Support Information

Synthesis and Characterization of the $\{Si(NHCH_2CH_2NH)_3[Mo(CO)_3]_2\}^{2-}$ Complex Comprising the $Si(NHCH_2CH_2NH)_3^{2-}$ Octahedron

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Experimental Section

All reactions were carried out in a nitrogen atmosphere dry box (Vacuum Atmosphere Co). EDX analyses were performed on Hitachi SU-70 SEM, operated at an acceleration voltage of 10 keV. ESI-MS (JEOL ACCUTOF-CS ESI-TOF) data were collected in a negative ion mode by dissolving the crystals in CH_3CN. The samples were made up inside a glovebox under an N_2 atmosphere and rapidly transferred to the spectrometer in an airtight syringe by direct infusion with a Harvard syringe. The ^1H and ^{13}C NMR were recorded in CD_3CN on a Bruker DRX600 spectrometer. Chemical shifts are reported in parts per million (ppm) were referenced to the residual proton resonance of the deuterated solvents and are reported relative to tetramethylsilane(TMS).

Chemicals. Melts of nominal composition of $K_{12}Si_{17}$ was prepared by fusion of stoichiometric ratios of the elements at high temperature (~1100 °C). The elements were loaded into quartz tubes in a nitrogen atmosphere dry-box and then sealed under vacuum. CAUTION: the fusion process can be very exothermic and the reactions should be conducted behind blast shields on small scales (<500 mg) using full protective gear. [2.2.2]Crypt was purchased from TCI. Ethylenediamine (en) were purchased from Acros Organics. $Mo(CO)_3(C_7H_8)$ (Tricarbonyl(Toluene)molybdenum(0)) [1] was prepared according to the literature procedures. Anhydrous ethylenediamine (en) vacuum distilled from K_4Sn_9 and stored under N_2. Toluene was distilled from sodium under N_2 and stored under N_2.

Synthesis of $[K([2,2,2]crypt)]_2\{Si[\mu_2\text{-}(NHCH_2CH_2NH)]_3[Mo(CO)_3]_2\}\bullet(tol)_2$. In vial 1, the precursor with the nominal composition "$K_{12}Si_{17}$"(92.9mg, 0.1mmol) and 2,2,2-crypt (21.5mg, 0.06mmol) were dissolved into 2ml ethylenediamine(en). After stirring for 2 h, a light yellow-green solution with plenty of gray precipitates was resulted. In vial 2, $Mo(CO)_3(C_7H_8)$(8.2mg, 0.03mmol) was dissolved in 2ml toluene(tol), giving a brown-yellow solution. The solution of vial 2 was added dropwise to vial 1 and the mixture were stirred for 2h, yielding a reddish-brown solution. The solution was then filtered through tightly packed glass wool. The filtrate was layered with another 3ml toluene. After about a week, brown-yellow plate-like crystals of $[K([2,2,2]crypt)]_2\{Si[\mu_2\text{-}(NHCH_2CH_2NH)]_3[Mo(CO)_3]_2\}\bullet(tol)_2$ precipitated, in a yield of ~25% (based on $Mo(CO)_3(C_7H_8)$).

Crystallographic Studies. A suitable single crystals of $C_{62}H_{106}K_2Mo_2N_{10}O_{18}Si$ (UM2831) was selected and measured on a Bruker Smart Apex II CCD diffractometer.[2] The crystal was kept at 150(2) K during data collection. The integral intensity was correct for absorption using SADABS software [3] using multi-scan method. Resulting minimum and maximum transmission are 0.897 and 0.984 respectively. The structure was solved with the ShelXT program and refined with the XL program and Least Squares minimisation using ShelX software package.[4]

Crystal structure determination. *Crystal Data* for $C_{62}H_{106}K_2Mo_2N_{10}O_{18}Si$ (M =1577.73 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 20.0662(11) Å, b = 24.3575(14) Å, c = 16.0618(9) Å, β = 112.0165(7)°, V = 7277.9(7) Å^3, Z = 4, T = 150(2) K, μ(MoKα) = 0.548 mm^{-1}, *Dcalc* = 1.440 g/cm^3, 64074 reflections measured (3.998° ≤ 2Θ ≤ 53°), 15034 unique (R_{int} = 0.0453, R_{sig} = 0.0442) which were used in all calculations. The final R_1 was 0.0405 (I > 2σ(I)) and wR_2 was 0.0985 (all data).

