, providing another potential route to the dihydride complex.

The complex $[O(SiMe_2C_5H_4)_2]Mo(SEt)_2$ (**4a**) was prepared by the reaction of **2a** with NaSEt in refluxing ethanol and purified by column chromatography to give air-stable orange crystals in 33% yield. The mononuclear nature of **4a** was confirmed by the molecular weight determination by mass spectrum (m/z 480 (M^+, ^{98}Mo)).

Disiloxane-bridged tungstenocene analogues were prepared by the same procedure as that for molybdenum. Pale-yellow crystals of $[O(SiMe_2C_5H_4)_2]WH_2$ (**1b**) were isolated in 8% overall yield. Dimethyl $[O(SiMe_2C_5H_4)_2]WMe_2$ (**3b**) and dithiolate $[O(SiMe_2C_5H_4)_2]W(SEt)_2$ (**4b**) were isolated as yellow-orange (14% yield) and orange crystals (16% yield), respectively. Dichloride $[O(SiMe_2C_5H_4)_2]WCl_2$ (**2b**) is less reactive than the molybdenum counterpart and complexes derived from it are obtained in lower yields. Once formed, as expected, the tungsten derivatives are much more stable in air than the molybdenum analogues. Photolysis of Cp_2WH_2 (**6b**) in the presence of aromatic solvents (ArH) has been known to produce $Cp_2WH(Ar)$ via C–H bond activation of aromatics [5]. Photolysis of **1b** in benzene solution similarly gave $[O(SiMe_2C_5H_4)_2]WH(Ph)$ (**5b**) in 86% yield.



Scheme 1.

The hydride absorption in ^1H NMR spectrum of **1a** was observed at $\delta - 8.70$ (s) which is very close to the value of -8.80 (s) for Cp_2MoH_2 (**6a**) but rather different from the corresponding resonances at δ -8.25 (s) and -8.18 (s) in $(MeC_5H_4)_2MoH_2$ [6] and $(Me_5C_5)_2MoH_2$ [7]. In the tungsten analogue, the value is $\delta - 11.82$ (t) for **1b** compared to -12.25 (t) for Cp_2WH_2 (**6b**). In the dimethyl complexes, the methyl proton resonances of **3a** and **3b** are at $\delta - 0.02$ and 0.02, respectively, which are comparable to the unbridged Cp_2MoMe_2 (δ 0.22) and Cp_2WMe_2 (δ 0.37). The ^{13}C NMR spectrum of **3a** exhibits the metal bonded Me absorption at $\delta - 12.1$ while the parent Cp_2MoMe_2 shows that absorption at -8.9 ppm. The ^{13}C NMR absorption for the W–Me in **3b** is observed at $\delta - 26.5$. The NMR peaks of methylene and methyl protons in **4a** (δ 2.19, 1.21) and **4b** (δ 2.29, 1.18) are observed at positions close to those of $Cp_2Mo(SEt)_2$ (δ 2.21, 1.21) and $Cp_2W(SEt)_2$ (2.33, 1.15) [8].

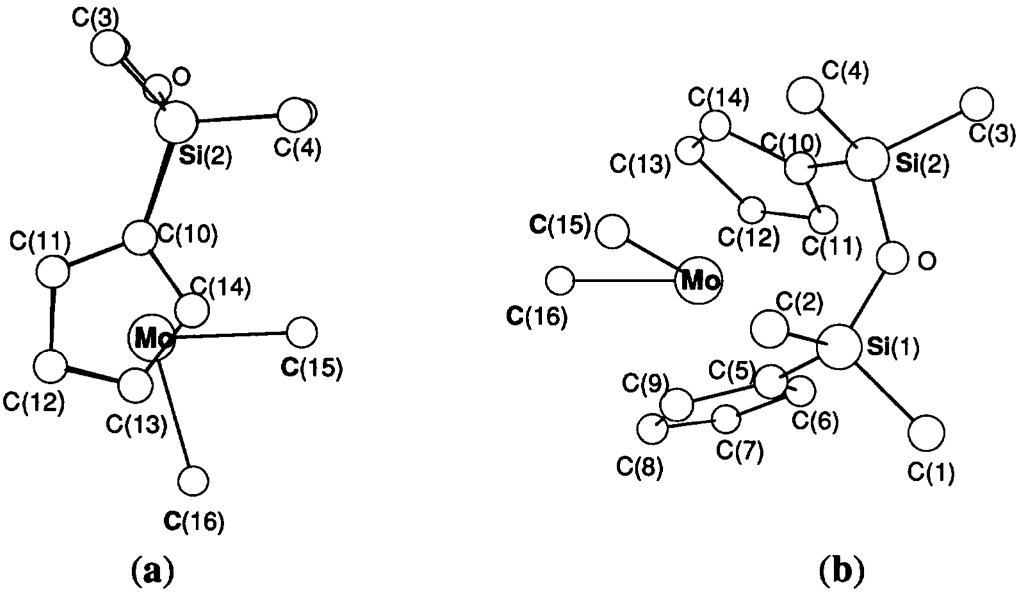
TABLE 1. Atomic coordinates and equivalent temperature factors (Å^2)

