First Crystal Structure of a Cyclohexasilyl Transition-Metal Derivative, $[(DIME)_2Li][Mo(CO)_5Si_6Me_{11}]$ (DIME = Diethylene Glycol Dimethyl Ether)[†]

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The reaction of $[(DIME)_2Li][Mo(CO)_5I]$ with KSi_6Me_{11} affords the novel complex $[(DIME)_2Li][W(CO)_5Si_6Me_{11}]$. Its crystal structure and chemical properties are discussed.

Introduction

The chemistry of $[M^0(CO)_5X]^-$ anions of group VI elements is encountered throughout the literature.[1] The ease of preparation from $M(CO)_6$ and $NR_4{}^+X^-$ makes them suitable as educts to obtain useful water-soluble complexes of these transition metals.[2] The preparation of water-soluble catalysts is an area of considerable current interest.[3] Furthermore, transition-metal silicon compounds may be useful precursors for metal silicides.[4] For this reason, the design of such compounds seems to be very important. We have synthesized previously stable iodopentacarbonylmetalate complexes of molybdenum and tungsten.[5] However, the chemistry of ionic transition-metal silyl derivatives is not very well explored. There are only a few compounds of this type derived from monosilanes.[6]

Some transition-metal compounds of undecamethylcyclohexasilane have been described in recent years,[7] but none of these compounds has been characterized by X-ray structure analysis. The X-ray structure of 1,4-bis(cyclopentadienyldicarbonylferrio)decamethylcyclohexasilane has been mentioned in the literature, but to our knowledge, the final data were never published.[8] Therefore, there is no information available about the bond parameters or conformation of the cyclohexasilyl system in such compounds. In the present study, we report further developments of the chemistry of $[RM(CO)_5]^-$ anions including the first X-ray structure of a cyclohexasilyl transition-metal derivative.

Results and Discussion

$[(DIME)_2Li][Mo(CO)_5I]$ (1), Molecular Structure. The preparation of $[(DIME)_2Li][Mo(CO)_5I]$ (**1**) has already been described.[5] To characterize this compound, we carried out an X-ray diffraction study on it (Figures 1 and 2). The molecular structure of **1** has been found to be analogous to that of $[(DIME)_2Li][W(CO)_5I]$.[5] Its cation part is shown in Figure 1. The lithium atom is coordinated by two molecules of DIME with a distorted octahedral geometry.

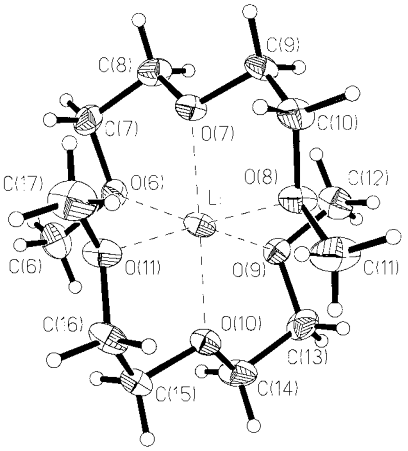

Figure 1. Structure of the $[Li(DIME)_2]^+$ cation in **1**.

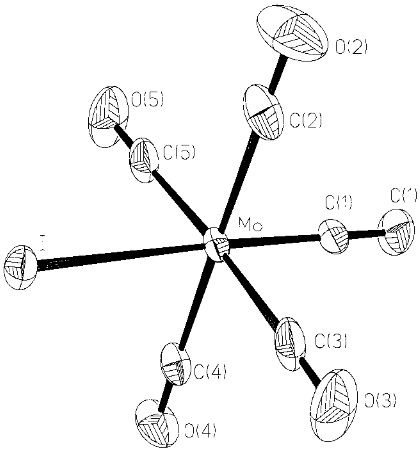

Figure 2. Structure of the $[Mo(CO)_5I]^-$ anion in **1**.

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[†] Dedicated to Prof. P. Jutzi on his 60th birthday.

[1] Atwood, J. L.; Bott, S. G.; Junk, P. C.; May, M. T. *J. Organomet. Chem.* **1995**, *487*, 7 and references therein.

[2] Abel, E. W.; Butler, I. S.; Reid, J. G. *J. Chem. Soc.* **1963**, 2068.