Refinement details: The structure contains heavily disordered toluene solvent which was accounted for using SQUEEZE routine from Platon software (Spek, 1990).[5] The removed solvent molecules were added to the total content in order to calculate correct density, absorption coefficient and F000. H atoms were positioned from geometric considerations and refined as riding on the attached atoms with Uiso constrained to be 20% larger than Ueqv of the attached atom. Exception are H atoms in NH groups of the ethylenediamine which were located from difference Fourier maps and freely refined.

References:

1. King, R.B. and Fronzaglia, A. (**1966**). *Inorg. Chem.* 5, 1837-1846.
2. Bruker (**2010**). Apex2. Bruker AXS Inc., Madison, Wisconsin, USA.
3. Sheldrick, G. M. (**2008**), *Acta Cryst*. A64, 112-122.
4. Sheldrick, G. M. (**2014**). SHELXL-2014. University of Gottingen, Germany.
5. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (**2009**), *J. Appl. Cryst.* 42, 339-341.

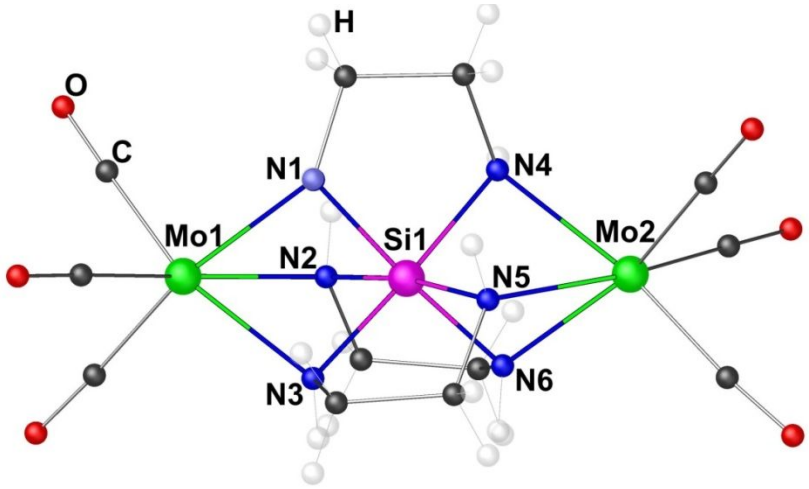

Figure S1 Crystal structure of **Λ**- $Si(NHCH_2CH_2NH)_3^{2-}$ draw in the ball & stick model.

