Bis(arylimido) Molybdenum(VI) Amidinate and Guanidinate Complexes; Molecular Structures of $[(ArN)_2MoMe\{N(Cy)C[N(i-Pr)_2]N(Cy)\}]$ (Ar = 2,6-*i*-Pr₂C₆H₃; Cy = Cyclohexyl) and $[(2,6-i-Pr_2C_6H_3N)_2MoCl_2] \cdot [NH=C(C_6H_5)CH(SiMe_3)_2]$

Haijun Hao, Chunming Cui, Guangcai Bai, Herbert W. Roesky*, Mathias Noltemeyer, Hans-Georg Schmidt, Yuqiang Ding

Göttingen, Institut für Anorganische Chemie der Universität

Received February 10th, 2000.

Dedicated to Professor Jerzy Haber on the Occasion of his 70th Birthday

Abstract. The reaction of $[(ArN)_2MoCl_2] \cdot DME$ (Ar = 2,6-*i*-Pr₂C₆H₃) (1) with lithium amidinates or guanidinates resulted in molybdenum(VI) complexes $[(ArN)_2-MoCl{N(R^1)C(R^2)N(R^1)}]$ (R¹ = Cy (cyclohexyl), R² = Me (2); R¹ = Cy, R² = N(*i*-Pr)₂ (3); R¹ = Cy, R² = N(SiMe_3)₂ (4); R¹ = SiMe_3, R² = C₆H₅ (5)) with five coordinated molybdenum atoms. Methylation of these compounds was exemplified by the reactions of 2 and 3 with MeLi affording the corresponding methylates $[(ArN)_2MoMe{N(R^1)C(R^2)N(R^1)}]$ (R¹ = Cy, R² = Me (6); R¹ = Cy, R² = N(*i*-Pr)₂ (7)). The ana-

logous reaction of **1** with bulky $[N(SiMe_3)C(C_6H_5)-C(SiMe_3)_2]Li \cdot THF$ did not give the corresponding metathesis product, but a Schiff base adduct $[(ArN)_2MoCl_2] \cdot [NH=C(C_6H_5)CH(SiMe_3)_2]$ (8) in low yield. The molecular structures of **7** and **8** are established by the X-ray single crystal structural analysis.

Keywords: Amidinates; Guanidinates; Imido ligands; Molybdenum; Schiff bases

Bis(arylimido) Molybdän(VI) Amidinat und Guanidinat Komplexe; Strukturbestimmungen von $[(ArN)_2MoMe\{N(Cy)C[N(i-Pr)_2]N(Cy)\}]$ (Ar = 2,6-*i*-Pr₂C₆H₃; Cy = Cyclohexyl) und $[(2,6-i-Pr_2C_6H_3N)_2MoCl_2] \cdot [NH=C(C_6H_5)CH(SiMe_3)_2]$

Inhaltsübersicht. Die Umsetzungen von $[(ArN)_2MoCl_2]$. DME (Ar = 2,6-*i*-Pr₂C₆H₃) (1) mit Lithium- Amidinaten oder Guanidinaten lieferten Molybdän(VI) Komplexe $[(ArN)_2MoCl{N(R^1)C(R^2)N(R^1)}]$ (R¹ = Cy (Cyclohexyl), R² = Me (2); R¹ = Cy, R² = N(*i*-Pr)₂ (3); R¹ = Cy, R² = N(SiMe₃)₂ (4); R¹ = SiMe₃, R² = C₆H₅ (5)) mit fünffach koordinierten Molybdän Atomen. Durch die Reaktion von 1 und 2 mit MeLi wurden die entsprechenden Methylate $[(ArN)_2MoMe{N(R¹)C(R²)N(R¹)}]$ (R¹ = Cy, R² = Me (6);

Introduction

Recently bis(arylimido) molybdenum complexes bearing C,N- or O,N- bidentate ligands have been found to be active for ring opening metathesis polymerization (ROMP) reaction [1]. Most of these compounds have five coordinated metal atoms. It is our recent interest to investigate this class of compounds having