[3] Herrmann, W. A.; Kohlpaintner, C. W. *Angew. Chem.* **1993**, *105*, 1588; *Int. Ed. Engl.* **1993**, *32*, 1524.

[4] *Organosilicon Chemistry II, From Molecules to Materials*; Auner, N.; Weis, J., Eds.; VCH: Weinheim, 1994.

[5] Palitzsch, W.; Böhme, U.; Roewer, G. *Chem. Commun.* **1997**, 803.

[6] (a) Isaacs, E. E.; Graham, W. A. G. *Can. J. Chem.* **1975**, *53*, 467. (b) Heyn, R. H.; Tilley, T. D. *Inorg. Chem.* **1990**, *29*, 4051.

[7] (a) Hengge, E.; Pinter, E.; Eibl, M.; Uhlig, F. *Bull. Soc. Chim. Fr.* **1995**, *132*, 509. (b) Hengge, E.; Eibl, M.; Schrank, F. *J. Organomet. Chem.* **1989**, *369*, C23.

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Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) for 1

Mo−C(1)	1.944(4)	C(4)−O(4)	1.139(4)
Mo−C(2)	2.047(4)	C(5)−O(5)	1.129(4)
Mo−C(3)	2.045(4)	Li−O(6)	2.272(6)
Mo−C(4)	2.029(3)	Li−O(7)	1.988(6)
Mo−C(5)	2.032(4)	Li−O(8)	2.128(6)
Mo−I	2.8693(6)	Li−O(9)	2.179(6)
C(1)−O(1)	1.153(4)	Li−O(10)	2.023(6)
C(2)−O(2)	1.094(5)	Li−O(11)	2.191(6)
C(3)−O(3)	1.126(4)		
C(2)−Mo−C(5)	90.4(2)	O(10)−Li−O(7)	170.0(3)
C(1)−Mo−C(5)	177.9(1)	O(7)−Li−O(8)	78.6(2)
C(4)−Mo−C(3)	90.8(2)	O(7)−Li−O(6)	76.9(2)
C(4)−Mo−C(5)	89.2(2)	O(7)−Li−O(11)	95.1(2)
C(2)−Mo−C(3)	89.7(2)	O(7)−Li−O(9)	110.6(2)
C(1)−Mo−I	177.9(1)		

Table 2. Selected Bond Lengths (Å) and Bond Angles (deg) for 2

Li−O(6)	2.258(7)	Si(1)−Si(6)	2.343(1)
Li−O(7)	2.041(6)	Si(1)−Si(2)	2.348(1)
Li−O(8)	2.142(7)	Si(2)−Si(3)	2.350(2)
Li−O(9)	2.240(7)	Si(3)−Si(4)	2.343(2)
Li−O(10)	1.990(7)	Si(4)−Si(5)	2.338(2)
Li−O(11)	2.107(7)	Si(5)−Si(6)	2.340(1)
Mo−C(1)	1.972(4)	Si(1)−C(6)	1.914(3)
Mo−C(2)	2.012(4)	Si(2)−C(7)	1.888(4)
Mo−C(3)	2.018(4)	Si(2)−C(8)	1.893(4)
Mo−C(4)	2.034(4)	Si(3)−C(10)	1.889(4)
Mo−C(5)	2.031(5)	Si(3)−C(9)	1.901(4)
Mo−Si(1)	2.666(1)	Si(4)−C(11)	1.888(5)
C(1)−O(1)	1.161(5)	Si(4)−C(12)	1.890(5)
C(2)−O(2)	1.161(5)	Si(5)−C(14)	1.881(4)
C(3)−O(3)	1.149(5)	Si(5)−C(13)	1.898(4)
C(4)−O(4)	1.137(5)	Si(6)−C(15)	1.895(4)
C(5)−O(5)	1.146(5)	Si(6)−C(16)	1.895(4)
O(10)−Li−O(7)	178.9(4)	C(3)−Mo−Si(1)	90.4(1)
O(7)−Li−O(8)	80.3(2)	C(4)−Mo−Si(1)	84.0(1)
O(7)−Li−O(6)	76.0(2)	C(5)−Mo−Si(1)	80.2(1)
O(7)−Li−O(11)	97.3(3)	Si(6)−Si(1)−Mo	113.16(4)
O(7)−Li−O(9)	104.2(3)	Si(2)−Si(1)−Mo	116.49(4)
C(2)−Mo−C(3)	90.6(3)	Si(6)−Si(1)−Si(2)	105.22(5)
C(2)−Mo−C(5)	89.8(2)	Si(1)−Si(2)−Si(3)	113.36(5)
C(4)−Mo−C(5)	89.8(2)	Si(4)−Si(3)−Si(2)	111.44(5)
C(4)−Mo−C(3)	89.8(2)	Si(5)−Si(4)−Si(3)	110.21(5)
C(1)−Mo−Si(1)	174.8(1)	Si(4)−Si(5)−Si(6)	111.06(5)
C(2)−Mo−Si(1)	96.1(1)	Si(5)−Si(6)−Si(1)	116.03(5)
Si−Si2−Si3−Si4	59.25(7)	Si4−Si5−Si6−Si1	−55.58(7)
Si2−Si3−Si4−Si5	−54.21(7)	Si2−Si1−Si6−Si5	55.61(6)
Si3−Si4−Si5−Si6	51.61(7)	Mo−Si1−Si6−Si5	−176.14(4)