	x	y	z	B_{eq}
Mo	0.5514(1)	0.43766(3)	0.3526(1)	2.3
Si(1)	0.2270(2)	0.3847(1)	0.1569(1)	2.8
Si(2)	0.5386(2)	0.2759(1)	0.1603(1)	2.8
O	0.3739(5)	0.3345(3)	0.1172(3)	2.8
C(1)	0.1037(10)	0.4503(7)	0.0582(5)	4.8
C(2)	0.1002(10)	0.2946(7)	0.2002(7)	5.0
C(3)	0.6493(10)	0.2602(7)	0.0642(6)	4.8
C(4)	0.4885(11)	0.1606(6)	0.2061(6)	4.9
C(5)	0.3147(8)	0.4690(5)	0.2492(4)	2.7
C(6)	0.4320(9)	0.5410(5)	0.2439(4)	3.0
C(7)	0.4676(10)	0.5921(5)	0.3291(5)	3.7
C(8)	0.3701(9)	0.5538(6)	0.3861(5)	3.7
C(9)	0.2787(8)	0.4792(6)	0.3401(5)	3.3
C(10)	0.6644(7)	0.3447(5)	0.2549(4)	2.6
C(11)	0.7185(8)	0.4402(6)	0.2500(5)	3.2
C(12)	0.8140(9)	0.4688(6)	0.3391(5)	4.0
C(13)	0.8221(8)	0.3880(6)	0.3955(5)	4.0
C(14)	0.7319(9)	0.3130(6)	0.3475(5)	3.5
C(15)	0.4413(11)	0.3130(6)	0.4126(6)	4.8
C(16)	0.6194(12)	0.4603(8)	0.5075(5)	5.4

2.2. *Structure of 3a and other derivatives*

The molecular structure of **3a** has been determined by a single-crystal X-ray diffraction analysis. Selected bond distances and angles are summarized in Tables 1 and 2. The bridged-bis(cyclopentadienyl) framework of **3a** (Fig. 1) is identical to that of $[O(SiMe_2C_5H_4)_2]TiCl_2$ [9] where the bridging $Me_2SiOSiMe_2$ group lies on one side of the bisector of the Cl–Ti–Cl or Me–Mo–Me angle. The Me–Mo–Me angle (75.7(4)°) and the Mo–Me bond lengths (2.264(10) and 2.278(7) Å) are very close to the C–Mo–C angle and the Mo–C bond lengths found in the unbridged complex $Cp_2Mo(^nBu)_2$, 76.6(2)°, 2.268(4) and 2.272(4) Å [10]. The Cp–Mo–Cp bite angle of 134.4(3)° is also comparable to the angle in $Cp_2Mo(^nBu)_2$ (135.2(1)°). Therefore, the bridging Si–O–Si group causes virtually no strain in the metallocene moiety.

The solid state structure shown in Fig. 1 indicates that the two methyl groups on the silicon are inequivalent. In ^1H NMR spectra of complexes **1–4**, the Si–Me resonances were observed as a sharp singlet showing that "to and fro" movement of the $Me_2SiOSiMe_2$



(a) (b)

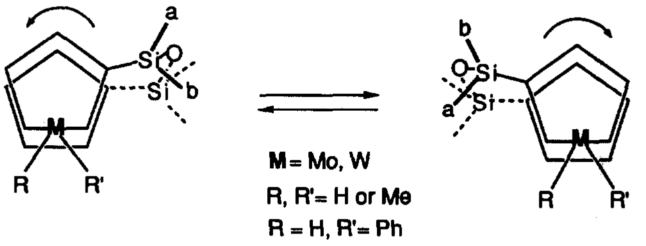
Fig. 1. Molecular structure of **3a**.