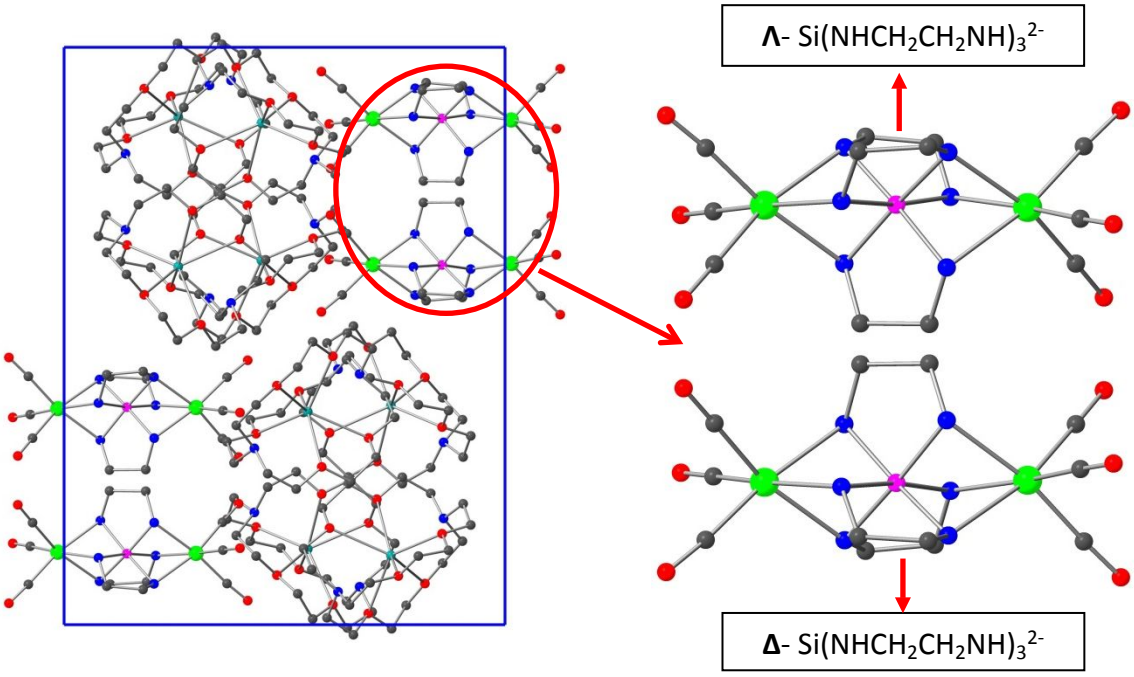

Figure S2 the chiral (Λ- and Δ- isomers) $Si(NHCH_2CH_2NH)_3^{2-}$ anion in the molecular unit cell of the compound $[K(2,2,2\text{-crypt})]_2\{Si(NHCH_2CH_2NH)_3[Mo(CO)_3]_2\}\bullet(tol)_2$, with all hydrogen atoms omitted for clarity, viewed from the *c* axis.

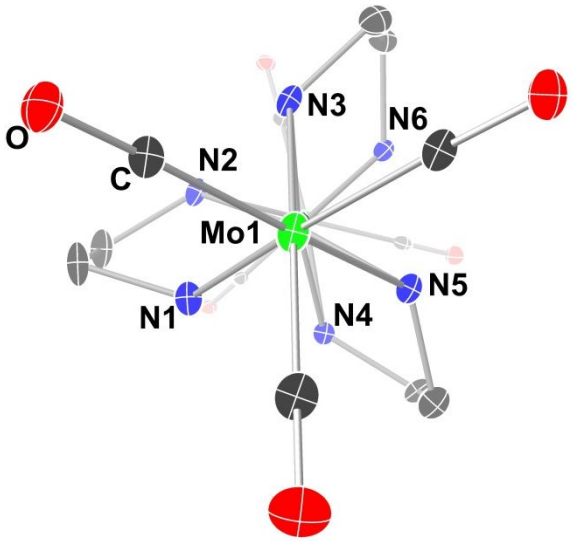

Figure S3 Side view of the $\{Si(NHCH_2CH_2NH)_3[Mo(CO)_3]_2\}^{2-}$ anion with the C_3 axis defined by Mo1, Si and Mo2.

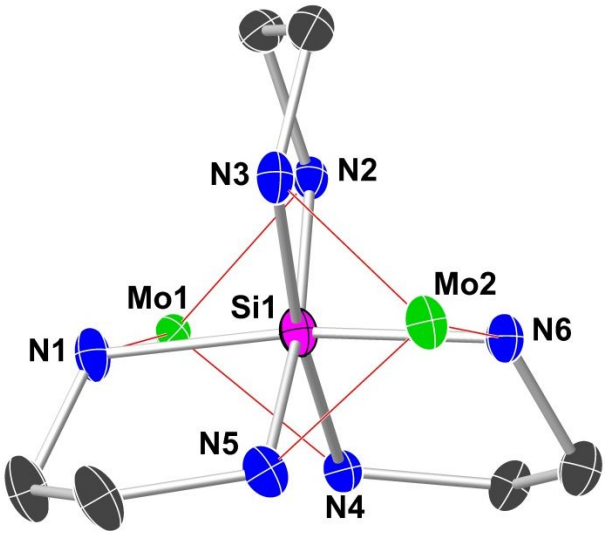

Figure S4 the SiN_6Mo_2 skeleton in $\{Si(NHCH_2CH_2NH)_3[Mo(CO)_3]_2\}^{2-}$.