The same geometry is also found for the cation in **2**. Figure 2 demonstrates the structure of the iodopentacarbonylmolybdenum(0) anion. The molybdenum atom resides in a nearly regular octahedron with CO_{eq}−Mo−CO_{eq} angles very close to 90° and a CO_{ax}−Mo−I_{ax} angle of 177.9(1)°. Important bond distances and angles are listed in Table 1. Crystallographic data and data collection parameters are listed in Table 4.

Synthesis of $[(DIME)_2Li][Mo(CO)_5Si_6Me_{11}]$ (2). The title compound was prepared according to Scheme 1. The reaction of 1 equiv of $[(DIME)_2Li][Mo(CO)_5I]$ (**1**) with $K[Si_6Me_{11}]$ in DME (DME = 1,2-dimethoxyethane) at ambient temperature results in the novel $[(DIME)_2Li][Mo(CO)_5Si_6Me_{11}]$ **2**.

Compounds **1** and **2** can be safely dried in vacuum at room temperature without loss of the DIME ligands. Complex **2** is prone to slow decomposition in air. These compounds show no sign of decomposition over extended periods under an inert atmosphere. **2** decomposes thermally at 170 °C. **2** is highly soluble in protic solvents (for example methanol) with no evidence of decomposition in solution, as checked by NMR. Recrystallization from dichloromethane/pentane at −20 °C gave analytically pure yellow crystals of **2** suitable for an X-ray crystallographic study.

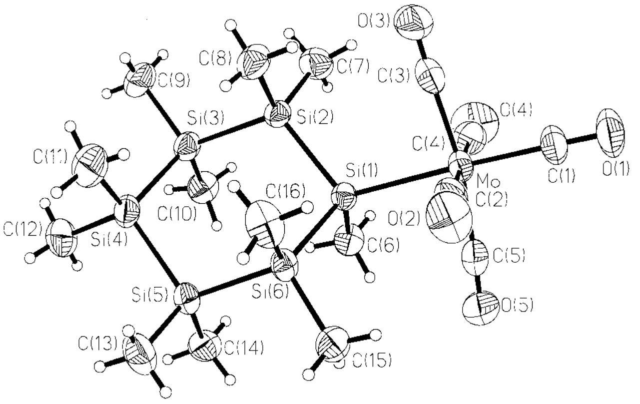

Figure 3. Structure of the $[Mo(CO)_5Si_6Me_{11}]^-$ anion in **2**.

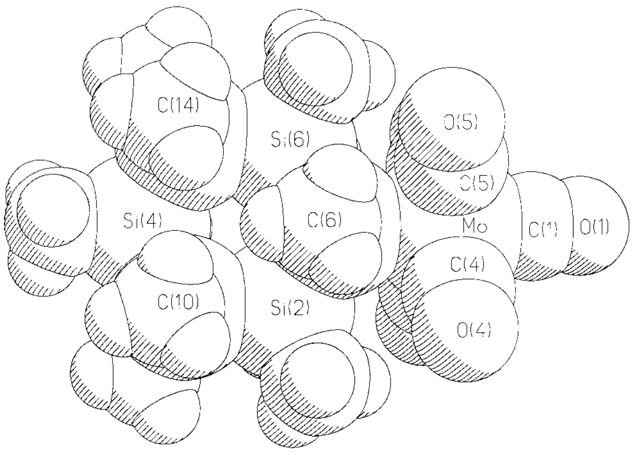

Figure 4. Space-filling plot of the $[Mo(CO)_5Si_6Me_{11}]^-$ anion in **2**.