TABLE 2. Selected bond distances (Å) and angles (°)

Bond distances			
Mo–C(15)	2.264(10)	Mo–C(16)	2.278(7)
Mo–C(5)	2.306(6)	Mo–C(10)	2.305(7)
Mo–C(6)	2.261(7)	Mo–C(11)	2.276(8)
Mo–C(7)	2.308(7)	Mo–C(12)	2.312(8)
Mo–C(8)	2.371(8)	Mo–C(13)	2.356(7)
Mo–C(9)	2.350(7)	Mo–C(14)	2.348(8)
C(5)–C(6)	1.437(10)	C(10)–C(11)	1.438(11)
C(6)–C(7)	1.437(10)	C(11)–C(12)	1.460(10)
C(7)–C(8)	1.404(12)	C(12)–C(13)	1.413(12)
C(8)–C(9)	1.404(11)	C(13)–C(14)	1.415(11)
C(9)–C(5)	1.449(10)	C(14)–C(10)	1.450(9)
Si(1)–O	1.641(5)	Si(2)–O	1.637(5)
Si(1)–C(5)	1.856(7)	Si(2)–C(10)	1.858(6)
Si(1)–C(1)	1.865(8)	Si(2)–C(3)	1.870(10)
Si(1)–C(2)	1.864(10)	Si(2)–C(4)	1.853(9)
Bond angles			
C(15)–Mo–C(16)	75.7(4)	Si(1)–O–Si(2)	136.6(3)
Cp(c) [a]–Mo–Cp(c)	140.1	Cp–Mo–Cp	134.4(3)
O–Si(1)–C(1)	106.2(3)	O–Si(2)–C(3)	106.3(3)
O–Si(1)–C(2)	110.8(4)	O–Si(2)–C(4)	110.7(3)
O–Si(1)–C(5)	109.0(3)	O–Si(2)–C(10)	109.9(3)
C(1)–Si(1)–C(2)	110.1(4)	C(3)–Si(2)–C(4)	111.2(5)
C(5)–C(6)–C(7)	109.6(6)	C(10)–C(11)–C(12)	109.9(6)
C(6)–C(7)–C(8)	106.9(6)	C(11)–C(12)–C(13)	105.2(7)
C(7)–C(8)–C(9)	109.3(7)	C(12)–C(13)–C(14)	110.9(6)
C(8)–C(9)–C(5)	109.3(7)	C(13)–C(14)–C(10)	108.2(7)
C(9)–C(5)–C(6)	104.9(6)	C(14)–C(10)–C(11)	105.8(6)

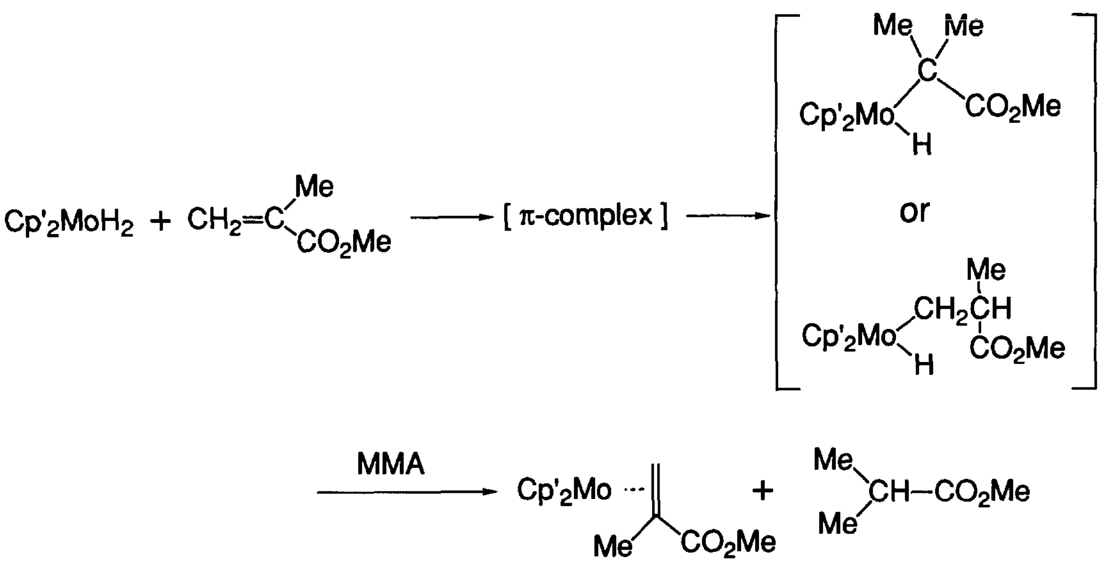
[a] Cp(c) = ring centroid.

