Electronic Supplementary Information:

Synthesis and Properties of $MoCl_4$ Complexes with Thio- and Seleno-ethers and Their Use for Chemical Vapour Deposition of $MoSe_2$ and MoS_2 Films

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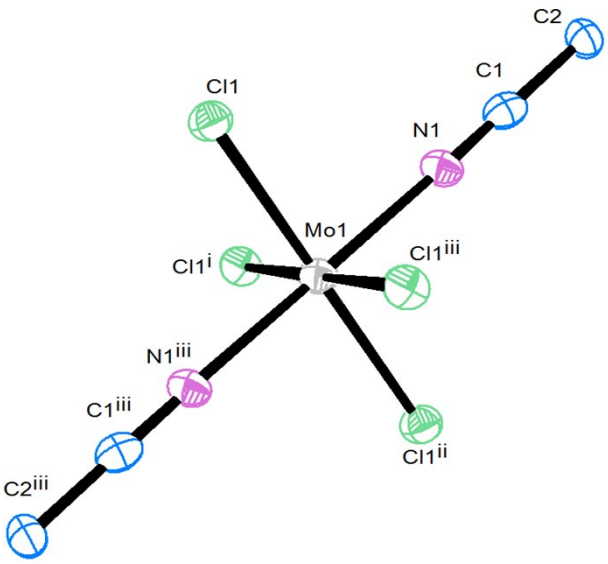

Fig. S1 The structure of $[MoCl_4(MeCN)_2]$ showing the atom numbering scheme and with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry operation: i = x, -y, z; ii = 1-x, -y, 1-z; iii = 1-x, y, 1-z. Selected bond lengths (Å) and angles (°) Mo1–Cl1 = 2.336(1), Mo1–N1 = 2.113(3), (cis) N–Mo–Cl = 89.28(13), 90.72(13).

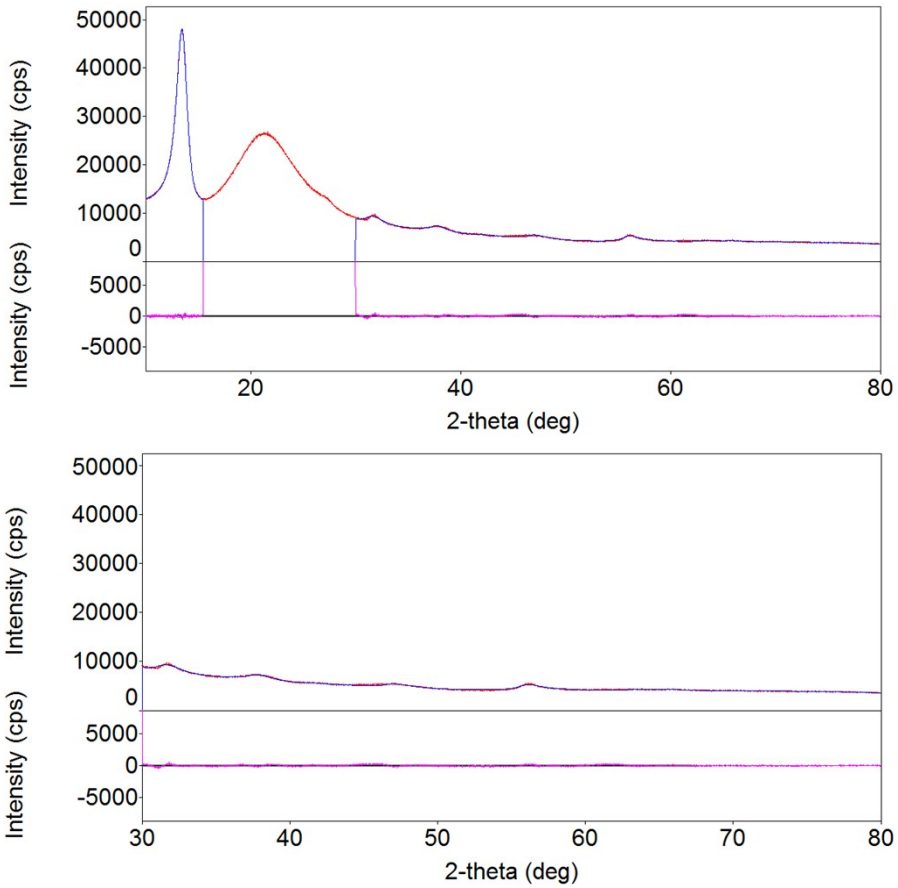

Fig. S2 Le Bail fit to the $MoSe_2$ pattern from a sample produced at 550 °C (as shown in Fig. 4), with an expansion of the higher angle region.