Molecular Structure of 2. The structure was solved and refined in space group $P2_1/n$. The lithium atom is coordinated by two molecules of DIME with a distorted octahedral coordination geometry. The tridentate ether molecules chelate the lithium atom in a meridional fashion. The Li−O bond distances in **2** of 2.041−2.258 Å are in the same range as the Li−O distances reported for $[(DIME)_2Li][Mo(CO)_5I]$. The structures of the cations are isomorphous (see also Figure 1).

The structure and atom-labeling scheme for the cyclohexasilylpentacarbonylmolybdenum(0) anion are shown in Figure 3. Bond distances and angles are listed in Table 2, and crystallographic data and data collection parameters are given in Table 4.

The $[Mo(CO)_5Si_6Me_{11}]^-$ anion has approximately C_s symmetry with a Mo−Si bond length of 2.666(1) Å. The structures deposited in the Cambridge Structural Database (CSD) have been analyzed for compounds containing molybdenum−silicon bonds.[9] Analysis of the 15 existing structures shows that the average values for Mo−Si bonds are in the range of 2.538−2.608 Å.[10]

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(8) The structure was cited as “Hengge, E.; Eibl, M. Unpublished results” In Hengge, E.; Janoschek, R. *Chem. Rev.* **1995**, *95*, 1495.

Table 3. ^{1}H, ^{13}C, and ^{29}Si NMR Data for Compound 2[a]

$\delta^{1}H$		$\delta^{13}C$			
DIME	Me−Si	DIME	CO	Si−Me	$\delta^{29}Si$
3.57, 3.72, (CH_2), 3.42 (CH_3)	0.25, 0.20, 0.15, 0.13	71.67, 69.72 (CH_2), 59.12 (CH_3)	211.46, 204.52	−2.07, −3.12, −3.72, −4.15, −4.35, −5.73, −6.42	−63.25, −41.44, −39.81, −30.14

[a] Recorded in $CDCl_3$, at 25 °C; data are given in ppm relative to Me_4Si at 0.0 ppm.