group across the R–M–R (M = Mo, W; R = H, Me, SEt) bisector is faster than the NMR time scale, the same fluxional phenomena already observed for $[O(SiMe_2C_5H_4)_2]TiCl_2$ [9]. To check if this motion is affected by the bulkiness of the group R which is directly bound to the metal, the low temperature NMR spectrum of **5b**, where R = H and R′ = Ph, was examined. Two sharp singlets in equal intensity at δ 0.32 and 0.23, however, remained unchanged from room temperature down to −80°C indicating that the motion illustrated below is fairly facile and this "to and fro" half rotation of the bridged Cp rings is not slowed down by substituting metal-bound hydrogen with the bulkier phenyl group [11*].



2.3. Reaction of 1a with methyl methacrylate

Stoichiometric hydrogenation of olefins bearing electron-withdrawing substituents by molybdenocene or tungstenocene dihydride has attracted interest as a model of transition metal-catalyzed olefin hydrogenations. Detailed mechanistic study by Nakamura and Otsuka [12] has suggested that **6a** and olefin form σ-DA and σπ-EDA complexes prior to insertion which



Scheme 2.

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* Reference number with asterisk indicates a note in the list of references.

makes the room temperature reaction kinetics very complicated. Yet a third π-complex has been suggested, which leads to the insertion product and whose formation is a rate-determining step. Based on molecular orbital considerations, they speculated that this π-complex formation would take place at the side position of the complex and not at the open side of the wedged metallocene, *i.e.* coordination of olefin at the position between the two hydrogen ligands is unlikely. In the case of hydrozirconation of olefins by $Cp_2Zr(H)Cl$, however, recent theoretical calculation has shown that ethylene attacks between the Cl and H ligands [13].

In the present bridged-molybdenocene dihydride the bridging group blocks efficiently one of the two side positions of the wedge shaped molecule without causing strain, as confirmed by X-ray analysis of **3a**. Further, direct steric interaction between the bridging group and hydride ligand must be negligible as inferred from Fig. 1(a). NMR based evaluation of electronic effect of the bridging $O(SiMe_2)_2$ group on the hydride ligand is difficult. However, comparison of IR ν (M–H) vibrations (**1a**, 1818; **6a** 1826 cm^{-1} in CH_2Cl_2) indicates that the M–H bond energy is virtually identical in the bridged and unbridged dihydride complexes. Complex **1a** should therefore be an ideal probe to check where an olefin will attack. If it attacks between the two hydride ligands, the bridged and unbridged molybdenocene dihydride should exhibit similar reaction rates while if it attacks the side positions, the rate will be slower in the bridged molybdenocene dihydride.

We chose the reactions of methyl methacrylate (MMA) with **1a** and **6a** (Scheme 2) since the reactions of 1,1-disubstituted olefins were found to be much slower than those of monosubstituted or 1,2-disubstituted olefins and suitable for rate measurement at elevated temperatures. The long induction period and S-shaped time-conversion curve observed by Nakamura and Otsuka in the room temperature reaction of **6a** with diethyl fumarate was found to be negligible in the present reaction system at 90.0°C. The reaction was carried out in C_6D_6 solution with a molar ratio MMA/(**1a** or **6a**) of 4 in sealed NMR tubes. The conversion was monitored by decrease of the peak intensities of the hydride protons of the starting complex **1a** or **6a**. The time-conversion curves thus obtained for the early stage of the reaction (up to *ca.* 15% conversion) are plotted in Fig. 2. Our finding that the reaction rate of **1a** towards MMA is about half that observed for **6a** is in full agreement with the side position attack of the olefin discussed above.