Institut für Anorganische Chemie der Universität Göttingen

E-mail: hroesky@gwdg.de

 $R^1 = Cy, R^2 = N(i-Pr)_2$ (7)) erhalten. In einer analogen Reaktion von 1 mit dem sterisch anspruchsvollen Lithiumsalz des 1-Azaallylliganden [N(SiMe_3)C(C_6H_5)C(SiMe_3)_2]Li · THF konnte nicht das entsprechende Metatheseprodukt, sondern ein Addukt an die Schiffsche Base in geringer Ausbeute dargestellt werden [(ArN)_2MoCl_2] · [NH=C(C_6H_5)-CH(SiMe_3)_2] (8). 7 und 8 wurden durch Einkristallröntgenstrukturanalysen charakterisiert.

other bidentate ligands with expectation to have an insight into the coordination sphere of Mo and the effect of ligand properties. Bidentate anionic amidinate and guanidinate ligands are very important ancillary ligands in transition and main group metal chemistry and have been widely used for Group 13 [2] and 14 [3] metals as well as for Group 4 [4], 5 [5], 6 [6] and 7 metals [7]. Due to the variability of the substituents on the backbone of these ligands, it seems that these ligands are suitable for our studies.

Herein, we report on the synthesis of bis(arylimido) molybdenum amidinate and guanidinate complexes.

^{*} Prof. Herbert W. Roesky

Tammannstrasse 4 D-37077 Göttingen

Telfax: Int. +5 51 39-33 73

Results and Discussion

Synthesis and Spectroscopic Characterization of compounds 2–7

The reaction of $[(ArN)_2MoCl_2]DME$ (1) (Ar = 2,6-*i*- $Pr_2C_6H_3$) with one equiv of the lithium salt of amidinate and guanidinate in THF yielded the compounds $[(ArN)_2MoCl{N(R^1)C(R^2)N(R^1)}]$ (R¹ = Cy (cyclohexyl), $R^2 = Me$ (2); $R^1 = Cy$, $R^2 = N(i-Pr)_2$ (3); $R^1 = Cy, R^2 = N(SiMe_3)$ (4); $R^1 = SiMe_3, R^2 = C_6H_5$ (5)) with five coordinated Mo atoms in modest yields. Compounds 2 and 3 have low solubility in diethyl ether, but can be recrystallized from toluene to afford orange crystals. However, compounds 4 and 5 are highly soluble in hydrocarbon solvents, even in *n*-pentane, and could not be recrystallized. Nevertheless, removing the volatiles from the *n*-pentane extract afforded the analytically pure brown product. These complexes can be methylated by MeLi, exemplified by the reaction of 2 and 3 with MeLi in THF affording $[(ArN)_2MoMe\{N(R^1)C(R^2)N(R^1)\}]$ (R¹ = Cy, R² = Me (6); $R^1 = Cy$, $R^2 = N(i-Pr)_2$ (7)). Attempts to methylate 2 and 3 using MeMgBr instead of MeLi are unsuccessful. The methylates 6 and 7 are resistant to the fluorinating reagent Me₃SnF, indicating that the two compounds are less reactive compared to [(ArN)₂MoMe₂] [8]. Compounds 2–7 are moisturesensitive but can be handled in air for a short time (several minutes) without any noticeable change.



Scheme 1

The compounds were characterized by elemental analysis, EI mass spectrometry and ¹H NMR spectroscopy. The EI-mass spectrum of each compound presents a very clear molecular ion and a peak attributed to the $[M^+-ArN]$ fragment. The ¹H NMR spectra of **2–7** show one septet and two doublet resonances for the *i*-Pr ortho substituents of the ArN ligands, and one septet and only one doublet for N(*i*-Pr)₂ of **2** and **7** due to the free rotation around C–N(*i*-Pr)₂ axis. The Si*Me*₃ groups in **4** show a doublet resonance most

likely due to the bulk of the SiMe₃ group that hampers the free rotation around the C–N(SiMe₃) axis. The Mo-*Me* resonance single peak of **6** and **7** appears at lower field (1.54 ppm and 1.60 ppm, respectively) compared to those found in the C,N-chelating congeners (1.03 or 1.13 ppm) [1 a, b] and at slightly higher field than that of the O,N-chelating complex (1.67 ppm) [1 c].