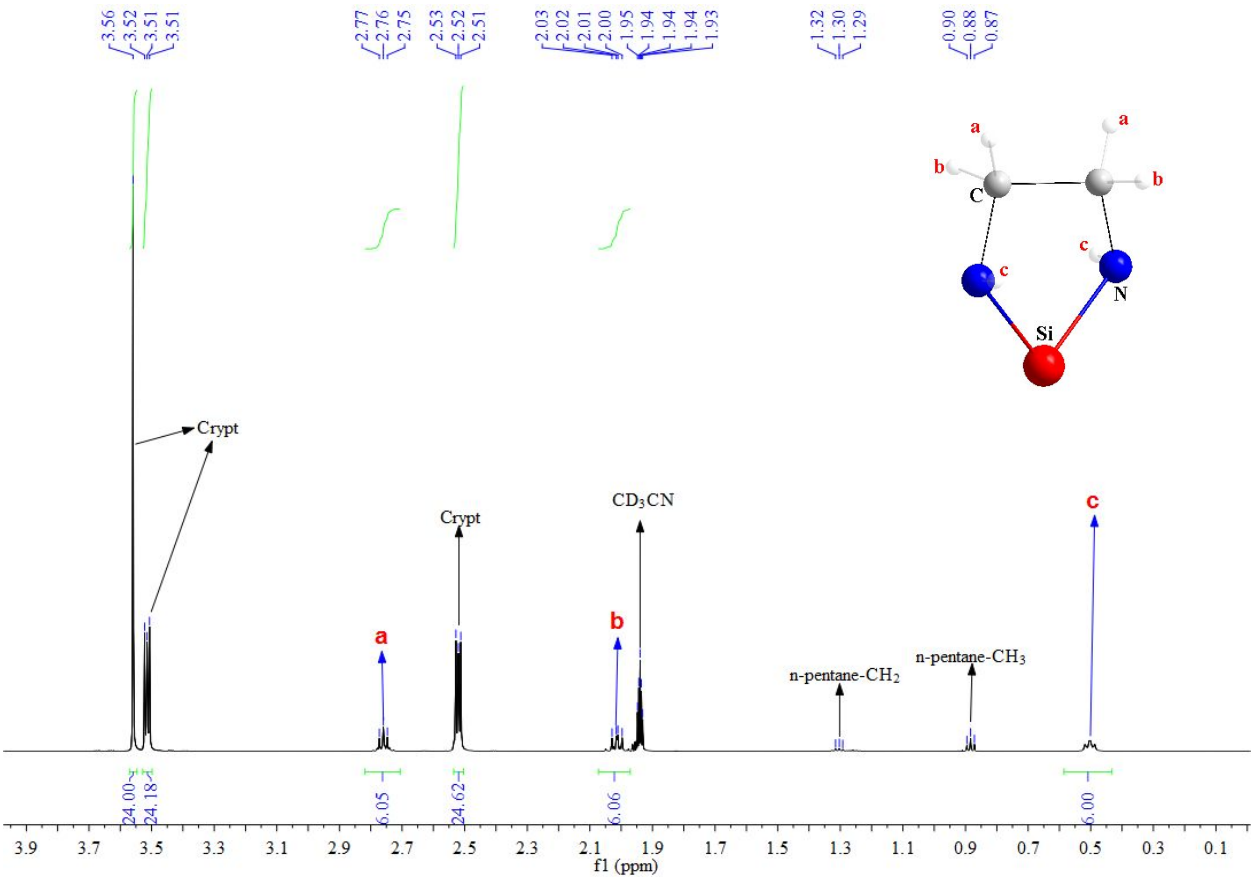

Figure S5 ^{1}H-NMR of crystals $[K([2,2,2]crypt)]_2\{Si[(NHCH_2CH_2NH)]_3[Mo(CO)_3]_2\}\bullet (tol)_2$ in CD_3CN. The crystals were washed by toluene and pentane, respectively, each for three times. δ=3.56(s, 24H; 2,2,2crypt), 3.51(m, 24H; 2,2,2-crypt), 2.52(m, 24H; 2,2,2-crypt); 0.50(tr, 6H, -$NHCH_2CH_2NH$-), 2.01(m, 6H, -$NHCH_2CH_2NH$-), 2.76(m, 6H, -$NHCH_2CH_2NH$-). The toluene solvates in the crystals are lost in the washing and drying of the crystalline compound.