3. Experimental details

3.1. General

Most manipulations were performed in a dry oxygen-free argon atmosphere. Solvents were purified by standard methods and freshly distilled (from Na-benzophenone or CaH_2) under argon before use. The starting materials and complexes $MoCl_4(THF)_2$ [14], $WCl_4(THF)_2$ [15], 1,1,3,3-tetramethyl-1,3-bis(cyclopentadienyl)disiloxane [9], $ZnMe_2$ [16], Cp_2MoH_2 [17],

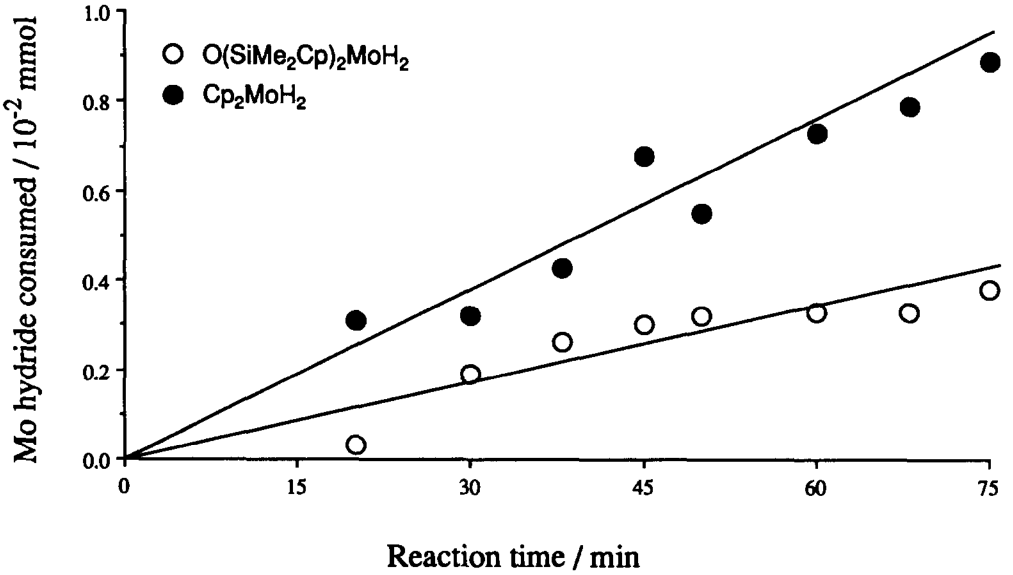

Fig. 2. Initial reaction rate for the reaction of MMA (4 molar excess) with **1a** (○) and **6a** (●) in C_6D_6 at 90.0°C.

Cp_2WH_2 [17] were obtained by published procedures. All other reagents were commercially obtained. ^1H- and ^{13}C-NMR spectra were measured on a JEOL EX-270 spectrometer and IR spectra were recorded on a Perkin Elmer FT-1650 spectrometer using CaF_2 liquid cell. EI-MS analyses were undertaken on a Hitachi M-80 spectrometer. Elemental analyses were performed by the Chemical Analysis Laboratory of this institute.

3.2. Preparation of dichloro [(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(η^5-cyclopentadienyl)]molybdenum (2a)

To a stirred suspension of NaH (1.0 g, 41.6 mmol) in THF (70 ml) was added 1,1,3,3-tetramethyl-1,3-bis(cyclopentadienyl)disiloxane (4.84 g, 18.4 mmol) at 0°C and the resulting mixture was stirred at room temperature for 4.5 h to give pink-red suspension. The suspension was added dropwise at 0°C to $MoCl_4(THF)_2$ (7.04 g, 18.4 mmol) in THF (80 ml) and stirred at room temperature for 15 h. The resulting maroon mixture was filtered and the filtrate was evaporated and washed with hexane (3 × 10 ml) and dried *in vacuo* to afford brown powder solid (4.63 g, crude yield 59%). The ^1H NMR spectrum of dichloride **2a** was measured using a sample prepared *in situ i.e.* treatment of dihydride **1a** with $CDCl_3$ at 60°C for 1 h in a sealed NMR tube: δ 6.00 and 5.40 (t, CpH, $J = 2.0$), 0.36 (s, SiMe).