The X-ray crystal structure of 7

An insight into the molecular geometry of this series of compounds with five coordinated molybdenum atoms was achieved by X-ray single crystal structural determinations of 6 and 7. Unfortunately, the crystal structural data of 6 is not so good to give credible bond lengths and angles. Nevertheless, good data are obtained for 7 (Selected bond lengths and angles are giv-

Table 1Bond lengths Å and angles ° for 7.

Mo(1)-N(1)	1.756(3)	N(1)-Mo(1)-N(3) 107.06(10)
Mo(1) - N(2)	1.757(2)	N(2)-Mo(1)-N(3) 142.45(11)
Mo(1)-N(4)	2.128(2)	N(4)-Mo(1)-N(3) = 60.66(9)
Mo(1)-C(1)	2.172(3)	C(1)-Mo(1)-N(3) = 84.72(10)
Mo(1)–N(3)	2.211(2)	C(11)–N(1)–Mo(1) 155.6(2)
N(1)-C(11)	1.398(4)	C(21)–N(2)–Mo(1) 175.5(3)
N(2)-C(21)	1.395(3)	C(2)–N(3)–C(31) 121.8(2)
N(3)-C(2)	1.325(3)	C(2)-N(3)-Mo(1) 92.8(2)
N(4)-C(2)	1.344(4)	C(31)–N(3)–Mo(1) 137.4(2)
N(5)-C(2)	1.391(4)	C(2)-N(4)-C(41) 122.1(3)
N(5)-C(6)	1.478(4)	C(2)-N(4)-Mo(1) 96.0(2)
N(5)-C(3)	1.481(5)	C(41)–N(4)–Mo(1) 132.6(2)
N(1)-Mo(1)-N(2)	109.56(13)	C(2)-N(5)-C(6) 116.0(3)
N(1)-Mo(1)-N(4)	110.87(10)	C(2)-N(5)-C(3) 118.6(3)
N(2)-Mo(1)-N(4)	98.06(11)	C(6)-N(5)-C(3) 125.0(3)
N(1)-Mo(1)-C(1)	102.59(11)	N(3)-C(2)-N(4) 110.5(2)
N(2)-Mo(1)-C(1)	95.1(2)	N(3)-C(2)-N(5) 126.7(3)
N(4)-Mo(1)-C(1)	137.13(10)	N(4)-C(2)-N(5) 122.9(3)



Fig. 1 The molecular structure of **7** in the crystal. Hydrogen atoms have been omitted for clarity.

en in table 1). The molecular structure of **7** is shown in figure 1.

Compound 7 has a distorted square pyramidal geometry around the Mo^{VI} atom, in which the arylimido ligand (ArN(1)) is arranged at the top vertex with an angle at N(1) of $155.6(2)^{\circ}$ and a Mo(1)-N(1) bond length of 1.756(3) Å. At the equatorial positions are a bidentate guanidinate ligand, a terminal methyl and an arylimido group with an angle at N(2) of $175.5(3)^{\circ}$ and a Mo(1)–N(2) bond length of 1.757(2) Å. The bond lengths of Mo(1)-N(1) and Mo(1)-N(2) are within the range for other arylimido ligand containing compounds [1 a, 1 b, 1 c]. The Mo(1)–N(3) bond length (2.211(2) Å) is slightly longer than that of Mo(1)–N(4) (2.128(2) Å). The backbone of the guanidinate ligand (N(3)-C(2)-N(4)) along with the Mo atom defines a plane (Mo(1)-N(3)-C(2)-N(4)). The relatively longer Mo-N distance (average 2.1695 Å) than that of C-N (average 1.3345 Å) leads to an acute N(3)-Mo-N(4) angle $(60.66(9)^{\circ})$. The Mo–Me bond length (2.172(3) Å) is similar to those found in the C,N- or O.N-chelating complexes [1a, 1b, 1c].

Formation and the structure of 8

Attempts to prepare a molybdenum complex bearing the 1-aza-allyl ligand ($[N(SiMe_3)C(C_6H_5)C(SiMe_3)_2]$) [8], which is isoelectronic with the amidinate and guanidinate, unexpectedly led to the formation of a Schiff base adduct [$(2,6-i-Pr_2C_6H_3N)_2MoCl_2$] · $[NH=C(C_6H_5)CH(SiMe_3)_2$] (8) in low yield. Presumably this is a hydrolyzed product (Scheme 2). The expected compound [$(2,6-i-Pr_2C_6H_3N)_2MoCl[N(SiMe_3) C(C_6H_5)C(SiMe_3)_2$]] was not obtained probably due to the bulkyness of this ligand.