Scheme 1

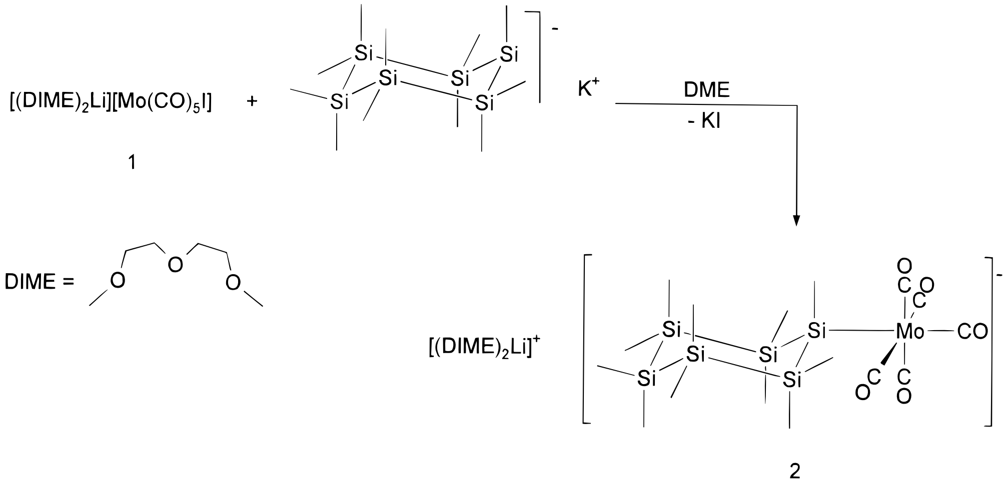

Table 4. Crystal Data and Structure Refinement for 1 and 2

	1	2
empirical formula	$C_{17}H_{28}ILiMoO_{11}$	$C_{28}H_{61}LiMoO_{11}Si_6$
fw	638.17	845.19
temp	190(2) K	190(2) K
wavelength	1.54180 Å	1.54180 Å
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
unit cell dimens	$a = 14.625(3)$ Å	$a = 16.127(2)$ Å
	$b = 13.234(2)$ Å	$b = 14.310(1)$ Å
	$c = 14.683(4)$ Å	$c = 20.256(2)$ Å
	$\beta = 113.02(2)°$	$\beta = 96.60(1)°$
vol.	2615.6(10) $Å^3$	4643.5(13) $Å^3$
Z	4	4
density (calcd)	1.619 Mg/m^3	1.209 Mg/m^3
abs coeff	13.782 mm^{-1}	4.163 mm^{-1}
$F(000)$	1264	1784
cryst size	0.5 × 0.4 × 0.4 mm	1.0 × 0.7 × 0.25 mm
θ range for data collection	3.28−75.78°	3.32−74.77°
index ranges	$-18 \le h \le 16$	$-20 \le h \le 20$
	$0 \le k \le 16$	$0 \le k \le 17$
	$0 \le l \le 18$	$-25 \le l \le 20$
no. of reflns collected	5410	18 514
no. of indep reflns	5410	9532 [$R(\text{int}) = 0.0567$]
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
data/restraints/params	5410/0/280	9532/0/439
goodness-of-fit on F^2	0.946	1.025
final R indices [$I > 2\sigma(I)$]	R1 = 0.0307	R1 = 0.0521
	wR2 = 0.0809	wR2 = 0.1422
R indices (all data)	R1 = 0.0362	R1 = 0.0597
	wR2 = 0.0846	wR2 = 0.1498
min transmission	0.717	0.665
max transmission	1.0	0.999
largest diff peak and hole	0.663 and −0.837 e × $Å^{-3}$	1.111 and −0.899 e × $Å^{-3}$

There is one very short Mo−Si bond in a molybdocene derivative ($Cp_2Mo(H)SiMe_2Cl$),[10d] and one example of an extremely long bond is in tetrakis(dimethylamino)-bis(tris(trimethylsilyl)silyl)dimolybdenum[10a] with a bond length of 2.669 Å. The bond length of **2** is also very long compared to the literature data. This is probably due to the distribution of the negative charge over the Mo−Si bond.

The Mo−C distances for the four equatorial CO ligands range from 2.012(4) to 2.034(4) Å, while the Mo−C bond to the axial CO ligand is only 1.972(4) Å. This reflects the stronger π-back-bonding to the CO ligand that is trans to the silyl group. Two of the four equatorial CO's are bent toward the Si_6Me_{11} ligand, resulting in Si(1)−Mo−C(4) and Si(1)−Mo−C(5) angles of 84.0(1)° and 80.2(1)°, respectively. This is probably caused by packing effects since these two CO groups fit well in the gap between the methyl groups of the cyclohexasilyl ligand as can be seen from the space-filling plot (Figure 4).

In contrast, the CO groups C(2)O(2) and C(3)O(3) have directly neighboring methyl groups, C(8) and C(16), which cause an enlargement of the bond angles Si(1)−Mo−C(2) and Si(1)−Mo−C(3) (96.1° and 90.4°, respectively). The different values of these two angles can be explained by the position of the six-membered ring in relation to the $Mo(CO)_5$ unit: the torsion angle C(3)−Mo−Si(1)−Si(2) has a value of 18.5° and the angle C(2)−Mo−Si(1)−Si(6) has a value of −12.9°. This means that there is a small deviation from ideal C_s symmetry. The group C(2)O(2) is near the neighboring Si(6)C(16), whereas C(3)O(3) is rotated away from Si(2)C(8) and, therefore, a smaller angle Si(1)−Mo−C(3) results.

The cyclohexasilyl ligand has a chair conformation with the $Mo(CO)_5$ group at an equatorial position. The ideal chair conformation should have torsion angles of

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(9) Cambridge Structural Database System, prepared by the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, England.