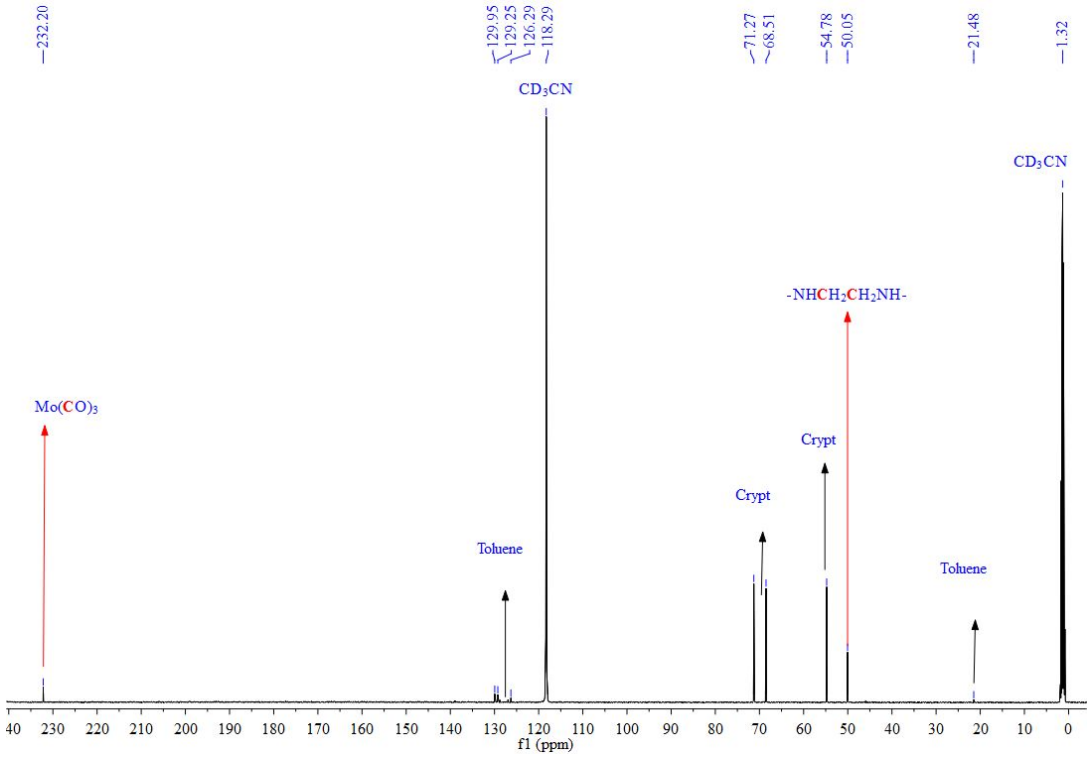

Figure S6 ^{13}C-NMR of crystals $[K([2,2,2]crypt)]_2\{Si[(NHCH_2CH_2NH)]_3[Mo(CO)_3]_2\}\bullet(tol)_2$ in CD_3CN, which was washed by toluene and hexane, respectively, each for three times.