Scheme 2

Single crystals of 8 suitable for X-ray diffraction analysis were obtained from diethyl ether solution. The elemental analysis are in agreement with the proposed structure. The EI mass spectrum shows the

Table 2Selected bond lengths Å and angles ° for 8.

Mo(1)–N(2)	1.749(2)	N(1)-Mo(1)-Cl(1)	81.89(6)
Mo(1)-N(3)	1.752(2)	N(2)-Mo(1)-Cl(2)	102.54(7)
Mo(1) - N(1)	2.255(2)	N(3)-Mo(1)-Cl(2)	92.38(7)
Mo(1)-Cl(1)	2.3940(10)	N(1)-Mo(1)-Cl(2)	81.04(6)
Mo(1)-Cl(2)	2.4415(10)	Cl(1)-Mo(1)-Cl(2)	148.89(2)
N(1)-C(1)	1.290(3)	C(1)-N(1)-Mo(1)	140.5(2)
C(1)-C(11)	1.477(3)	N(1)-C(1)-C(11)	119.6(2)
C(1)-C(2)	1.490(3)	N(1)-C(1)-C(2)	121.5(2)
N(2)-C(21)	1.405(3)	C(11)-C(1)-C(2)	118.8(2)
N(3)-C(31)	1.381(3)	C(1)-C(2)-Si(2)	113.1(2)
N(2)-Mo(1)-N(3)	108.07(8)	C(1)-C(2)-Si(1)	110.0(2)
N(2)-Mo(1)-N(1)	94.46(8)	Si(2)-C(2)-Si(1)	119.38(13)
N(3)-Mo(1)-N(1)	157.43(8)	C(21)-N(2)-Mo(1)	151.1(2)
N(2)-Mo(1)-Cl(1)	104.55(7)	C(31)-N(3)-Mo(1)	176.6(2)
N(3)-Mo(1)-Cl(1)	93.52(7)		



Fig. 2 The molecular structure of 8 in the crystal. Hydrogen atoms except those two at N(1) and C(1) have been omitted for clarity.

peak of $[M^+-Cl]$ (m/z 745) and an ion (m/z 570) ascribed to the $[M^+-Cl-ArN]$ fragment.

The molecular structure of **8** is best described as a distorted trigonal bipyramid as shown in figure 2 (selected bond lengths and angles are given in table 2), in which two chlorine atoms and an imido ligand $(C(21)-N(2)-Mo(1) 151.1(2)^{\circ})$ occupy the equatorial positions. Opposite to the apical linear imido ligand $(C(31)-N(3)-Mo(1) 176.6(2)^{\circ})$, the Schiff base is coordinated to the Mo atom with a bond length of 2.255(2) Å. The slightly shorter Mo(1)–N(1) bond length compared to that of Mo(1)–N(2) is presumably due to the long Mo–N bond of the *trans*-coordinated Schiff base. The average Mo–Cl bond length is 2.418 Å.

Experimental Section

All manipulations were performed on a high vacuum line or in a glovebox under a purified N_2 atmosphere. Diethyl ether was distilled from Na/benzophenone ketyl, toluene and THF from K prior to use. [(ArN)₂MoCl₂] · DME (1) [9] and the lithium salts of amidinate and guanidinate [3 a, 5 a] were prepared by literature methods.

Elemental analyses were performed by the Analytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen. Finnigan MAT 8230 was used for mass spectra (EI 70 eV). Bruker AM 200 and Bruker 250 spectrometers were used to record ¹H NMR (200.131 MHz) and ²⁹Si NMR (99.362 MHz) spectra. The chemical shifts were externally referenced to SiMe₄. Melting points were measured in sealed glass tubes and were not corrected.

$[(2,6-i-Pr_2C_6H_3N)_2MoCl\{N(Cy)C(Me)N(Cy)\}]$ (2).

