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Synthesis and structures of silicon-, germanium-, and tin-containing imido-alkyl molybdenum complexes $(ArN)_2Mo(CH_2EMe_3)_2$ (E = Si, Ge, Sn)

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New silicon-, germanium-, and tin-containing imido-alkyl molybdenum complexes $(ArN)_2Mo(CH_2EMe_3)_2$ (Ar is 2,6-diisopropylphenyl; E = Si (**1**), Ge (**2**), Sn (**3**)) were prepared in the crystalline state in 58—66% yields by the reactions of the $(ArN)_2MoCl_2(DME)$ complex with alkyllithium derivatives Me_3ECH_2Li (E = Si or Ge) or the Grignard reagents Me_3ECH_2MgCl (E = Ge or Sn). The structures of complexes **1**—**3** and the known analog $(ArN)_2Mo(CH_2Bu^t)_2$ (**4**) were established by X-ray diffraction analysis. Complexes **1**—**3** were found to be isostructural. The coordination environment about the Mo atom can be described as a distorted tetrahedron. Complex **4** has a similar structure. The Mo—C distance tends to decrease with increasing electron-donating ability of the EMe_3 group.

Key words: imido-alkyl molybdenum complexes, silicon-, germanium-, and tin-containing; synthesis, structure, X-ray diffraction analysis.

The imido-alkyl molybdenum complexes $(ArN)_2Mo(CH_2R)_2$ (Ar is 2,6-diisopropylphenyl; R = Bu^t, CMe_2Ph)[1–4] are used as the starting compounds in the synthesis of carbene complexes, which serve as active catalysts for olefin metathesis. Data on analogous imido-alkyl derivatives of molybdenum with heteroatom-containing alkyl groups are scarce,[5] and the possibility of using these compounds for the synthesis of carbene complexes is poorly studied. In the present study, we synthesized and structurally characterized the silicon-, germanium-, and tin-containing imido-alkyl molybdenum complexes $(ArN)_2Mo(CH_2EMe_3)_2$ (E = Si, Ge, Sn).

The new imido-alkyl molybdenum complexes were prepared by the reaction of molybdenum diimido chloride with heteroatom-containing alkyllithium derivatives or Grignard reagents (Scheme 1).

Scheme 1

$$(ArN)_2MoCl_2(DME) + \underset{E\,=\,Si,\ Ge}{2\ Me_3ECH_2Li} \xrightarrow{i}$$

$$\longrightarrow \underset{\mathbf{1},\ \mathbf{2}}{(ArN)_2Mo(CH_2EMe_3)_2} + 2\ LiCl$$

$$(ArN)_2MoCl_2(DME) + \underset{E\,=\,Ge,\ Sn}{2\ Me_3ECH_2MgCl} \xrightarrow{i}$$

$$\longrightarrow \underset{\mathbf{2},\ \mathbf{3}}{(ArN)_2Mo(CH_2EMe_3)_2} + 2\ MgCl_2$$

E = Si (**1**), Ge (**2**), Sn (**3**) *i*. Diethyl ether, –30—+20 °C.

Complexes **1**—**3** were isolated in pure form in 58—66% yields as dark-red crystals, which are unstable in air and readily soluble in organic solvents. Compounds **1**—**3** were characterized by elemental analysis, IR spectroscopy, and ^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectroscopy.

The structures of complexes **1**—**3** were established by X-ray diffraction analysis. To compare the structural parameters of the complexes, we also determined the structure of the known $(ArN)_2Mo(CH_2Bu^t)_2$ compound (**4**).[1] X-ray diffraction analysis demonstrated that complexes **1**—**3** are isostructural (Fig. 1). Complex **4** has a similar structure but crystallizes in a different modification (Fig. 2). In complexes **1**—**4**, the Mo atoms have tetrahedral coordination. The Mo(1)—C(25) and Mo(1)—C(29) distances are, respectively, 2.115(2) and 2.117(2) Å for **1**, 2.118(1) and 2.116(2) Å for **2**, and 2.099(3) and 2.100(3) Å for **3**. The C(25)—E(1) and C(29)—E(2) distances are, respectively, 1.860(2) and 1.870(2) Å for **1**, 1.960(1) and 1.958(1) Å for **2**, and 2.157(3) and 2.156(3) Å for **3**, which are slightly larger than the sum of the covalent radii of the carbon and the corresponding sp^3-hybridized heteroatom. In complex **4**, the Mo(1)—C(13) distance is 2.126(4) Å. Analysis of the Mo—C distances in a series of