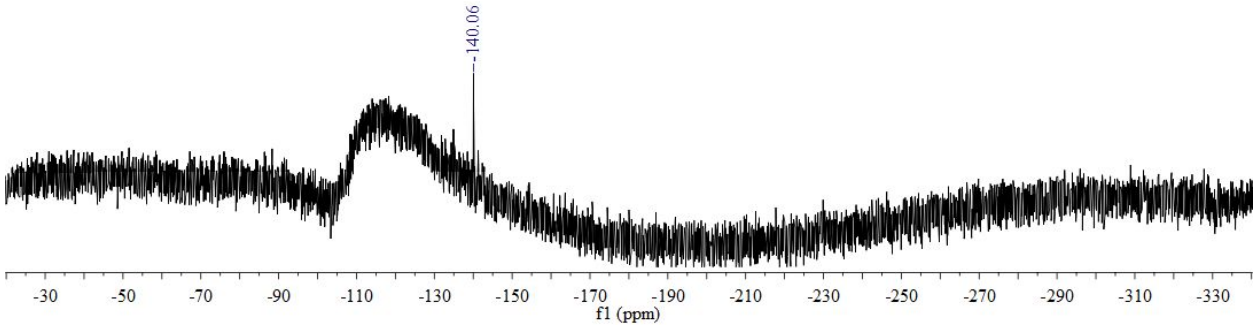

Figure S7 ^{29}Si-NMR of crystals $[K([2,2,2]crypt)]_2\{Si[\mu^2\text{-}(NHCH_2CH_2NH)]_3[Mo(CO)_3]_2\}\bullet(tol)_2$ in CD_3CN. The broad peak is the background ^{29}Si signal arising from glass and quartz.

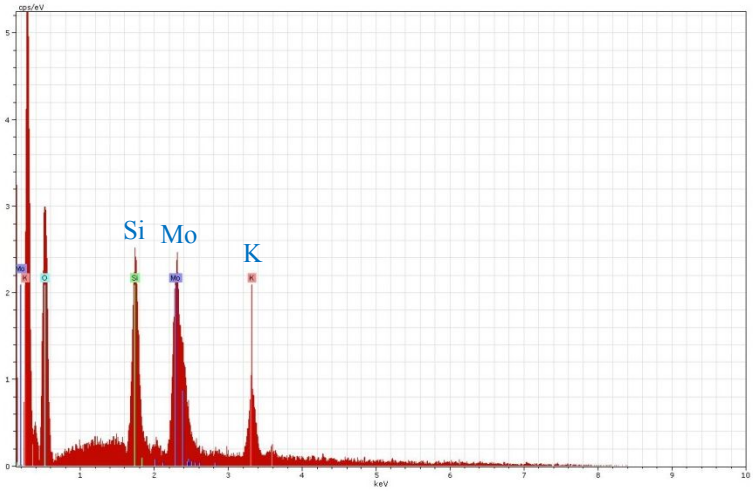

Figure S8 EDX analysis of the crystal $[K([2,2,2]crypt)]_2\{Si[(NHCH_2CH_2NH)]_3\,[Mo(CO)_3]_2\}\bullet(tol)_2$. It shows the presence of K, Si, and Mo.

