Chalcogen stabilized trimetallic clusters: synthesis, structures, and bonding of [(Cp*M)$_3$(E)$_{6+m}$(BH)$_n$] (M = Nb or Ta; E = S or Se; m = 0 or 1 or 2; n = 0 or 1)

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I Experimental

I.2 Spectroscopic details

II Computational

Supplementary data

Figure S1. Molecular structure and labeling diagram for compound **1**. Selected bond lengths (Å) and bond angles (°) of **1**: Nb1-Nb2 3.1750(9), Nb1-Nb1 3.1390(9), Nb1-S2 2.5514(18), Nb1-S1 2.3840(18), Nb2-S2 2.5337(17), Nb2-S1 2.3837(15), Nb1-S3 2.5336(18), B1-S3 1.937(15), S5-S2 1.941(4), S5-B1 1.880(14), B1-S2 2.086(13); Nb1-Nb2-Nb1 59.25(2), Nb1-Nb1-Nb2 60.373(11), Nb1-S3-Nb1 76.56(6), B1-S5-S2 90.7(4), B1-S3-Nb1 91.7(4).
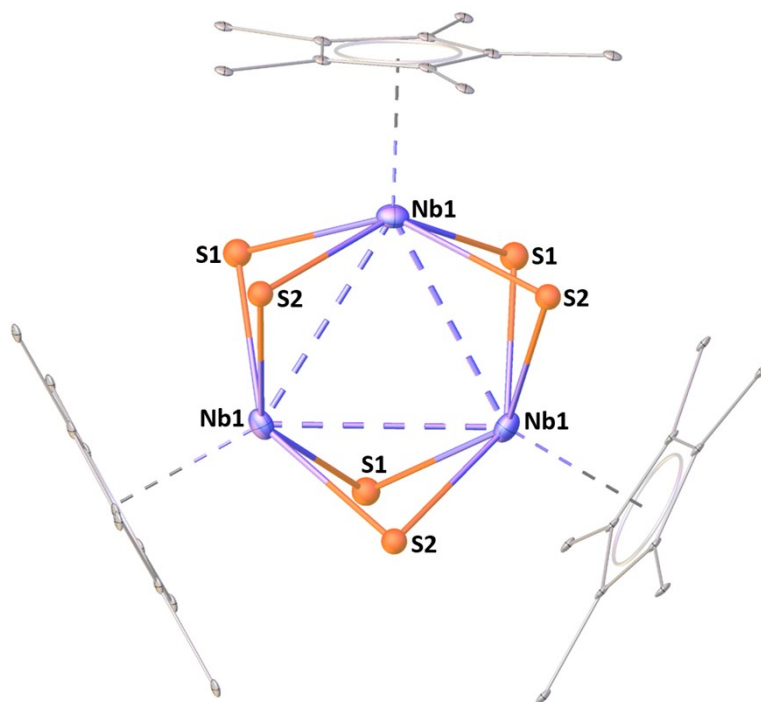
Figure S2. Molecular structure and labeling diagram for compound **2**.[1]
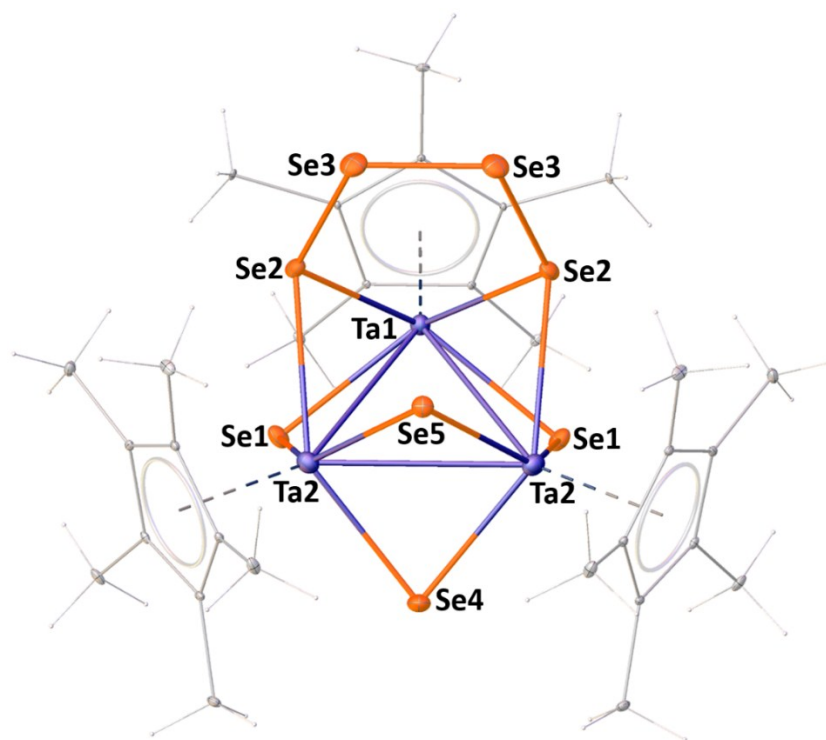
Figure S3. Molecular structure and labelling diagram of **3**. Selected bond lengths (Å) and angles (°) of **3**: Ta2-Ta2 3.085(11), Ta1-Ta2 3.3499(9), Se1-Ta1 2.4790(14), Se1-Ta2 2.5488(17) Ta2-Se2 2.7095(13), Ta1-Se2 2.6201(15), Se4-Ta2 2.5045(16), Se5-Ta2 2.5303(16) Se2-Se3 2.248(3), Se3-Se3 1.938(7); Ta2-Se2-Se3 118.33(11), Ta1-Se2-Se3 115.76(11), Ta1-Se2-Ta2 77.86(4), Se3-Se3-Se2 110.03(9), Ta2-Se4-Ta2 76.03(6), Ta2-Se5-Ta2 75.12(6), Ta2-Ta2-Ta1 62.584(12), Ta2-Ta1-Ta2 54.83(2).