[N(C₆H₁₁)C(Me)N(C₆H₁₁)]Li · O(C₂H₅)₂ (1.5 g, 5.0 mmol) was added in serveral portions to a solution of **1** (3.0 g, 5.0 mmol) in THF (35 mL) at -78 °C. After warming slowly to ambient temperature (about 2 h), the solution was stirred at 22 °C for 48 h. After removal of all the volatiles, the residue was extracted with toluene (20 mL). Removing the toluene from the extract, washing the residue with ether (20 mL) and drying the residue *in vacuo* for 2 h, resulted in a yellow powder (1.2 g, 40%). M. p. 218–222 °C.

C₃₈H₅₉ClMoN₄ (703.30 g/mol)

Analyses: C 64.64 (calc 64.90); H 8.45 (8.46); N 7.97(7.97)%.

¹H NMR (200 MHz, C₆D₆ solution): δ (ppm) = 6.90–7.10 (m, 6 H, 2,6-*i*-Pr₂C₆H₃), 4.00 (m, 4 H, CHMe₂), 3.30 (m, 2 H, Cy), 1.60 (s, 3 H, NC(CH₃)N), 1.1–2.5 (m, 20 H, Cy), 1.24 (d, 12 H, CH(CH₃)₂), 1.18 (d, 12 H, CH(CH₃)₂).

MS (98 Mo): m/z (%) = 704(10) [M⁺]; 529(55) [M⁺-ArN]; 83(100) [Cy].

[$(2,6-i-Pr_2C_6H_3N)_2MoCl\{N(Cy)C(N(i-Pr)_2)N(Cy)\}$] (3). The synthetic procedure is similar to that described for **2**. [N(C₆H₁₁)C(N(*i*-Pr)_2)N(C₆H₁₁)]Li · O(C₂H₅)₂ (5.9 g, 15.5 mmol) was added in several portions to a solution of **1** (9.1 g, 15 mmol) in THF (100 mL) at -78 °C. Yield: 4.5 g (37%). M. p. 218–220 °C.

C₄₃H₇₀ClMoN₅ (788.45 g/mol)

Analyses: C 65.45 (calc 65.50); H 8.88 (8.95); N 8.78(7.88)%.

¹H NMR (200 MHz, C₆D₆ solution): δ (ppm) = 6.90–7.10 (m, 6H, *i*-Pr₂C₆H₃), 4.19 (m, 4H, CHMe₂), 3.65 (m, 2H, Cy), 3.55 (m, 2H, NC(N(CHMe₂))N), 1.31 (d, 12H, CHMe₂), 1.23 (d, 12H, CHMe₂), 1.20 ppm (d, 12 H, NC(N(CHMe₂))N), 1.10–2.70 (m, 20 H, Cy). MS (⁹⁸Mo): m/z (%) = 789(100) [M⁺]; 614(68) [M⁺–ArN].

 $[(2,6-i-Pr_2C_6H_3N)_2MoCl[N(Cy)C(N(SiMe_3)_2)N(Cy)]]$ (4). A solution of $[N(C_6H_{11})C(N(SiMe_3)_2)N(C_6H_{11})]Li \cdot O(C_2H_5)_2$ (0.75 g, 2.0 mmol) in THF (20 mL) was added dropwise to **1** (1.20 g, 2.0 mmol) in THF (20 mL) at -70 °C over a period of 10 min. After warming slowly to ambient temperature, the resulting solution was stirred at 22 °C for 16 h. After removal of all the volatiles, the residue was extracted with *n*-pentane (20 mL). Removing of *n*-pentane from the extract afforded **4** as brown-yellow powder. Yield: 1.2 g (70%). M. p. 82–84 °C.

C₄₃H₇₄ClMoN₅Si₂ (848.65 g/mol)

Analyses: C 60.61 (calc 60.85); H 9.08 (8.78); N 8.92 (8.35)%.

¹H NMR (200 MHz, C₆D₆ solution): δ (ppm) = 6.85–7.10 (m, 6 H, *i*-Pr₂C₆H₃), 4.08 (m, 4 H, CHMe₂), 3.73 (m, 2 H, Cy), 1.10–2.10 (m, 20 H, Cy), 1.28 (d, 12 H, CHMe₂), 1.27 (d, 12 H, CHMe₂), 0.27 (d, 18 H, SiMe₃). MS (⁹⁸Mo): m/z = 849 [M⁺]; 674 [M⁺–ArN].