(10) (a) Chisholm, M. H.; Chiu, H.−T.; Folting, K.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 4097. (b) Hseu, T. H.; Chi, Y.; Liu, C.-S. *Inorg. Chem.* **1981**, *20*, 199. (c) Berry, D. H.; Chey, J.; Zipin, H. S.; Carroll, P. J. *Polyhedron* **1991**, *10*, 1189. (d) Koloski, T. S.; Pestana, D. C.; Carroll, P. J.; Berry, D. H. *Organometallics* **1994**, *13*, 489. (e) Malisch, W.; Lankat, R.; Fey, O.; Reising, J.; Schmitzer, S. *Chem. Commun.* **1995,** 1917.

60° and tetrahedral coordination of the silicon atoms with bond angles of 109.5°. The torsion angles along the Si−Si bond skeleton vary between 51.6° and 59.2° (positive or negative sign). This means that the ring is slightly flattened.

The silicon−silicon bond lengths in **2** are in the range from 2.338 to 2.350 Å. There is no elongation of the Si(1)−Si(6) and Si(1)−Si(2) bonds as might have been expected due to substitution with molybdenum in this position. For dodecamethylcyclohexasilane, bond lengths of 2.332−2.342 Å were reported.[11] Simple monosubstituted cyclohexasilyl derivatives such as bis(undecamethylcyclohexasilane) and bis(undecamethylcyclohexasilyl)dimethylsilane have Si−Si bond lengths in the range from 2.341 to 2.366 and 2.327 to 2.364 Å, respectively.[12] Therefore, it can be concluded that the cyclohexasilyl ligand in **2** has normal Si−Si bond lengths. There is no significant effect of bond elongation due to displacement of the negative charge into the six-membered ring. The silicon−carbon bond lengths range from 1.881 to 1.901 Å, which fits well with the sum of the atomic radii of 1.88 Å. Only the Si(1)−C(6) distance is longer than the other Si−C bonds (1.914 Å). This is another suggestion of the displacement of the negative charge to Si(1).

Spectroscopic Properties of 1 and 2. Infrared spectra of **1** in the carbonyl streching frequency region exhibit four bands. While only three infrared-active bands are expected for a $RM(CO)_5^-$ molecule of C_{4v} symmetry, a rather weak band at 2045 cm^{-1} in a related complex has been assigned as the formally infrared-inactive B_1 mode.[13] The ^1H NMR signals of the diethylene glycol dimethyl ether ligands are observed at 3.41 ppm (s, $-CH_3$) and 3.53 and 3.71 ppm (m, $-CH_2-CH_2-$). The ^{13}C NMR data of **1** are in agreement with the proposed structure.

The infrared spectrum of **2** has four metal carbonyl bands at 2020 (w), 1915 (m), 1890 (s), and 1860 (m) cm^{-1}, which are characteristic for metal pentacarbonyl anions, $RM(CO)_5^-$.[14] The IR bands are assigned to the three IR-active fundamental vibrations ($2A_1 + E$) expected for a C_{4v} metal pentacarbonyl species and to the B_1 vibration, which is IR inactive in the case of rigorous C_{4v} geometry. This assignation follows that given by Casey for the alkylpentacarbonyltungsten anions.[15] This fourth band is also observed in many other $M(CO)_5R^-$ species.[16]

The electronic spectra of the complexes **1** and **2** (Figure 5) show intensive absorptions below 280 nm, which originate mainly from a charge-transfer Mo → CO (MLCT). A detailed analysis of the absorption bands is impossible due to the intensive solvents absorption of dichloromethane in this region. The solution of $Mo(CO)_6$ in pentane shows maxima at 227 and 288 nm. Si_6Me_{12} in pentane absorbs at 232 nm with a shoulder at 258 nm.[17] The ionic pentacarbonyl molybdates **1** and **2** show additional maxima at 398 (**1**) and 336 nm (**2**), respectively. These maxima can be assigned as charge-transfer bands of LMCT type ($I^- \rightarrow Mo$ and $Si_6Me_{11}^- \rightarrow Mo$). The low energy of the charge-transfer band in the case of $Mo(CO)_5I^-$ arises from the low ionization potential of the iodide ion. The substitution of iodide by $Si_6Me_{11}^-$ leads to a strong hypsochromic shift of the LMCT band. The appearance of this UV band confirms the location of the negative charge at the $Si_6Me_{11}^-$ ligand. This conclusion is in agreement with the data of the X-ray structure. There is no evidence for charge delocalization or σ-aromaticity in the six-membered silicon ligand.