I.2 Spectroscopic details

Figure S4. ESI-MS of compound **1**

SGG-NB-HOMO
05122018-04-SGG-NB-HOMO 15 (0.378) AM (Cen,5, 80.00, Ar,5000.0,0.00,1.00); Sb (1,40.00); Sm (Mn, 1x5.00); Cm (4:22)   TOF MS ES+
                                                                                                                                                          1.79e+002
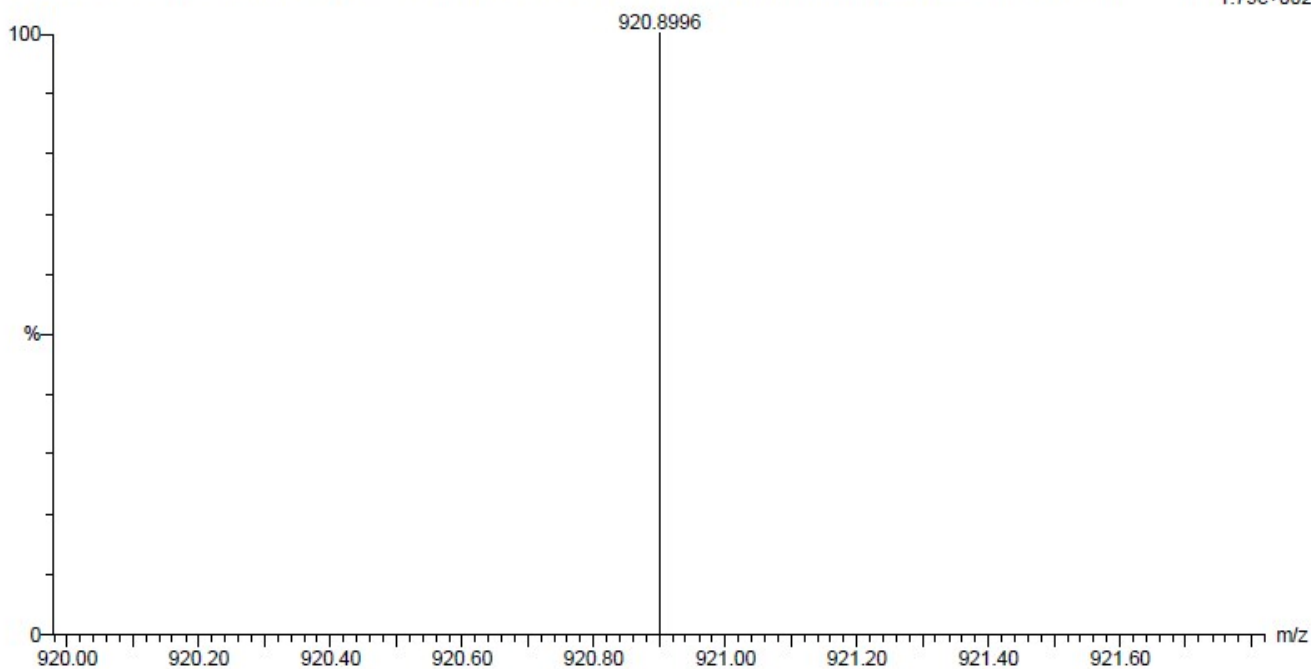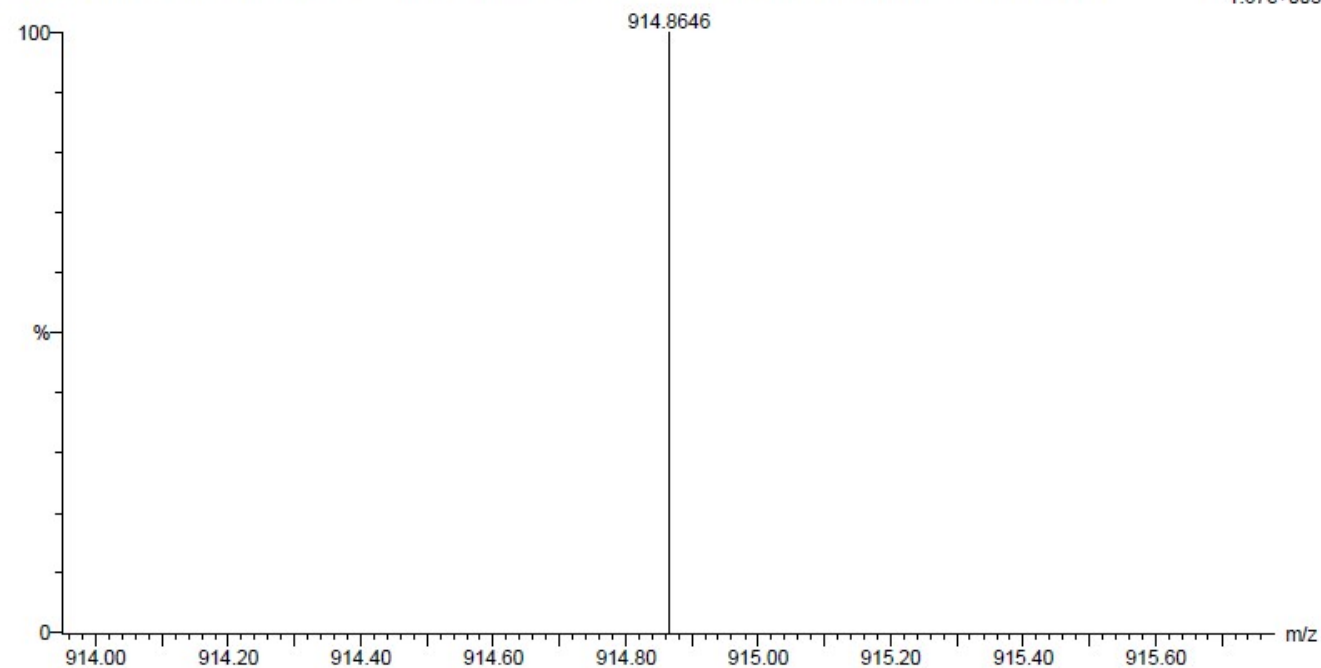
Minimum:			-1.5		
Maximum:	5.0	10.0	50.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
920.8996	920.9007	-1.1	-1.2	8.0	n/a	C30 H47 B S7 Nb3