3.3. Preparation of dichloro [(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(η^5-cyclopentadienyl)]tungsten (2b)

To a stirred suspension of NaH (0.28 g, 11.7 mmol) in THF (25 ml) was added 1,1,3,3-tetramethyl-1,3-bis(cyclopentadienyl)disiloxane (1.36 g, 5.1 mmol) at 0°C and the resulting mixture was stirred at room temperature for 5 h to give a purple suspension. The suspension was added dropwise at 0°C to $WCl_4(THF)_2$ (2.35 g, 5.0 mmol) in THF (30 ml) and stirred at room temperature for 40 h. The resulting dark-brown mixture was filtered and the filtrate was evaporated, washed with hexane (3 × 10 ml) and dried *in vacuo* to afford a brown powder (1.80 g, crude yield 70%).

3.4. Synthesis of [(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(η^5-cyclopentadienyl)] dimethylmolybdenum (3a)

To a stirred suspension of crude **2a** (0.50 g, 1.2 mmol) in toluene (40 ml) was added $ZnMe_2$/toluene 1 M solution (5.0 ml) at 0°C and the mixture was stirred at room temperature for 5.5 h. The resulting dark-brown mixture was filtered and washed with toluene (5 × 10 ml). The orange-brown filtrate was evaporated to dryness to yield orange solid (0.39 g, 0.99 mmol, 85%). MS: m/z 388 (M^+, ^{98}Mo), 373 (M − Me), 358 (M − 2Me). ^1H NMR (C_6D_6): δ 4.47 and 3.87 (t, CpH, $J = 2.3$), 0.27 (s, SiMe), −0.02 (s, Me). ^{13}C NMR (C_6D_6): δ 97.2, 93.8 and 78.4 (Cp), 0.7 (SiMe), −12.1 (MoMe).

The analytically pure sample (mp 173–174°C) was obtained by vacuum sublimation (100°C/10^{-2} mmHg). Anal. Found: C, 49.29; H, 6.84. $MoC_{16}H_{26}OSi_2$ calcd.: C, 49.72; H, 6.78%.

3.5. Synthesis of [(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(η^5-cyclopentadienyl)] dimethyltungsten (3b)

A stirred suspension of crude **2b** (0.40 g, 0.8 mmol) in toluene (30 ml) was treated with $ZnMe_2$/toluene 2 M solution (1.6 ml) at 0°C and stirred at room temperature for 23 h. The resulting yellow-black mixture was filtered and washed with toluene (3 × 10 ml). The yellow-black filtrate was evaporated to dryness and purified by vacuum sublimation (120°C/10^{-2} mmHg) to yield yellow-orange crystals (0.05 g, 0.11 mmol, 14%). ^1H NMR (C_6D_6): δ 4.49 and 3.63(t, CpH, $J = 2.3$), 0.31 (s, SiMe), 0.02 (s, Me). ^{13}C NMR (C_6D_6): δ 93.7, 91.1, and 71.8 (Cp), 0.7 (SiMe), −26.5 (WMe).

The analytically pure sample was obtained by recrystallization from toluene as orange needles (mp 189–190°C). Anal. Found: C, 40.57; H, 5.44. $WC_{16}H_{26}OSi_2$ calcd.: C, 40.51; H, 5.52%.

3.6. Preparation of [(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(η^5-cyclopentadienyl)]bis(ethanethiolate)molybdenum (4a) and tungsten (4b)

To a suspension of crude **2a** (0.50 g, 1.2 mmol) in ethanol (30 ml) were added ethanethiol (0.16 ml, 2.1 mmol) and sodium hydroxide (0.08 g, 2.0 mmol) in water (5 ml) and the mixture was heated under reflux for 3 h. The solvent was removed under vacuum and the residue was extracted with dichloromethane (150 ml) and water (100 ml), washed with water (2 × 50 ml) and dried on Na_2SO_4. Dichloromethane was evaporated and the residue was washed with hexane (7 × 10 ml) and dried under vacuum to give dark-brown solid. The solid was resolved in a minimum amount of dichloromethane and chromatographed on an alumina column (Al_2O_3/10 wt% H_2O) to give an orange band. The orange band eluted with dichloromethane was collected and evaporated to dryness to yield air-stable orange crystals (0.18 g, 0.38 mmol, 33%). MS: m/z 480 (M^+, ^{98}Mo), 419 (M − SEt), 358 (M − 2SEt). ^1H NMR ($CDCl_3$): δ 5.55 and 4.98 (t, CpH $J = 2.3$), 2.19 (q, SCH_2), 1.21 (t, SCH_2Me), 0.36 (s, SiMe).