 $[(2,6-i-Pr_2C_6H_3N)_2MoCl{C_6H_5C}(NSiMe_3)_2]$ (5). The synthetic procedure is similar to that of **4**. $[C_6H_5C(NSi-Me_3)_2]Li \cdot THF$ (1.26 g, 3.68 mmol) was dissolved in THF

(20 mL) and was added dropwise to a solution of 1 (2.23 g, 3.68 mmol) in THF (20 mL) at -57 °C. Yield: 1.90 g (69%). M. p. 120–124 °C.

 $C_{37}H_{57}ClMoN_4Si_2$ (745.45 g/mol)

Analyses: C 60.08 (calc. 59.62); H 7.98 (7.31); N 7.41 (7.59)%.

¹H NMR (200 MHz, C₆D₆ solution): δ (ppm) = 6.85–7.30 (m, 11 H, 2,6*i*-Pr₂C₆H₃ and C₆H₅), 4.08 (m, 4 H, CHMe₂), 1.33 (d, 12 H, CHMe₂), 1.25 (d, 12 H, CHMe₂), 0.26 (s, 9 H, SiMe₃), 0.12 (2, 9 H, SiMe₃).

MS (⁹⁸Mo): m/z (%) = 746(10) [M⁺]; 571(15) [M⁺-ArN], 175(100) [ArN].

 $[(2,6-i-Pr_2C_6H_3N)_2MoMe[N(Cy)C(Me)N(Cy)]]$ (6). MeLi (0.34 mL, 0.54 mmol, 1.6 M solution in ether) was added dropwise to a solution of **2** (0.37 g, 0.52 mmol) in THF (20 mL) at -57 °C. After warming slowly to ambient temperature, the solution was stirred at 22 °C for 16 h. After removal of all the volatiles, the residue was extracted with toluene (40 mL). After concentration and cooling to -32 °C for several days, orange crystals were formed (0.26 g, 73%). M. p. 190–195 °C.

 $C_{39}H_{62}MoN_4$ (682.88 g/mol)

Analyses: C 68.13 (calc 68.60); H 9.12 (9.15); N 7.88 (8.20)%.

¹H NMR (200 MHz, C₆H₆ solution): δ (ppm) = 6.85–7.10 (m, 6 H, 2,6-*i*-Pr₂C₆H₃), 4.02 (m, 4 H, CHMe₂), 3.20 (m, 2 H, Cy), 1.57 (s, 3 H, Mo–Me), 1.54 (s, 3 H, NC(Me)N), 1.10–2.10 (m, 20 H, Cy), 1.27 (d, 12 H, CHMe₂), 1.17 (d, 12 H, CHMe₂).

MS (98 Mo): m/z (%) = 684(100) [M⁺].

 $[(2,6-i-Pr_2C_6H_3N)_2MoMe[N(Cy)C(N(i-Pr)_2N(Cy))]$ (7). The synthetic procedure is similar to that of **6**. MeLi (0.63 mL, 1.0 mmol, 1.6 M in solution in ether) was added dropwise to a solution of **3** (0.79 g, 1.0 mmol) in THF (20 mL) at -57 °C. Yield: 0.54 g (70%). M. p. 190–195 °C.

C₄₄H₇₃MoN₅ (768.01 g/mol)

Analyses: C 68.45 (calc 68.75); H 9.60 (9.58); N 8.96 (9.12)%.

¹H NMR (200 MHz, C₆H₆ solution): δ (ppm) = 6.85–7.10 (m, 6 H, 2,6-*i*-Pr₂C₆H₃), 4.08 (m, 4 H, CHMe₂), 3,65 (m, 2 H, Cy), 3.55 (m, 2 H, NC(N(CHMe₂)₂)N), 1.60 (s, 3 H, Mo–*Me*), 1.10–2.10 (m, 20 H, Cy), 1.31 (d, 12 H, CH*Me*₂), 1.24 (d, 12 H, CH*Me*₂), 1.11 (d, 12 H, NC(N(CHMe₂)₂)N).