Figure S5. HR-MS of compound **1**

Figure S6. ESI-MS of compound **2**

Figure S7. HR-MS of compound **2**
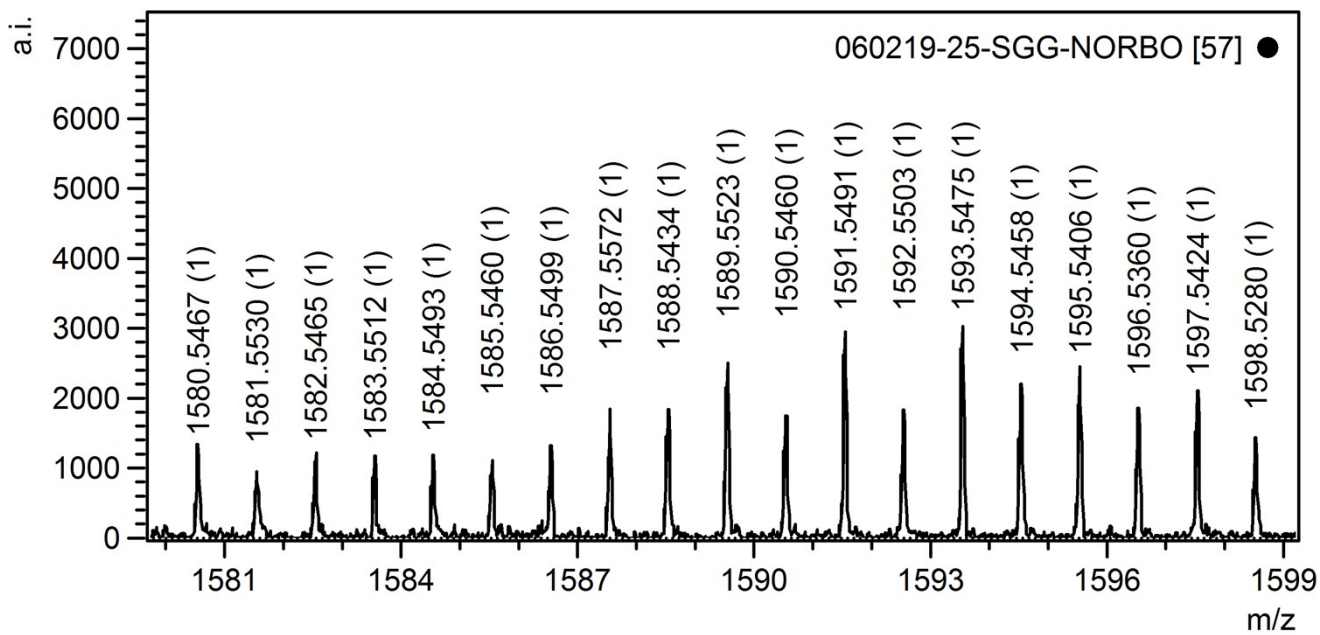
Figure S8. ESI-MS of compound **3**
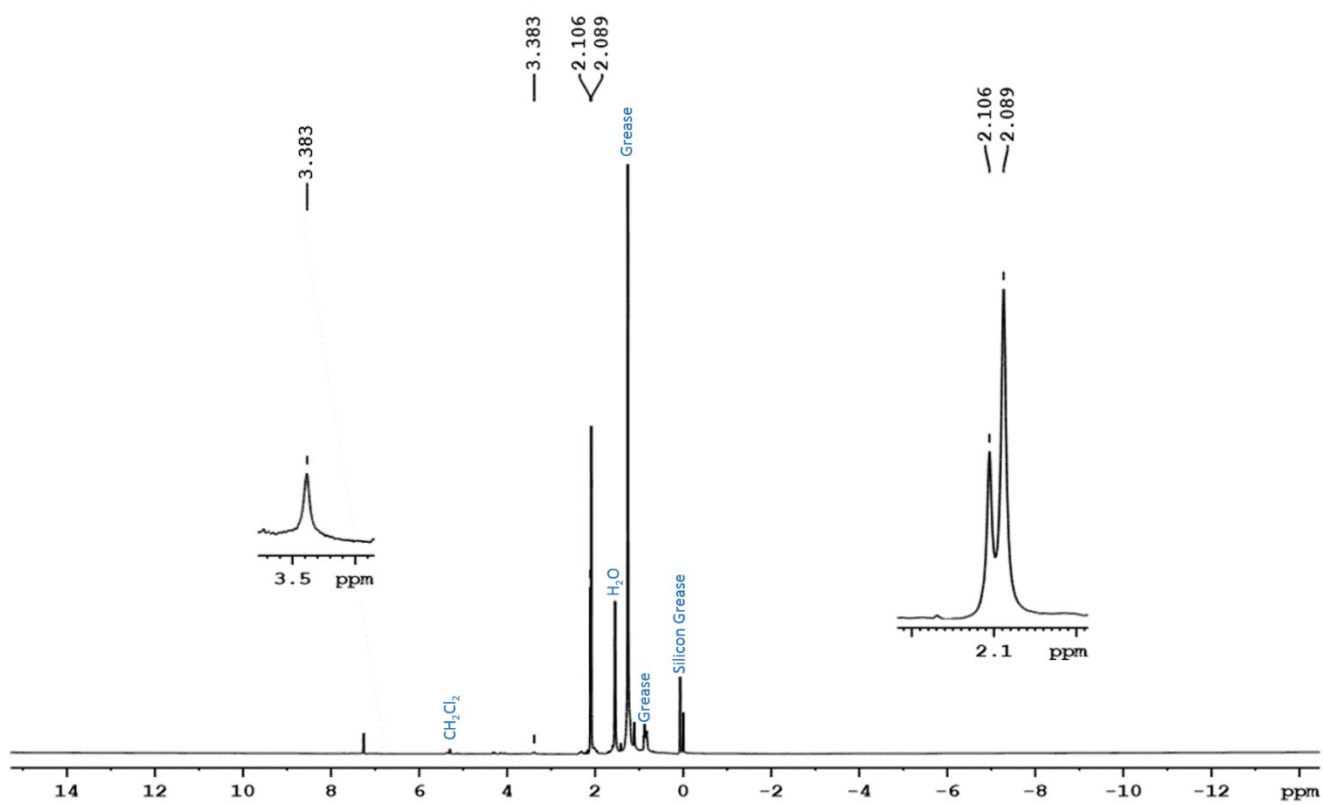
Figure S9. $^1H\{^{11}B\}$ NMR spectrum of compound **1** in $CDCl_3$