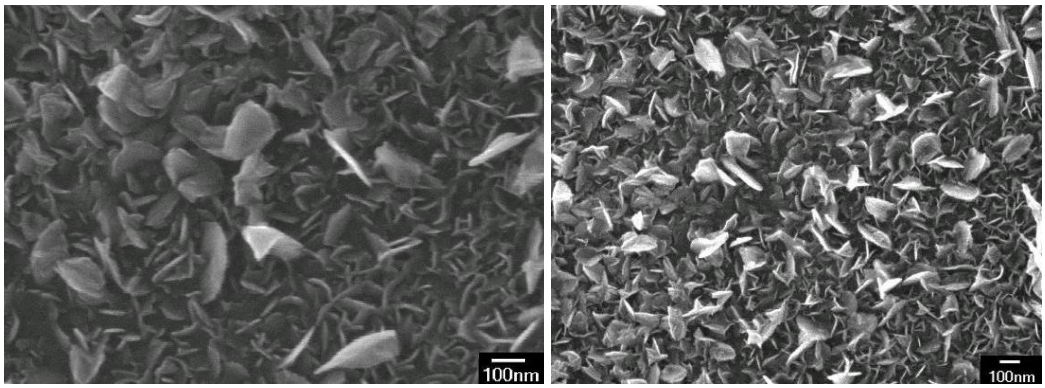

Fig. S3 SEM images of an $MoSe_2$ film grown at 550 °C using 200 mg $[MoCl_4(Se^nBu_2)_2]$.

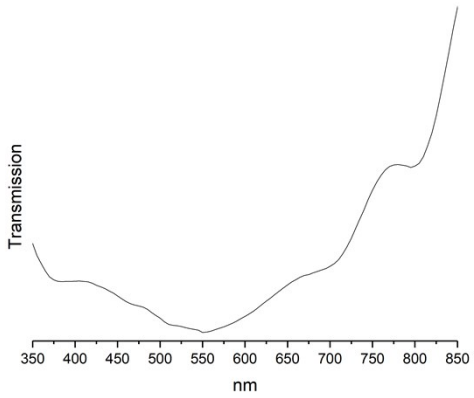

Fig. S4 Transmission spectrum of a $MoSe_2$ thin film.

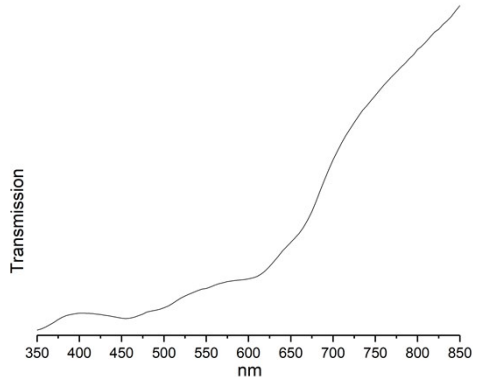

Fig. S5 Transmission spectrum of a MoS_2 thin film.