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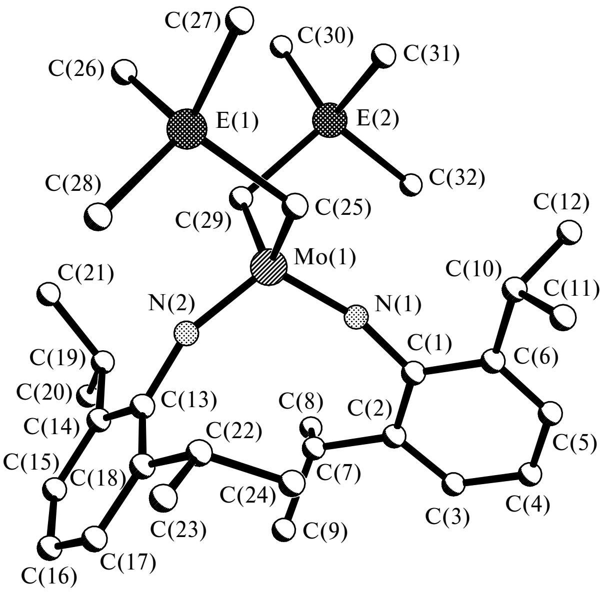

Fig. 1. Molecular structures of complexes **1** (E = Si), **2** (E = Ge), and **3** (E = Sn).

related compounds **4** and **1**—**3** shows that the Mo—C distances tend to decrease (2.126(4)—2.099(3) Å) with increasing electron-donating ability of the EMe_3 group (E = Si (**1**), Ge (**2**), Sn (**3**), C (**4**)).

The Mo—N distances in molecules **1**—**4** are in the range of 1.745(1)—1.758(1) Å, which is comparable with the Mo—N distance (1.759(2) Å) in the 2,6-Pr^i_2-C_6H_3N=Mo fragment in the $Mo(NC_6H_3$-2,6-$Pr^i_2)(NBu^t)(CH_2Bu^t)_2$ complex.[6]

To summarize, we synthesized and structurally characterized the new imido-alkyl molybdenum complexes $(ArN)_2Mo(CH_2EMe_3)_2$ (E = Si (**1**), Ge (**2**), Sn (**3**)) and the known hydrocarbon analog $(ArN)_2Mo(CH_2Bu^t)_2$ (**4**) by X-ray diffraction. The Mo—C distances were found to decrease with increasing electron-donating ability of the EMe_3 group.

Experimental

All operation were carried out in evacuated sealed tubes using the standard Schlenk technique. Thoroughly dried and deaerated solvents were used. The starting reagents, *viz*., $(ArN)_2MoCl_2(DME)$,[7] Me_3SiCH_2Li,[8] Me_3GeCH_2Li,[8] Me_3GeCH_2MgCl,[9] Me_3SnCH_2MgCl,[9] and the $(ArN)_2Mo(CH_2Bu^t)_2$ complex (**4**),[1] were synthesized according to known procedures. The IR spectra were recorded on a Perkin—Elmer-577 spectrometer. Samples were prepared under argon as Nujol mulls. The ^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR spectra were measured on a Bruker DPX-200 spectrometer in C_6D_6 using Me_4Si as the internal standard for ^1H and ^{29}Si NMR spectroscopy and Me_4Sn as the internal standard for ^{119}Sn NMR spectroscopy.

The decomposition temperatures were determined in evacuated sealed tubes and are uncorrected.

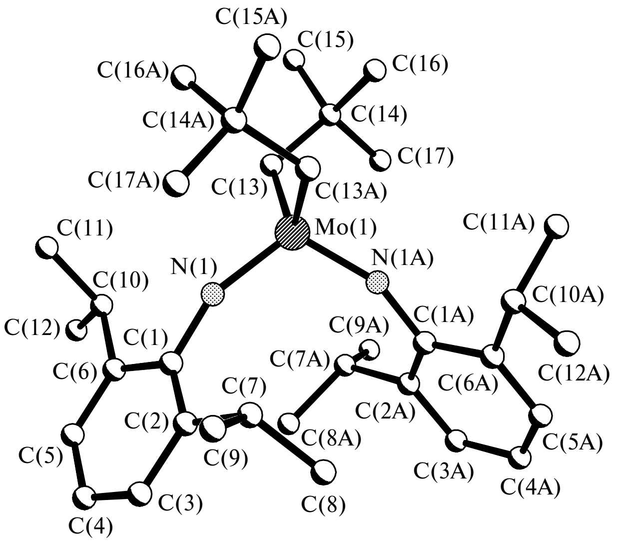

Fig. 2. Molecular structure of complex **4**.