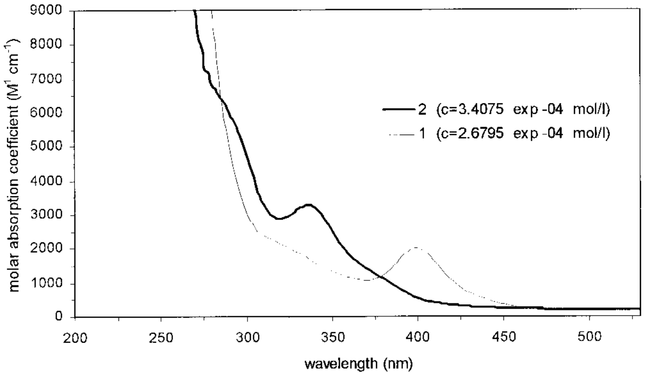

Figure 5. UV−vis absorption spectra of **1** and **2**.

The ^1H NMR signals of the DIME ligands are located at 3.42 (s, $-CH_3$), 3.57, and 3.72 ppm (m, $-CH_2-CH_2-$). The ^1H NMR resonances of the methyl groups bonded to the silicon appear in the typical δ range near zero (see Table 3). Seven signals for the silicon-bonded methyl groups in the ^{13}C NMR point to the fact that the silicon ring has occupied the chair conformation (Table 3). The single-crystal stucture analysis confirms this assumption. The ^{29}Si NMR spectrum of compound **2** exhibits four resonances which are caused by the cyclosilyl ligand bonded to the metal atom (Table 3). Dodecamethylcyclohexasilane shows one ^{29}Si NMR signal at −41.8 ppm. The signal at −63.25 ppm in the ^{29}Si NMR spectrum of **2** can be assigned to the Si(1) atom. Its significant high-field shift in comparison to the other signals also indicates accumulation of the negative charge on the silicon atom which is connected with the molybdenum pentacarbonyl fragment.

Conclusions

In summary, the preparation and characterization of $[(DIME)_2Li][Mo(CO)_5I]$ **(1)** and $[(DIME)_2Li][Mo(CO)_5Si_6Me_{11}]$ **(2)** are reported. Compound **2** represents the first cyclohexasilyl transition-metal derivative which has been characterized by X-ray structure analysis. The X-ray data show a cyclohexasilyl ring with a chair conformation and normal bond lengths. Elongated bonds at Mo−Si(1) and Si(1)−C(6) suggest the location of the negative charge is at Si(1) in the Si_6Me_{11} ligand. The occurrence of an LMCT band (Si → Mo) in the UV−vis spectrum and the high-field shift of the ^{29}Si NMR signal of Si(1) support this assumption.

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[11] Carrell, H. L.; Donohue, J. *Acta Crystallogr., Sect. B* **1972**, *28*, 1566.

[12] Hassler, K.; Mitter, F. K.; Hengge, E.; Kratky, C.; Wagner, U. G. *J. Organomet. Chem.* **1987**, *333*, 291.

[13] Dobson, G. R.; Stolz, I. W.; Sheline, R. K. *Adv. Inorg. Nucl. Chem.* **1966**, *8*, 1.

[14] Ellis, J. E.; Hagen, G. P. *Inorg. Chem.* **1977**, *16*, 1357.

[15] Casey, C. P.; Polichnowski, S. W. *J. Am. Chem. Soc.* **1978**, *100*, 7565.

[16] Ruff, J. K. *Inorg. Chem.* **1967**, *6*, 1502.

[17] West, R. In *Comprehensive Organometallic Chemistry;* Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 2, 391.

Both compounds (**1** and **2**) are unusually stable in protic solvents and will, therefore, be useful for further investigations.

Experimental Section

All preparative work and handling of the samples was carried out under Ar, using dry glassware and dry solvents. DIME (diethylene glycol dimethyl ether) and DME (1,2-dimethoxyethane) were repeatedly distilled from fresh Na until no effervescence was observed. DIME was distilled once more and then stored in a sealed flask in a drybox prior to use. Mo($CO)_6$ starting material was purchased from Fluka Chemie AG and vacuum sublimed prior to use. Synthesis of $Si_6Me_{11}K$ was carried out according to an established procedure.[18]

NMR spectra were recorded on Bruker MSL 200. Elemental analyses were performed on a CHN-O-RAPID (Heraeus). Carbon values are lower due to formation of carbide. Infrared spectra were recorded using a Specord 75 IR instrument in the range 4000−400 cm^{-1} using the KBr disk method. Electronic spectra were obtained with a M500-Zeiss UV−vis spectrometer from dichloromethane solutions.