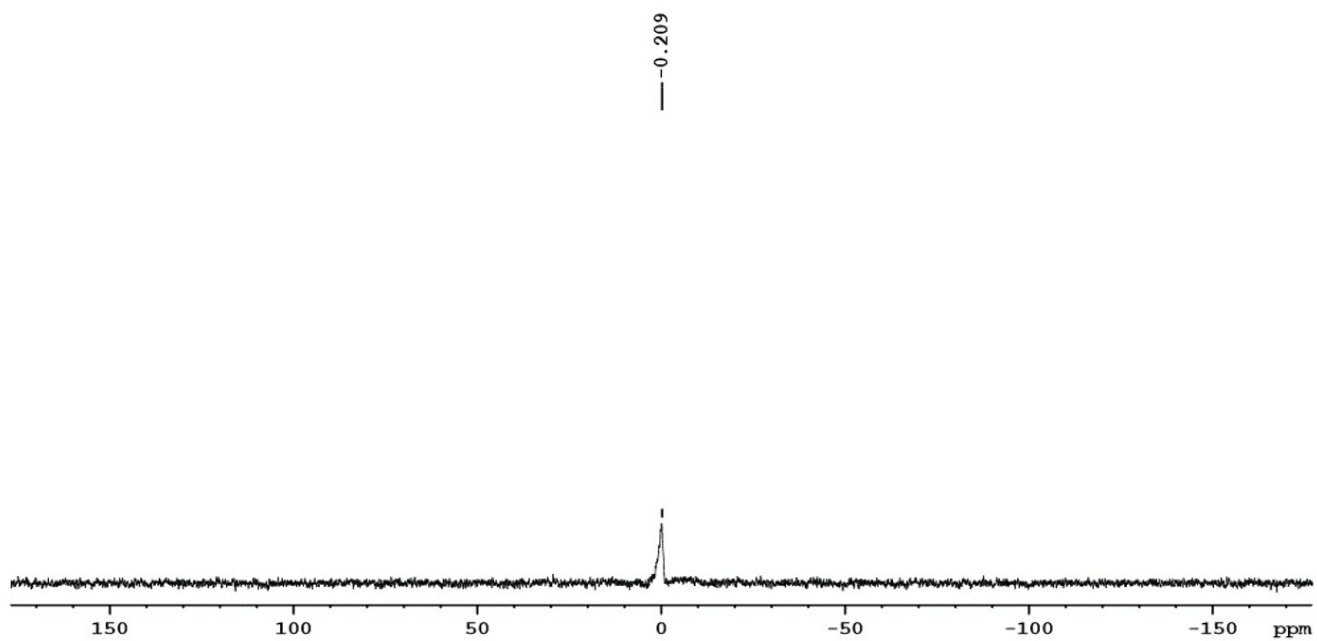
Figure S10. $^{11}B\{^{1}H\}$ NMR spectrum of compound **1** in CDCl$_3$.[2,3]
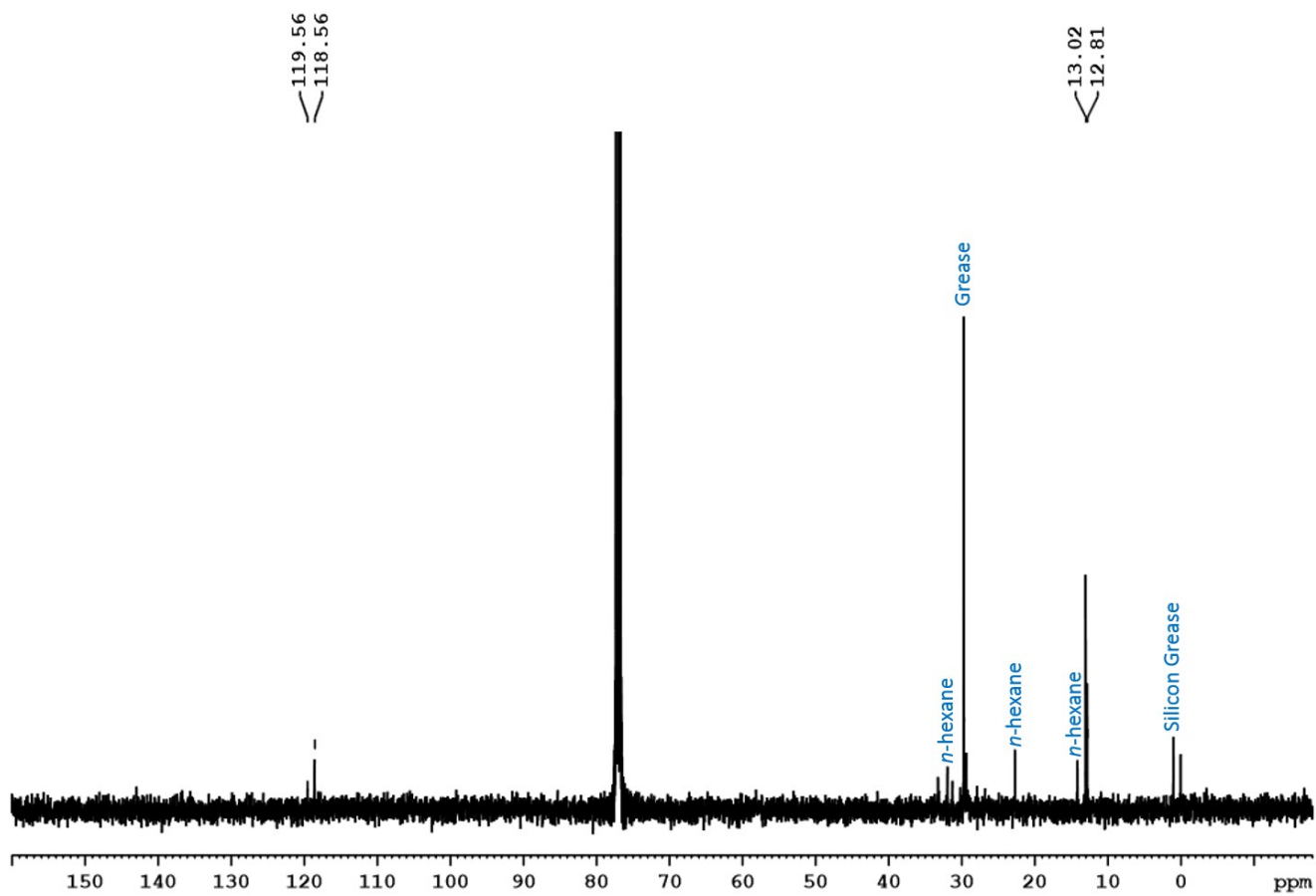
Figure S11. $^{13}C\{^1H\}$ NMR spectrum of compound **1** in CDCl$_3$
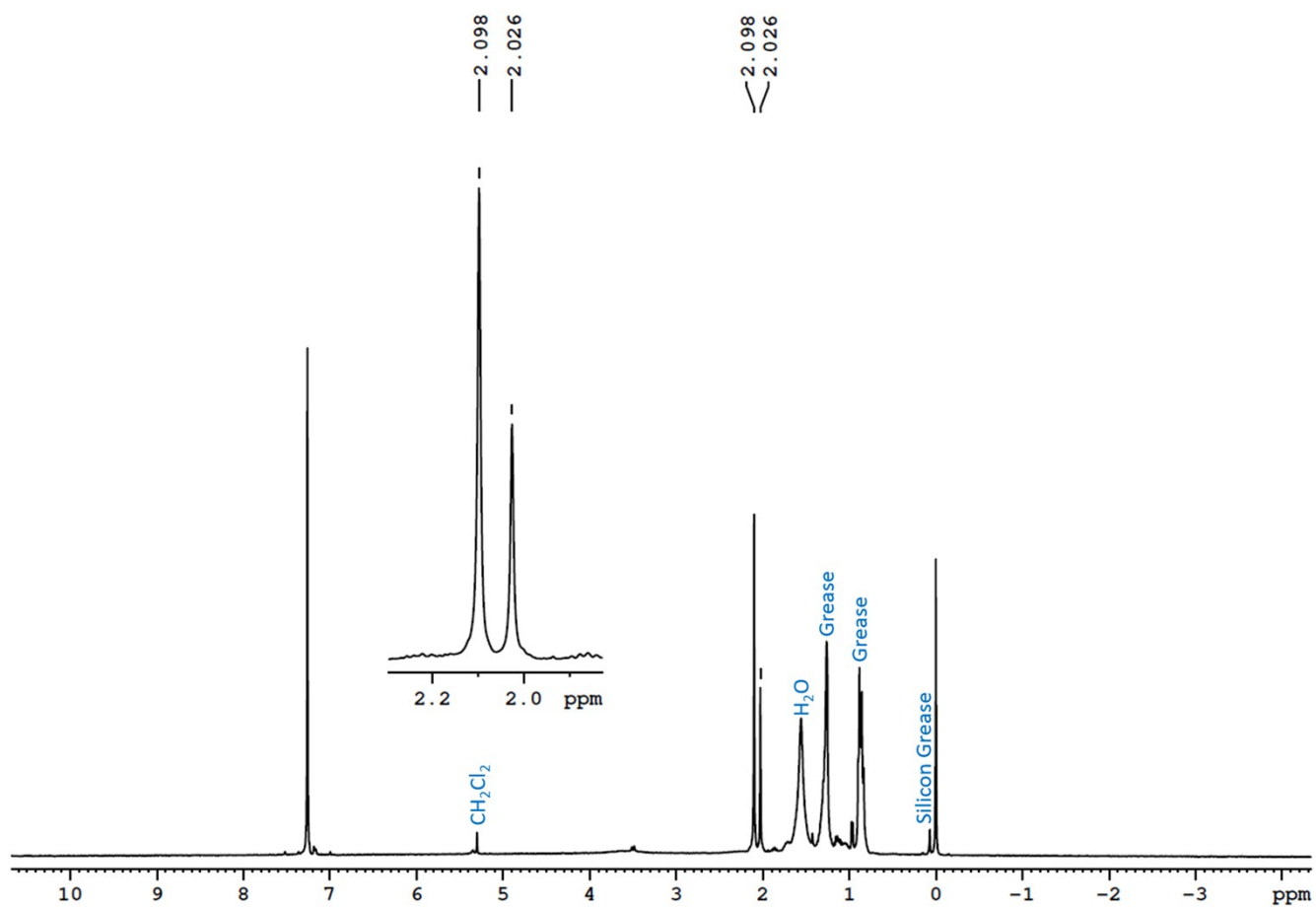