The X-ray diffraction data sets were collected on an automated Smart APEX diffractometer. Principal crystallographic characteristics and parameters of structure refinement are given in Table 1. All 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. The H atoms in complexes **1**, **3**, and **4** were placed in geometrically calculated positions and refined using a riding model. The H atoms in complex **2** were located from difference Fourier syntheses and refined isotropically. The refinement revealed disorder of the C(11) and C(12) atoms in **1** (Me groups in the Pr^i substituent), the C(11) atom in **3** (Me group in the Pr^i substituent), and the isopropyl groups and the *tert*-butyl substituent in **4**. Molecules **1**—**3** occupy general positions. The Mo atom in molecule **4** is located on the C_2 axis.

All calculations were carried out with the use of the SHELXTL v. 6.10 program package.[10] Selected bond lengths and bond angles are given in Table 2.

Bis(2,6-diisopropylphenylimido)bis(trimethylsilylmethyl)molybdenum $(ArN)_2Mo(CH_2SiMe_3)_2$ (1). A solution of Me_3SiCH_2Li (0.6 g, 6.38 mmol) in diethyl ether (10 mL) was added with stirring to a dark-cherry solution of $(ArN)_2MoCl_2(DME)$ (1.98 g, 3.26 mmol) in diethyl ether (30 mL) at −30 °C. The reaction mixture was gradually heated to room temperature. The colorless precipitate that formed was separated from the solution by centrifugation. The precipitate contained LiCl (0.27 g, 100.0%). Slow evaporation of the solvent from the reaction solution at room temperature afforded compound **1** in a yield of 1.34 g (66.4%) as dark-red crystals, which melt with decomposition at temperatures higher than 180 °C. Found (%): C, 61.98; H, 9.08. $C_{32}H_{56}MoN_2Si_2$. Calculated (%): C, 61.94; H, 9.03. IR, ν/cm^{-1}: 3060, 1170, 760 (2,6-diisopropylphenyl); 1275, 1245, 840, 700, 630 (CH_2SiMe_3). ^1H NMR, δ: 0.28 (s, 18 H, CH_2SiMe_3); 1.14 (d, 24 H, $CH\underline{Me}_2$); 1.55 (s, 4 H, $C\underline{H}_2SiMe_3$); 3.69 (sept, 4 H, $C\underline{H}Me_2$); 6.8—7.0 (m, 6 H, H(3), H(4)). DEPT ^{13}C NMR, δ: 1.87 (CH_2SiMe_3, $J_{C,^{29}Si}$ = 51.0 Hz); 23.5 ($\underline{C}HMe_2$); 28.7 ($CH\underline{Me}_2$); 50.3 ($\underline{C}H_2SiMe_3$); 122.9 (CH(3)); 126.3 (CH(4)); 142.8 (C(2)); 152.9 (C(1)). ^{29}Si NMR, δ: −0.5.

Table 1. Crystallographic data and parameters of structure refinement of complexes **1—4**