 $MS^{(98}Mo): m/z^{(\%)} = 769(100) [M^+].$

 $[(2,6-i-Pr_2C_6H_3N)_2MoCl_2]([NH=C(C_6H_5)CH(SiMe_3)_2]$ (8). A solution of $[N(SiMe_3)C(C_6H_5)C(SiMe_3)_2]Li \cdot THF$ (0.205 g, 0.49 mmol) in ether (15 mL) was added dropwise to a solution of **1** (0.30 g, 0.49 mmol) in ether (100 mL) at $-78 \,^{\circ}C$. After warming slowly to ambient temperature, the reaction mixture was stirred for 16 h at 22 °C. After removing all the volatiles, the residue was extracted with *n*-pentane (15 mL). The extract was cooled at $-5 \,^{\circ}C$ for 18 h to afford yellow crystals. Yield: 0.034 g (9%). M. p. 147–150 °C.

C₃₈H₅₉Cl₂MoN₃Si₂ (780.90 g/mol)

Analyses: C 58.37 (58.45); H 7.63 (7.62); N 5.57 (5.38)%.

²⁹Si NMR: δ (ppm) = 7.47.

MS (⁹⁸Mo): m/z (%) = 745(18) [M⁺-Cl]; 570(18) [M⁺-Cl-ArN]; 175(100) [ArN].

Single crystal X-ray structral determination and refinement

A summary of the crystal data, data collection, solution and refinement parameters for 7 and 8 is given in table 3. The

	7	8
Empirical formula	C44H73M0N5	C38H59Cl2M0N3Si2
Formula weight	768.01	780.90
Temperature	132(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	orthorhombic	triclinic
Space group	$P \operatorname{na2}(1)$	$P\overline{1}$
Unit cell dimensions	a = 20.459(3) Å	a = 12.832(4) Å
	b = 12.778(12) Å	b = 13.493(4) Å
	c = 16.916(2)Å	c = 14.071(5) Å
	$\alpha = 90^{\circ}$	$\alpha = 74.89(2)^{\circ}$
	$\beta = 90(3)^{\circ}$	$\beta = 73.061(15)^{\circ}$
	$\gamma = 90(2)^{\circ}$	$\gamma = 66.709(11)^{\circ}$
Volume, Z	4422.4(9) Å ³ , 4	2111.2(12) Å ³ , 4
Density (calculated)	1.153 Mg/m^3	1.228 Mg/m^3
Absorption coefficient	0.330 mm^{-1}	0.522 mm^{-1}
F(000)	1656	824
Crystal size	$0.60 \times 0.40 \times 0.20 \text{ mm}$	$1.00 \times 0.60 \times 0.40 \text{ mm}$
Theta range for data collection	3.51-25.02°	3.54–25.03°
Limiting indices	$-24 \le h \le 24, -15 \le k \le 15, -20 \le l \le 20$	$-15 \le h \le 15, -16 \le k \le 16, -16 \le l \le 16$
Reflections collected	9689	14824
Independent reflections	7782 ($R_{\rm int} = 0.0227$)	7412 ($R_{\rm int} = 0.0639$)
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7772/1/464	7410/1/433
Goodness-of-fit on F^2	1.068	1.058
Final R indices $[I > 2\sigma(I)]$	R1 = 0.0300, wR2 = 0.058	R1 = 0.0312, wR2 = 0.0811
R indices (all data)	R1 = 0.0397, wR2 = 0.0649	R1 = 0.0339, wR2 = 0.0836
Largest diff. peak and hole	0.228 and -0.264 eÅ ⁻³	0.354 and $-0.622 \text{ e}\text{\AA}^{-3}$

Table 3Crystal data and structure refinement parameters for compounds 7 and 8.

data collection was carried out on a Stoe-Siemens four-circle diffractometer using MoK α radiation. The structures were solved by direct methods (SHELXS-96) [10] and refined against F^2 using SHELXL-97 [11]. All heavy atoms were refined anisotropically. Hydrogen atoms were included using the riding model with U_{iso} tied to the U_{iso} of the parent atoms. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC 139641 (7) and CCDC 139642 (8). Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-(0)12 23-33 60 33 or e-mail: deposit@ccdc.cam.ac.uk)

Acknowledgment: We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft.

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