Figure S12. ^{1}H NMR spectrum of compound **2** in CDCl$_3$
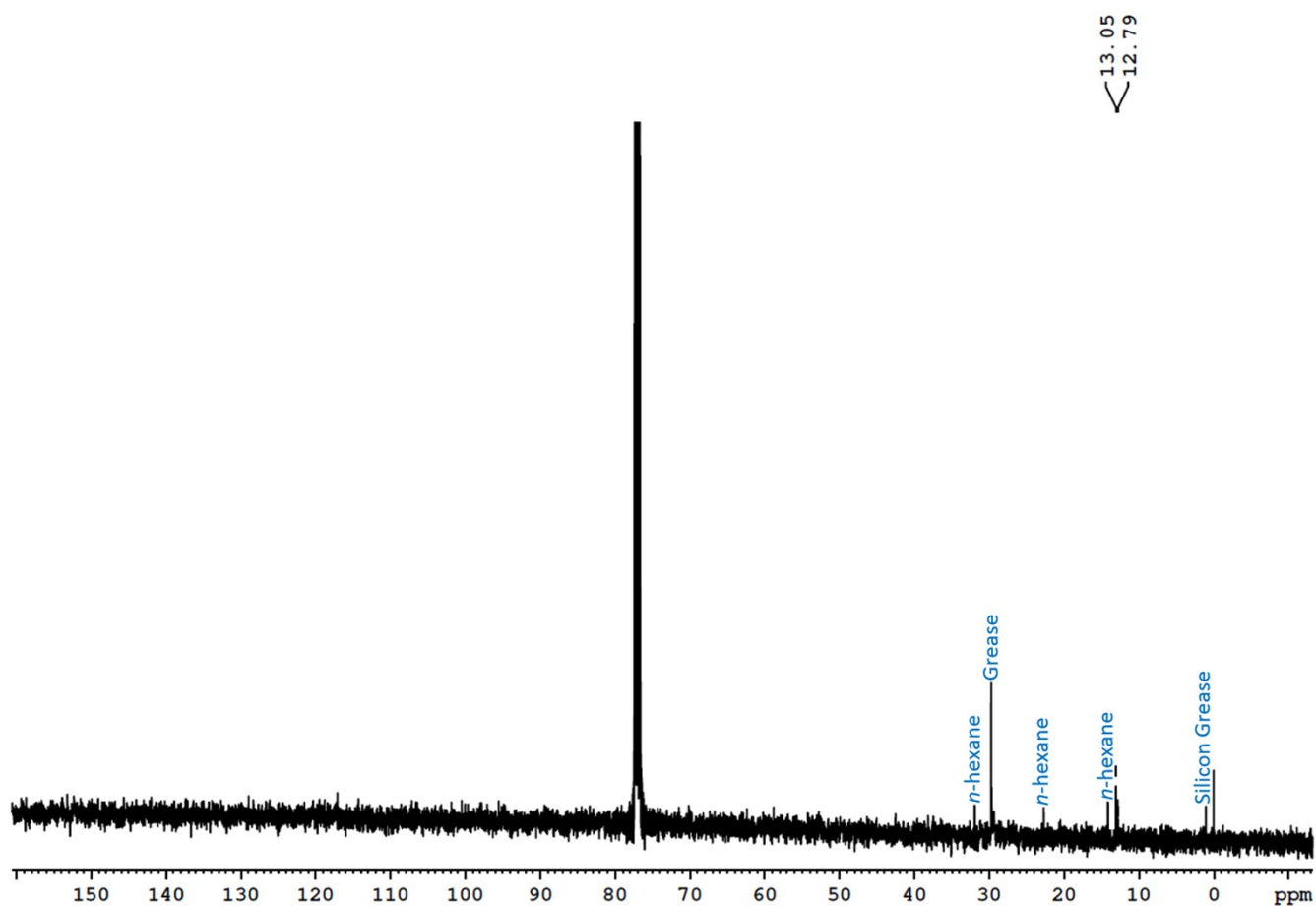
Figure S13. $^{13}C\{^1H\}$ NMR spectrum of compound **2** in CDCl$_3$ (due to less yield of **2** tertiary carbon peak of Cp* are not visible in spectrum)