Parameter	**1**	**2**	**3**	**4**
Molecular formula	$C_{32}H_{56}MoN_2Si_2$	$C_{32}H_{56}Ge_2MoN_2$	$C_{32}H_{56}MoN_2Sn_2$	$C_{34}H_{56}MoN_2$
Molecular weight	620.91	709.91	802.11	588.75
Crystal dimensions/mm	0.5×0.2×0.2	0.2×0.1×0.08	0.18×0.12×0.08	0.10×0.08×0.08
T/K	183(2)	100(2)	150(2)	100(2)
Space group	$P2_1/c$	$P2_1/n$	$P2_1/n$	$C2/c$
a/Å	11.158(2)	11.106(1)	11.360(1)	18.243(3)
b/Å	16.382(3)	16.367(1)	16.420(1)	10.9685(15)
c/Å	20.154(3)	19.969(1)	20.114(1)	18.372(3)
β/deg	103.081(3)	103.286(1)	103.229(1)	111.083(3)
V/Å^3	3588(1)	3533(1)	3652(1)	3430.2(8)
Z	4	4	4	4
d_{calc}/g cm^{-3}	1.149	1.335	1.459	1.140
μ/mm^{-1}	4.53	20.61	17.15	—
Absorption correction	SADABS program			
$T_{\text{min}}/T_{\text{max}}$	0.805/0.915	0.7815/0.9310	0.7477/0.8750	0.9607/0.9684
F(000)	1328	1472	1616	1264
2θ$_{\text{max}}$/deg	58	58	52	48
Number of measured reflections	25744	48332	22299	12049
Number of independent reflections (R_{int})	9444 (0.026)	9350 (0.0281)	7171 (0.0324)	2701 (0.0622)
R_1 (based on F for reflections with $I > 2\sigma(I)$)	0.0341	0.0214	0.0306	0.0549
wR_2 (based on F^2 for all reflections)	0.0883	0.0551	0.0739	0.1374
Number of parameters in refinement	353	558	500	253
Weighting scheme	$w^{-1} = \sigma^2(F_o^2) + (\alpha P)^2 + \beta P$, where $P = 1/3(F_o^2 + 2F_c^2)$			
α	0.0433	0.0270	0.0422	0.0499
β	0.8411	1.5994	0	15.561
GOOF	1.064	1.046	1.004	1.123
$(e_{\text{min}}/e_{\text{max}})$/e·Å^{-3}	−0.370/0.678	−0.338/0.609	−0.559/0.904	−1.854/1.170

Bis(2,6-diisopropylphenylimido)bis(trimethylgermylmethyl)molybdenum $(ArN)_2Mo(CH_2GeMe_3)_2$ (2). ***A.*** The synthesis and isolation of complex **2** were carried out as described above. The synthesis starting from $(ArN)_2MoCl_2(DME)$ (2.19 g, 3.60 mmol) and Me_3GeCH_2Li (1.0 g, 7.21 mmol) afforded LiCl in a yield of 0.28 g (93.3%) and complex **2** in a yield of 1.48 g (58.3%) as dark-red crystals, which melt with decomposition at a temperature higher than 175 °C. Found (%): C, 54.13; H, 7.96. $C_{32}H_{56}Ge_2MoN_2$. Calculated (%): C, 54.15; H, 7.90. IR, ν/cm^{-1}: 3060, 1170, 760 (2,6-diisopropylphenyl); 1270, 1240, 810, 590, 560 (CH_2GeMe_3). ^{1}H NMR, δ: 0.41 (s, 18 H, $CH_2Ge\underline{Me}_3$); 1.16 (d, 24 H, $CH\underline{Me}_2$); 1.88 (s, 4 H, $C\underline{H}_2GeMe_3$); 3.73 (sept, 4 H, $C\underline{H}Me_2$); 6.90—7.15 (m, 6 H, H(3), H(4)). ^{13}C NMR, δ: 1.4 ($CH_2Ge\underline{Me}_3$); 23.3 ($\underline{C}HMe_2$); 28.6 ($CH\underline{Me}_2$); 51.9 ($\underline{C}H_2GeMe_3$); 122.8 (CH(3)); 126.1 (CH(4)); 142.7 (C(2)); 153.1 (C(1)).

B. A solution of Me_3GeCH_2MgCl (1.24 g, 6.52 mmol) in diethyl ether (16.6 mL, 0.39 mol L^{-1}) was added with stirring to a dark-cherry solution of $(ArN)_2MoCl_2(DME)$ (1.98 g, 3.26 mmol) in diethyl ether (30 mL) at −30 °C. The reaction mixture was gradually warmed to room temperature. The colorless precipitate that formed was separated by centrifugation. The precipitate contained $MgCl_2$ (0.58 g, 93.6%). Slow evaporation of the solvent from the reaction solution at room temperature afforded compound **2** in a yield of 1.51 g (65.3%).