Synthesis of [(DIME)$_2$Li][Mo(CO)$_5$I] (1). A sample of $Mo(CO)_6$ (5.28 g, 0.02 mol) was added to a solution of LiI·Et_2O (4.15 g, 0.02 mol) in diethylene glycol dimethyl ether. The mixture was heated at 80 °C for 2 days. The solution became bright yellow. IR monitoring showed the formation of a species with a ν(CO) pattern typical of [$Mo(CO)_5X$] species: 2045, 1981, 1930, 1858 cm^{-1}. The solvent was removed under vacuum to give a yellow residue. It was dissolved in dichloromethane, then treated with *n*-pentane to give yellow crystals of **1** (isolated yield 9.95 g, 78 %). Spectroscopic data for **1**: ^{1}H NMR ($CDCl_3$/TMS) 3.71, 3.59, 3.41 ppm; ^{13}C NMR ($CDCl_3$/TMS) 219.59, 204.56, 70.49, 69.25, 59.44 ppm; UV−vis (λ_{max}, nm (log ϵ), dichloromethane) 398 (3.3022). Anal. Calcd for $C_{17}H_{28}ILiMoO_{11}$: C, 31.99; H, 4.38. Found: C, 31.48; H, 4.27.

Synthesis of [(DIME)$_2$Li][Mo(CO)$_5$Si$_6$Me$_{11}$] (2). $Si_6Me_{11}K$ was prepared from Si_6Me_{12} (2.6 g, 0.007 mol) and KOC($CH_3)_3$ (0.78 g, 0.007 mol) in DME (10 mL) and then added dropwise at room temperature within 15 min to a stirred solution of **1** (4.46 g, 0.007 mol) in DME (20 mL). After the reaction mixture was stirred at room temperature for 12 h, the solvent was removed under reduced pressure, a mixture of *n*-pentane/dichloromethane 1:1 (20 mL) was added to the residue, and the precipitate was filtered off.

The solvents were evaporated under reduced pressure. A 20 mL amount of *n*-pentane was added to the residue to form a slighty yellow suspension. After the addition of ca. 10 drops of dichloromethane, an orange liquid clathrate separated from the mixture. Yellow crystals of **2** deposited from the liquid clathrate layer after 1 day at −20 °C. Yield: 4.02 g (68%). The NMR data are shown in Table 3. IR (Nujol) ν(CO) 2020 (w), 1915 (m), 1890 (s), 1860 (m); UV−vis (λ_{max}, nm (log ϵ), dichloromethane) 336 (3.5145). Anal. Calcd for $C_{28}H_{61}LiO_{11}Si_6W$: C, 39.79; H, 7.21. Found: C, 38.87; H, 7.26.

Experimental Procedure for X-ray Crystallography. Suitable single crystals of **1** and **2** were mounted on glass fibers under paraffin oil and transferred to the diffractometer. Diffraction measurements were made on an Enraf-Nonius CAD-4 diffractometer at −83 °C using graphite-monochromated Cu−Kα radiation ($\lambda = 1.5418$ Å) with $\omega-2\theta$ scans. The structures were solved from a three-dimensional Patterson function for the heavy atoms; non-hydrogen atoms were located from difference Fourier synthesis and refined by full-matrix least squares on F^2 with anisotropic thermal parameters. Hydrogen atoms were calculated and allowed to ride on their corresponding carbon atoms. An empirical absorption correction was performed using ψ scans. Crystallographic data and the results of refinements are summarized in Table 4.

Atomic coordinates, bond length and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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Supporting Information Available: Tables giving crystal data and structure refinement details, atomic coordinates, thermal parameters, and bond distances and angles for **1** and **2** (14 pages). Ordering information is given on any current masthead page.

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[18] Uhlig, F.; Gspatl, P.; Trabi, M.; Hengge, E. *J. Organomet. Chem.* **1995**, *493*, 33.