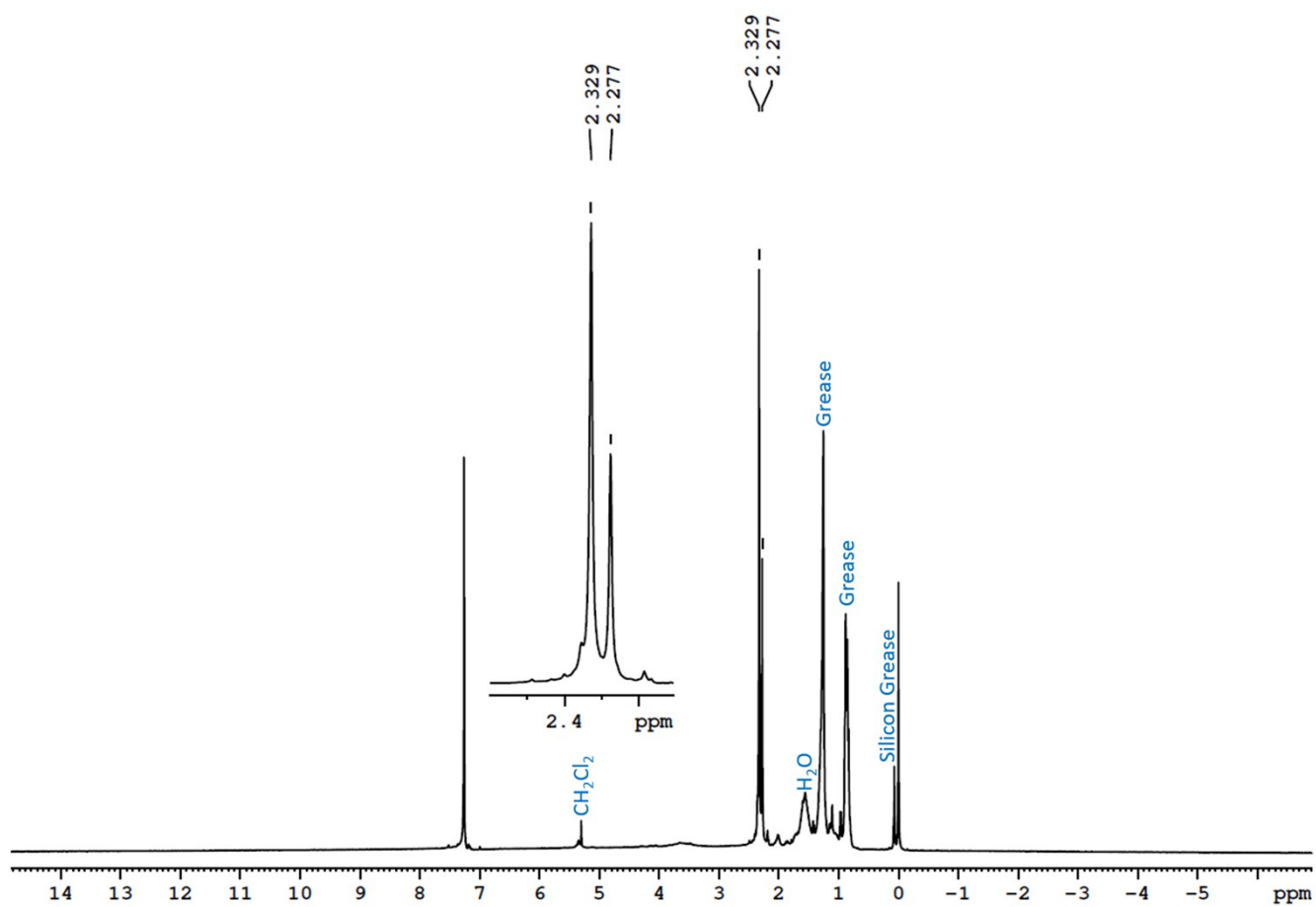
Figure S14. ^{1}H NMR spectrum of compound **3** in CDCl$_3$
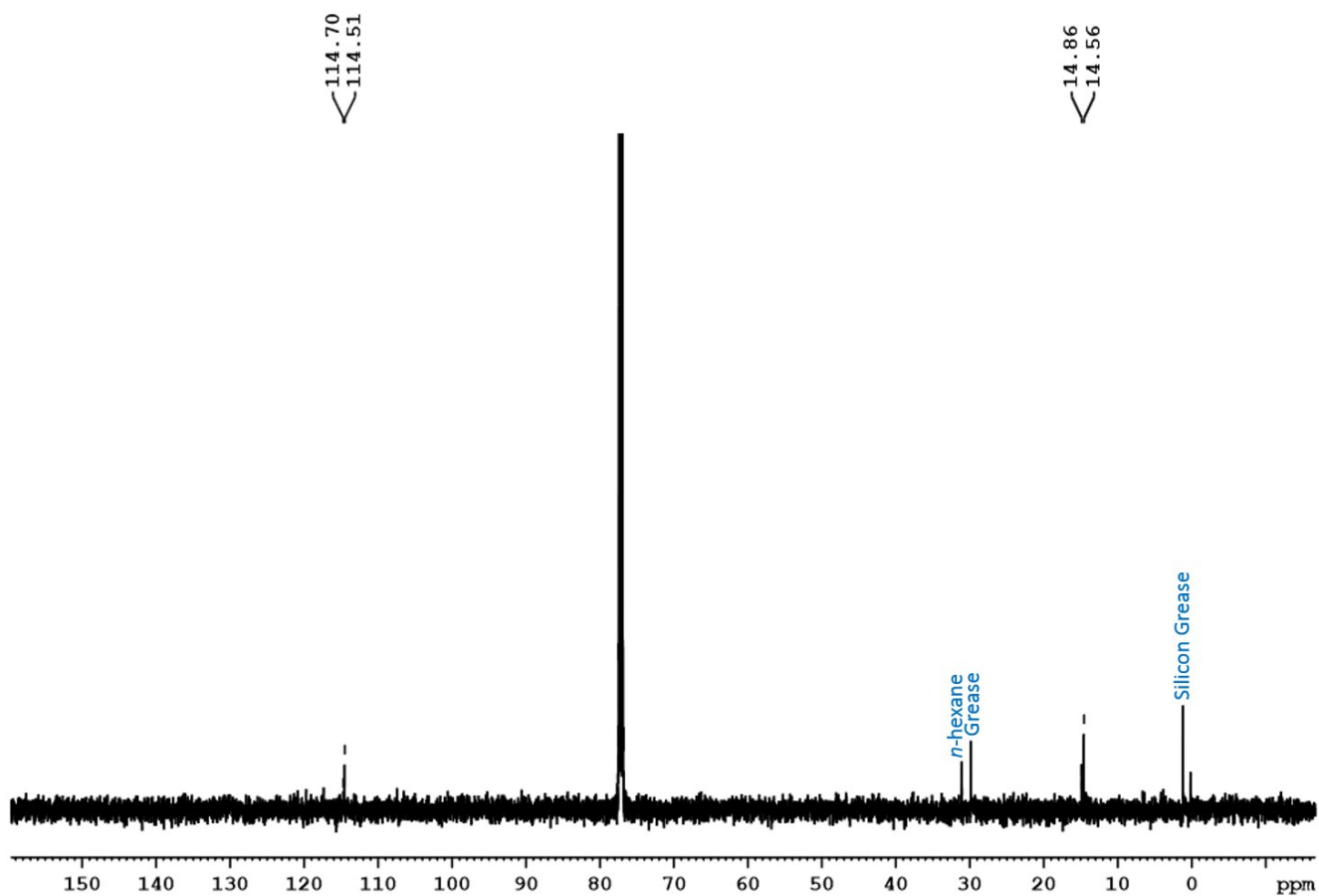
Figure S15. $^{13}C\{^1H\}$ NMR spectrum of compound **3** in CDCl$_3$
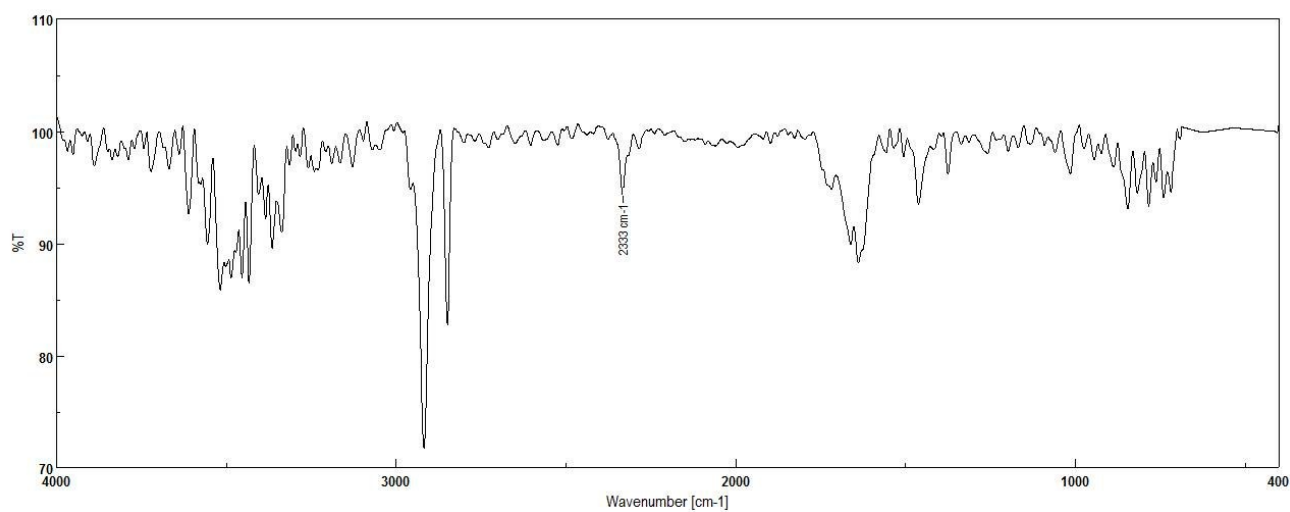
Figure S16. IR spectrum of compound **1**