Bis(2,6-diisopropylphenylimido)bis(trimethylstannylmethyl)molybdenum $(ArN)_2Mo(CH_2SnMe_3)_2$ (3). The synthesis and isolation of complex **3** were carried out as described above (method *B*). The synthesis starting from $(ArN)_2MoCl_2(DME)$ (2.12 g, 3.50 mmol) and a solution of Me_3SnCH_2MgCl (1.66 g, 3.49 mmol) in diethyl ether (12.7 mL, 0.55 mol L^{-1}) afforded $MgCl_2$ in a yield of 0.63 g (60.0%) and complex **3** in a yield of 1.48 g (58.3%) as dark-red crystals, which melt with decomposition at a temperature higher than 152 °C. Found (%): C, 47.95; H, 7.07. $C_{32}H_{56}MoN_2Sn_2$. Calculated (%): C, 47.92; H, 6.99. IR, ν/cm^{-1}: 3060, 1170, 760 (2,6-diisopropylphenyl); 1205, 800, 600, 520, 510 (CH_2SnMe_3). ^{1}H NMR, δ: 0.29 (s, 18 H, $CH_2Sn\underline{Me}_3$, $^2J_{\text{H},^{117}/^{119}\text{Sn}}$ = 51.0/53.2 Hz); 1.13 (d, 24 H, $CH\underline{Me}_2$); 2.25 (s, 4 H, $C\underline{H}_2SnMe_3$, $^2J_{\text{H},^{117}/^{119}\text{Sn}}$ = 54.2/54.7 Hz); 3.68 (sept, 4 H, $C\underline{H}Me_2$); 6.8—7.0 (m, 6 H, H(3), H(4)). ^{13}C NMR, δ: −7.04 ($CH_2Sn\underline{Me}_3$, $J_{\text{C},^{117}/^{119}\text{Sn}}$ = 313.9/328.5 Hz); 23.5 ($\underline{C}HMe_2$); 28.7 ($CH\underline{Me}_2$); 48.8 ($\underline{C}H_2SnMe_3$, $^2J_{\text{C},^{117}/^{119}\text{Sn}}$ = 162.3/169.6 Hz); 122.7 (CH(3)); 125.9 (CH(4)); 142.6 (C(2)); 153.2 (C(1)). ^{119}Sn NMR, δ: 2.4.

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

Parameter	**1** (E = Si)	**2** (E = Ge)	**3** (E = Sn)	**4** (E = C)
Bond		*d*/Å		
Mo(1)—N(1)	1.745(1)	1.745(1)	1.752(2)	1.750(4)
Mo(1)—N(2)	1.753(1)	1.758(1)	1.755(2)	—
Mo(1)—C(25)	2.115(2)	2.118(1)	2.099(3)	—
Mo(1)—C(29)	2.117(2)	2.116(2)	2.100(3)	—
E(1)—C(25)	1.860(2)	1.960(1)	2.157(3)	—
E(2)—C(29)	1.870(2)	1.958(1)	2.156(3)	—
N(1)—C(1)	1.393(2)	1.396(2)	1.392(3)	1.392(6)
N(2)—C(13)	1.393(2)	1.391(1)	1.396(3)	—
Mo(1)—C(13)	—	—	—	2.126(4)
Angle*		ω/deg		
N(1)—Mo(1)—N(2)	112.49(6)	112.38(5)	113.00(9)	—
N(1)—Mo(1)—C(25)	104.24(6)	106.39(6)	106.51(10)	—
N(2)—Mo(1)—C(25)	107.23(6)	107.19(6)	107.05(10)	—
N(1)—Mo(1)—C(29)	107.22(6)	104.84(6)	104.75(10)	—
N(2)—Mo(1)—C(29)	107.73(6)	107.33(6)	107.50(10)	—
C(25)—Mo(1)—C(29)	118.05(6)	118.83(6)	118.23(11)	—
C(1)—N(1)—Mo(1)	164.74(12)	164.83(10)	164.91(18)	158.7(3)
C(13)—N(2)—Mo(1)	156.53(10)	157.25(10)	157.82(17)	—
E(1)—C(25)—Mo(1)	116.95(8)	114.60(7)	114.19(12)	—
E(2)—C(29)—Mo(1)	116.88(8)	114.16(7)	113.29(13)	—
N(1)—Mo(1)—N(1A)	—	—	—	112.6(2)
N(1)—Mo(1)—C(13)	—	—	—	106.24(16)
N(1)—Mo(1)—C(13A)	—	—	—	108.46(17)
N(1A)—Mo(1)—C(13A)	—	—	—	106.24(16)
N(1A)—Mo(1)—C(13)	—	—	—	108.46(17)
C(13)—Mo(1)—C(13A)	—	—	—	115.0(3)
Mo(1)—C(13)—C(14)	—	—	—	120.9(3)

* Symmetry code: $-x$, y, $-z + 1/2$.

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