The analytically pure sample was obtained by recrystallization from ether as orange needles (mp 194–195°C). Anal. Found: C, 45.15; H, 6.32. $MoC_{18}H_{30}OS_2Si_2$ calcd.: C, 45.17; H, 6.32%.

The tungsten analogue **4b** was prepared by a similar procedure to give air-stable orange crystals in 16%

yield. ^{1}H NMR ($CDCl_3$): δ 5.56 and 4.76 (t, CpH $J = 2.3$), 2.29 (q, SCH_2), 1.18 (t, SCH_2Me), 0.40 (s, SiMe).

3.7. Synthesis of [(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(η^5-cyclopentadienyl)] dihydridomolybdenum (1a)

To a stirred suspension of NaH (0.90 g, 41.6 mmol) in DME (100 ml) was added 1,1,3,3-tetramethyl-1,3-bis(cyclopentadienyl)disiloxane (4.35 g, 16.6 mmol) at 0°C and the resulting mixture was stirred at room temperature for 4 h to give a pale-pink suspension. The suspension was added at 0°C in dropwise to a solution of $MoCl_4$ $(THF)_2$ (3.90 g, 10.2 mmol) in DME (100 ml) and the mixture was gradually warmed to room temperature to give a red-brown suspension which was stirred at room temperature for a further 16 h. To the resulting maroon mixture was added $NaBH_4$ (1.21 g, 32 mmol) and it was refluxed for 7 h. The solvent was evaporated and the residue was extracted with toluene (150 ml) and filtered through a glass filter. The dark red-brown filtrate was evaporated to dryness to yield dark-brown solid **1a** (2.46 g). A pure sample of **1a** was obtained by vacuum sublimation at 120°C/10^{-2} mmHg as pale-yellow crystals (mp158–160°C, 0.66 g, 1.8 mmol, 18% yield based on $MoCl_4$ $(THF)_2$ used). ^{1}H NMR (C_6D_6): δ 4.71 and 4.20 (t, CpH, $J = 2.0$), 0.29 (s, SiMe), -8.70 (s, H). ν(Mo–H): 1818 cm^{-1} (CH_2Cl_2). Anal. Found: C, 47.34; H, 6.31. $MoC_{14}H_{22}OSi_2$ calcd.: C, 46.91; H, 6.19%.

3.8. Synthesis of [(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(η^5-cyclopentadienyl)] dihydridotungsten (1b)

To a stirred suspension of NaH (1.83 g, 76.3 mmol) in DME (100 ml) was added 1,1,3,3-tetramethyl-1,3-bis(cyclopentadienyl)disiloxane (9.53 g, 36.3 mmol) at 0°C and the resulting mixture was stirred at room temperature for 4 h to give a pale-pink suspension. The suspension was added dropwise at 0°C to a solution of $WCl_4(THF)_2$ (17.0 g, 36.3 mmol) in DME (210 ml) and the mixture was gradually warmed to room temperature, which turned to red-brown, and stirred at room temperature for 24 h. The resulting dark-brown mixture was treated with $NaBH_4$ (3.57 g, 94.4 mmol) and refluxed for 14 h. The solvent was evaporated and the residue was extracted with toluene (150 ml) and then filtered through a glass filter. The dark yellow-orange filtrate was evaporated to dryness to yield pale-yellow solid **1b** (1.97 g, 4.4 mmol, 12%). A pure sample of **1b** was obtained by vacuum sublimation at 120°C/10^{-2} mmHg as pale-yellow crystals (1.27 g, 2.8 mmol, 8% yield based on $WCl_4(THF)_2$ used). ^{1}H NMR (C_6D_6): δ 4.68 and 3.91 (t, CpH, $J = 2.0$), 0.32 (s, SiMe), -11.82 (t, H, $J(^{193}W\text{–}H) = 36.9/36.3$). The analytically pure sample was obtained by recrystallization from toluene as pale yellow plates (mp 178–180°C). Anal. Found: C, 37.67; H, 4.97. $WC_{14}H_{22}OSi_2$ calcd.: C, 37.66; H, 4.88%.