II Computational

Supplementary data

Table S1. Calculated natural charges (q_M, q_E, and q_B), natural valence population (**Pop**) and HOMO – LUMO gaps of **1**, **2**, **2^{Se}**, **4^s**, **4**, and **3**.The transition metal and chalcogen atoms are indicated by **M** and **E** respectively.

	q_M	q_E	q_B	Pop(M_{val})	Pop(E_{val})	Pop(B_{val})	ΔE_{H-L} (ev)
1	-0.545	0.173	-0.290	5.465	5.784	3.262	2.61
	-0.522	0.195		5.437	5.767		
		0.243			5.706		
		-0.041			5.994		
2	-0.553	0.115	--	5.474	5.844	--	2.60
	-0.531	0.250		5.434	5.698		
		0.166			5.790		
		0.071			5.888		
2^{Se}	-0.877	0.288	--	5.797	5.677	--	2.08
	-0.833	0.281		5.763	5.685		
		0.351			5.606		
		0.356			5.600		
4^s	-0.002	-0.113	--	4.898	6.075	--	2.23
	-0.138	0.026		5.058	5.934		
		0.173			5.754		
		-0.117			6.086		
4	-0.481	0.141	-	5.375	5.822	--	2.45
	-0.454	0.148		5.352	5.814		
		0.269			5.682		
		0.267			5.684		
3	-0.505	0.279	--	5.403	5.674	--	2.35
	-0.467	0.174		5.356	5.782		
		0.177			5.783		
		-0.073			6.039		

Table S2. Selected Wiberg bond index (WBI) of **1**

	Nb1	Nb2	Nb1
Nb1	0.0000	0.3886	0.4332
Nb2	0.3886	0.0000	0.4323
Nb1	0.4332	0.4323	0.0000
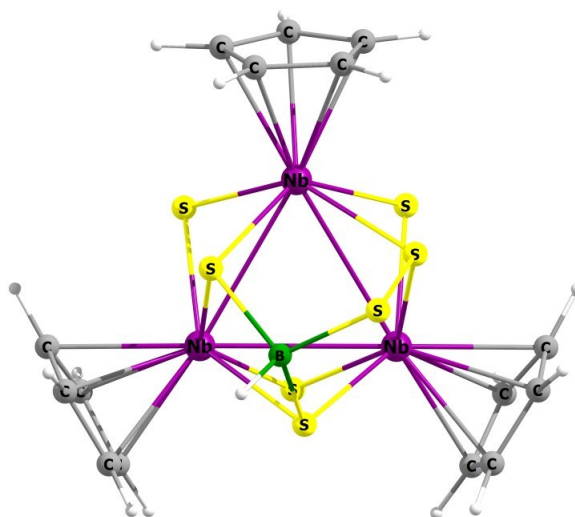
Figure S17. Optimized geometry of **1**

Total energy = -3565.42502489 a.u.