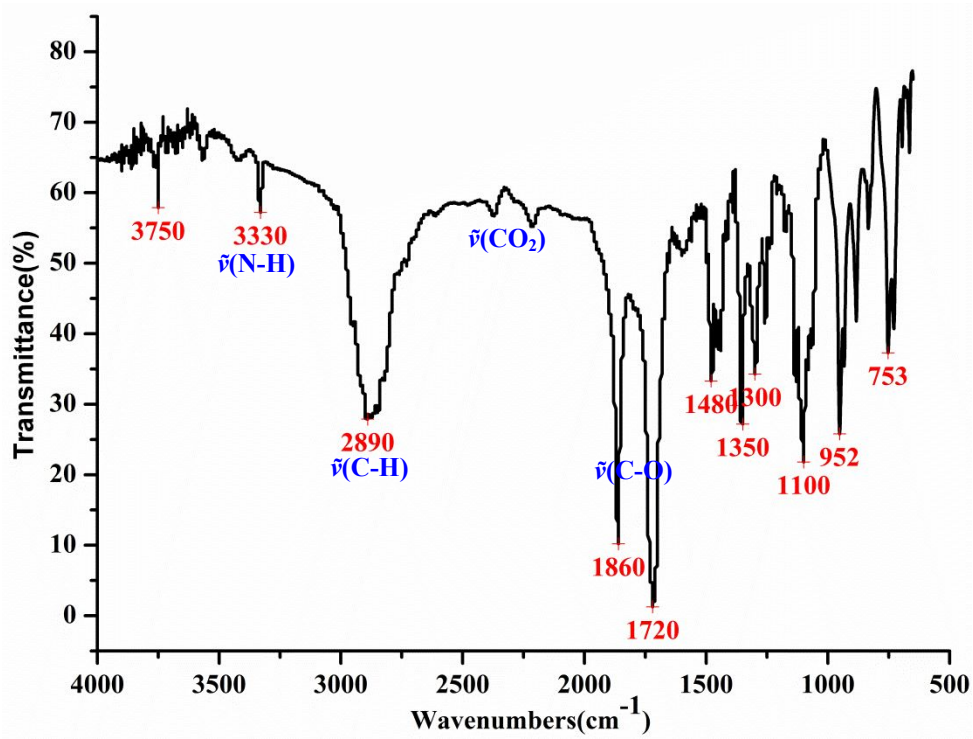

Figure S9 Infrared (IR) spectrum of $[K([2,2,2]crypt)]_2\{Si[\mu_2\text{-}(NHCH_2CH_2NH)]_3\,[Mo(CO)_3]_2\}\bullet\,(tol)_2$ (1) recorded in a Praying Mantis™ Reaction Chamber: $\tilde{\nu}$=3330cm^{-1}**, N-H** stretching vibration; $\tilde{\nu}$=2370 and 2210cm^{-1} originate from the carbon dioxide from residual CO_2 in the purge gas; $\tilde{\nu}$(CO)=1860 and 1720 cm^{-1}; broad absorbance around $\tilde{\nu}$=1600cm^{-1} is from the bending vibration of N-H and C-C stretches in the toluene aromatic ring; 4000-3500 cm^{-1} and 1480-500cm^{-1} are attributed to vibrational frequency of $[K(2,2,2\text{-crypt})]^+$ and toluene molecules.