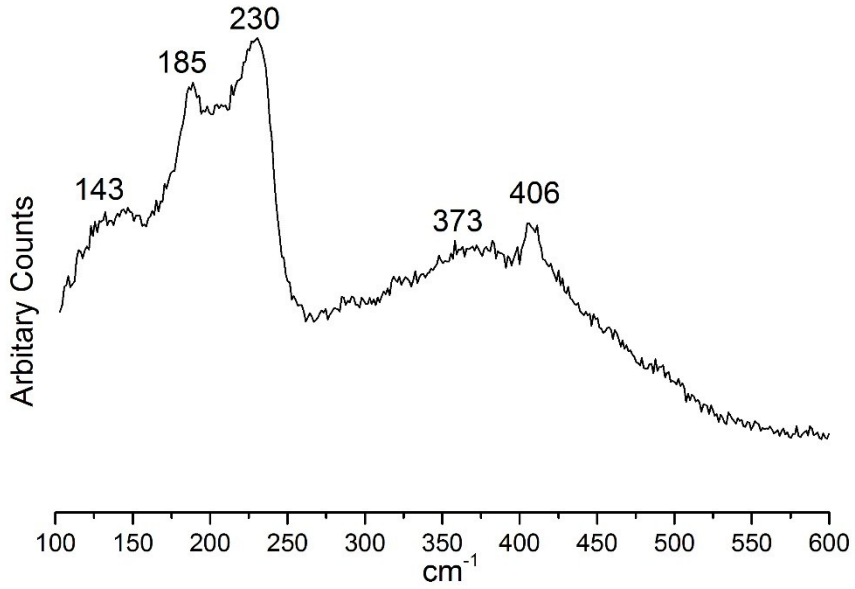

Fig. S6 Raman spectrum of MoS_2 deposited by LPCVD from $[MoCl_4(S^nBu_2)_2]$ at 750 °C

Table S1 X-Ray crystallographic Data

Compound	$[MoCl_4(MeCN)_2]$	$[MoCl_4(Me_2S)_2]$	$[MoCl_5(Me_2S)]$ $[Me_2SCH_2SMe]$	$[MoCl_4(MeSCH_2CH_2SMe)]$
Formula	$C_4H_6Cl_4MoN_2$	$C_4H_{12}Cl_4MoS_2$	$C_6H_{17}Cl_5MoS_3$	$C_4H_{10}Cl_4MoS_3$
Formula weight	319.85	362.00	458.57	359.98
Crystal system	Monoclinic	Orthorhombic	Orthorhombic	Monoclinic
Space group (no.)	C2/m (12)	Pbca (61)	$Pna2_1$ (33)	$P2_1$ (4)
a/ Å	11.622(9)	10.7754(4)	11.1611(3)	7.1386(6)
b/ Å	7.507(4)	8.6531(4)	23.676(1)	11.1622(6)
c/ Å	5.825(4)	13.0339(7)	12.6813(3)	7.8033(7)
α/ deg	90	90	90	90
β/ deg	102.27(2)	90	90	115.91(1)
γ/ deg	90	90	90	90
U/ $Å^3$	496.6(6)	1215.3(1)	3351.1(2)	559.27(9)
Z	2	4	8	2
μ(Mo-Kα)/mm^{-1}	2.336	2.248	1.925	2.442
F(000)	308	712	1824	352
Total no. reflections	5422	5273	14898	5766
Unique reflections	534	1195	6472	2142
R_{int}	0.0637	0.0325	0.0340	0.0603
No. parameters, restraints	34, 0	54, 0	281, 184	103, 1
R_1[b] [Io>2σ(Io)]	0.0231	0.0208	0.0340	0.0471
R_1 (all data)	0.0256	0.0270	0.0431	0.0556
wR_2[b] [Io >2σ(Io)]	0.0570	0.0439	0.0700	0.1177
wR_2 (all data)	0.0579	0.0457	0.0735	0.1223

[a] Common items: temperature =100 K; wavelength (Mo-K_α) = 0.71073 Å; θ(max)= 27.5°.

[b] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F\sigma|$. $wR_2=[\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{1/2}$

Table S1 cont.

Compound	$[MoCl_4(^iPrSCH_2CH_2S^iPr)]$	$[MoCl_4(MeSCH_2CH_2CH_2SMe)]$
Formula	$C_8H_{18}Cl_4MoS_2$	$C_5H_{12}Cl_4MoS_2$
Formula weight	416.08	374.01
Crystal system	Monoclinic	Triclinic
Space group (no.)	$P2_1/c$ (14)	P-1 (2)
a/ Å	8.6773(2)	6.9578(3)
b/ Å	9.1092(2)	7.3230(2)
c/ Å	19.7049(4)	12.5840(5)
α/ deg	90	77.457(3)
β/ deg	98.465(2)	81.727(3)
γ/ deg	90	72.082(3)
U/ $Å^3$	1504.57(6)	593.49(4)
Z	4	2
μ(Mo-Kα)/mm^{-1}	1.786	2.305
F(000)	832	368
Total no. reflections	12891	12279
Unique reflections	3018	2335
R_{int}	0.0215	0.0223
No. of parameters, restraints	140, 0	111, 0
$R_1{}^b$ [Io>2σ(Io)]	0.0256	0.0194
R_1 (all data)	0.0259	0.0218
$wR_2{}^b$ [Io >2σ(Io)]	0.0575	0.0516
wR_2 (all data)	0.0577	0.0528