3.9. Synthesis of [(1,1,3,3-tetramethyldisiloxane-1,3-diyl)bis(η^5-cyclopentadienyl)] hydrido(phenyl)tungsten (5b)

The compound **1b** (0.106 g, 0.24 mmol) in benzene (70 ml) was irradiated with a Riko 100 W high-pressure mercury lamp through Pyrex apparatus at room temperature for 10 h according to the reported method [5]. The initially pale-yellow solution became yellow. The solvent was evaporated and the residual yellow oil was dried *in vacuo* giving crystalline solid (0.12 g, 0.23 mmol). This was chromatographed on alumina (Al_2O_3/5 wt% H_2O, length 15 cm, diameter 2 cm) and elution with hexane/toluene (4 : 1) gave a yellow band which was collected and evaporated to dryness to yield yellow crystals (0.11 g, 0.20 mmol, 86%). ^{1}H NMR (C_6D_6): δ 7.86 (bs, Ph, 2H), 7.01 (m, Ph, 3H), 4.93 (bs, CpH, 2H), 4.78 (d, CpH, 2H, $J = 2.0$), 4.19 (m, CpH, 2H), 3.35 (m, CpH, 2H), 0.32 (s, SiMe, 6H), 0.23 (s, SiMe, 6H), -10.35 (t, H, $J(^{193}W\text{–}H) = 43.6$).

The analytically pure sample was obtained by recrystallization from hexane as yellow needles (mp 120–

TABLE 3. Crystallographic and experimental data for $[O(SiMe_2C_5H_4)_2]MoMe_2$ (**3a**)

Mw	386.49	μ (cm^{-1})	8.63
Crystal system	Monoclinic	F (000)	800
Space group	Cc	2θ range (°)	4.0–55.0
a (Å)	8.454(2)	range of h, k, l	$-10 \le h \le 10$
b (Å)	14.191(3)		$0 \le k \le 18$
c (Å)	14.840(3)		$0 \le l \le 19$
β (°)	101.64(2)	No. of unique reflections	1952 ($\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$)
V (Å^3)	1744(6)	R	0.0258
Z	4	R_w	0.0358
d_{calc} (g cm^{-3})	1.472	S	2.82
Cystal size (mm)	0.22 × 0.23 × 0.99		

122°C). Anal. Found: C, 46.08; H, 5.12. $WC_{20}H_{26}OSi_2$ calcd.: C, 45.98; H, 5.02%.

3.10. Reaction of methyl methacrylate (MMA) with **1a** *and* **6a**

A sample of the Mo complex (0.05 mmol) was placed in an NMR tube under argon. Into this tube was added a mixture of MMA (0.2 mmol)-toluene (0.1 mmol)-benzene-d_6 (0.45 ml), which had been degassed by three freeze-pump-thaw cycles. After the NMR tube was sealed, it was heated at 90.0°C in a thermostat oil bath and periodically subjected to ^{1}H NMR measurement. The reaction was monitored by decrease of the peak intensity of the hydride protons of the starting complexes **1a** or **6a** relative to that of the methyl protons of toluene used as an internal standard.

3.11. X-ray crystallographic study of **3a**

Yellow-orange air-unstable crystals of complex **3a** suitable for X-ray crystallography were grown from toluene solution and mounted in a capillary tube. Crystal data are summarized in Table 3. X-ray measurements were carried out with a Nonius CAD4 four-circle diffractometer equipped with graphite monochromator using ω–2θ scans. Absorption correction was made. A total of 2030 unique reflections in the range $\pm h$, $+k$, $+l$ and $2° < 2\theta < 55°$ was measured, of which 1952 independent reflections having $I > 3\sigma(I)$ were used in subsequent analysis. The structure was solved from direct and Fourier methods and refined by block-diagonal least squares with anisotropic thermal parameters in the last cycles for all non-hydrogen atoms. Hydrogen atoms for the cyclopentadienyl rings were located from difference Fourier map. In the refinements the weighting scheme $1/(\sigma F)$ was applied. The function minimized in the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$. The computational program package used in the analysis was UNICS 3 [18]. Neutral atomic scattering factors were taken from the *International Tables* [19]. Final atomic parameters for the non-hydrogen atoms and important bond lengths and angles are given in Tables 1 and 2, respectively.

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