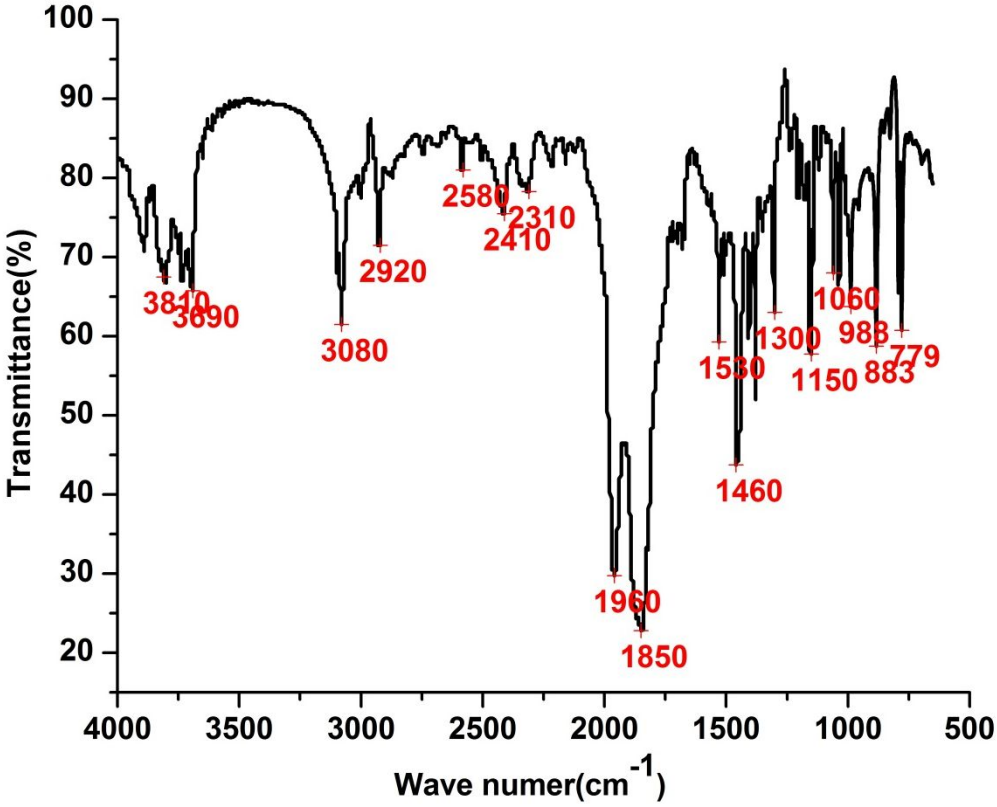

Figure S10 Infrared (IR) spectroscopy of $Mo(CO)_3(C_7H_8)$.

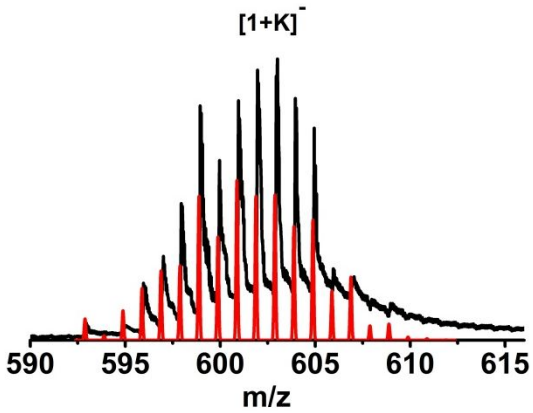

Figure S11 Measured (black) and simulated (red) K^+- coordinated molecular ions from ESI-MS in negative ion mode (**1**=$Si[(NHCH_2CH_2NH)]_3[Mo(CO)_3]_2$).

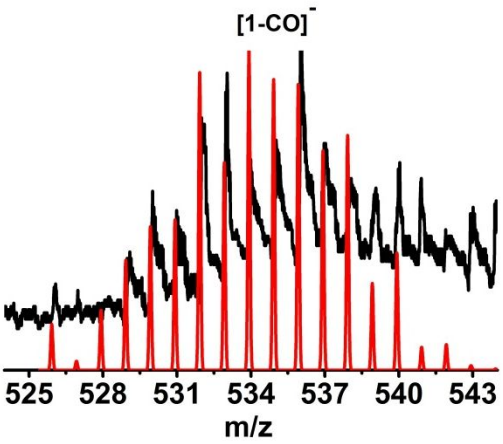

Figure S12 Measured (black) and simulated (red) molecular ions by losing one CO fragment from ESI-MS in negative ion mode (**1**=$Si[(NHCH_2CH_2NH)]_3[Mo(CO)_3]_2$).

Table S1 Selected Crystallographic, Data Collection, and Refinement Data for $[K([2,2,2]crypt)]_2\{Si[(NHCH_2CH_2NH)]_3[Mo(CO)_3]_2\}\bullet(tol)_2$[a].

Empirical formula	$C_{62}H_{106}K_2Mo_2N_{10}O_{18}Si$
Formula weight	1577.73
Temperature/K	150(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	20.0662(11)
b/Å	24.3575(14)
c/Å	16.0618(9)
α/°	90
β/°	112.0165(7)
γ/°	90
Volume/Å^3	7277.9(7)
Z	4
ρ_{cal} cg/cm^3	1.440
μ/mm^{-1}	0.548
F(000)	3312.0
Crystal size/mm^3	0.30 × 0.24 × 0.03
Radiation	Mo*Kα* (λ = 0.71073)
2ϑ range for data collection/°	3.998 to 53
Index ranges	-24 ≤ h ≤ 25, -30 ≤ k ≤ 30, -20 ≤ l ≤ 20
Reflections collected	64074
Independent reflections	15034 [R_{int} = 0.0453, R_{sigma} = 0.0442]
Data/restraints/parameters	15034/0/754
Goodness-of-fit on F^2	1.019
R_1/wR_2 [$I>=2\sigma$ (I)]	0.0405, 0.0910
R_1/wR_2 [all data]	0.0645, 0.0985

[a]See the Crystallographic Studies Section for details on the refinement .