Cartesian coordinates for the calculated structure **1** (in Å)

S	0.07277200	1.49719700	3.17134500
B	-0.01535500	-0.32635200	2.75392600
C	3.29437300	2.43198900	0.45207500
C	3.91160900	1.16531400	0.60454200
C	4.10584100	0.61783400	-0.68364600
C	3.60287400	1.54093700	-1.63475300
C	3.11265300	2.66651600	-0.93083800
C	-3.43131700	1.89226000	-1.63576700
C	-2.83723900	2.95843500	-0.91954800
C	-3.04761000	2.73066700	0.46046800
Nb	1.66068100	0.74319300	-0.33941600
Nb	-1.58159900	0.89916500	-0.33926700
S	0.09093400	1.88945000	-1.75039100
S	0.10305700	2.13431500	1.18665400
S	1.47748200	-0.84607500	1.62068800
S	1.70938700	-1.30235000	-1.57216000
S	-1.55203500	-0.69970000	1.62121400
C	-4.02638300	1.01421400	-0.69525700
C	-3.78619400	1.52897200	0.59872000
C	0.51935000	-3.99071900	1.04307600
C	0.94576400	-4.13515600	-0.29695100

|			
C	-0.20285900	-4.14118200	-1.12632000
C	-1.34199300	-4.02419500	-0.29205200
C	-0.89788200	-3.92204400	1.04604400
Nb	-0.09163700	-1.89424000	-0.11931300
S	-1.82701300	-1.13221000	-1.57225900
H	1.96684200	-4.20784800	-0.63099200
H	-0.20916000	-4.22478600	-2.20079500
H	-2.36671100	-3.99718100	-0.62173200
H	-1.52360600	-3.81016000	1.91533900
H	1.15665200	-3.94053900	1.90965300
H	4.54341600	-0.34095500	-0.90423600
H	4.17779600	0.70121700	1.53909300
H	3.01160100	3.09597800	1.25142000
H	2.65965200	3.53947400	-1.36929700
H	3.59633200	1.40827900	-2.70446600
H	-2.29925600	3.78687100	-1.34816100
H	-2.70536100	3.35679200	1.26712000
H	-3.43234800	1.76894500	-2.70660800
H	-4.55420400	0.10461100	-0.92651000
H	-4.10054900	1.08453100	1.52791100
H	-0.04882400	-1.01936300	3.73028100
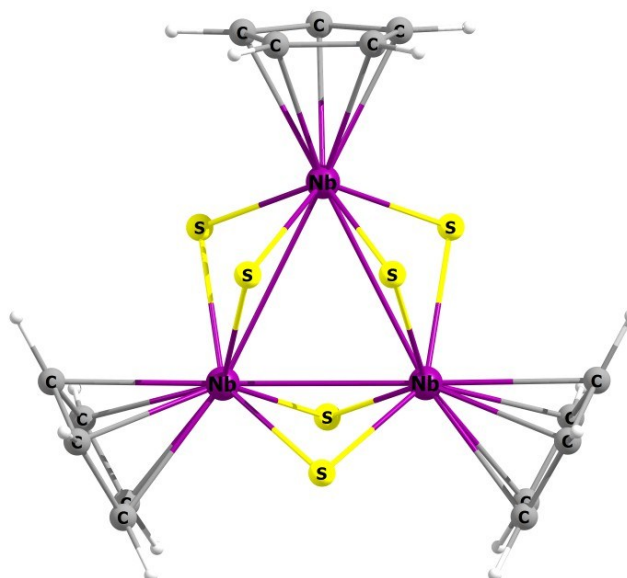
Figure S18. Optimized geometry of **2**

Total energy = -3141.65688904 a.u.

Cartesian coordinates for the calculated structure **2** (in Å)

C	2.89017300	2.92209300	0.65898700
C	1.70879200	3.57517800	1.08992000
C	0.99242100	3.98134800	-0.06041400
C	1.71874900	3.56812700	-1.20177000
C	2.89488100	2.91544500	-0.75680900
S	1.78204800	-0.00417600	-1.77698400
S	2.10041100	-0.00338000	1.51601200
Nb	1.02149800	1.48029200	-0.05480400
C	-4.12037700	1.12934000	-0.53055200
C	-4.13062900	0.77284800	0.83504400
C	-4.13260700	-0.64454100	0.91909800
C	-4.12343800	-1.15975400	-0.39494300
C	-4.09960100	-0.06434200	-1.29420200
S	-1.09866100	1.83698900	-1.28224900
S	-0.88353300	1.05706800	1.88317400
Nb	-1.95533700	0.00385000	-0.08653800
C	0.97576600	-3.98468100	-0.06393200
C	1.69006800	-3.58310100	1.08922900
C	2.87550000	-2.93427100	0.66304100
C	2.88492400	-2.92591000	-0.75271900

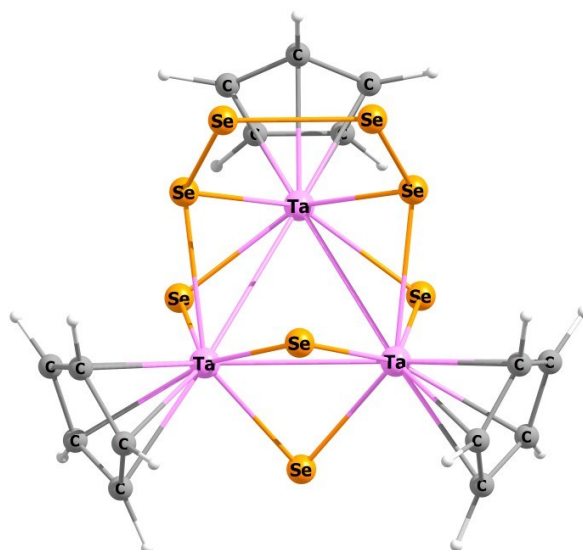|			
C	1.70749100	-3.57291800	-1.20239000
S	-1.10873900	-1.83340400	-1.28074100
S	-0.88598800	-1.05219900	1.88257400
Nb	1.01561700	-1.48358600	-0.05505400
H	0.02440000	-4.48974100	-0.07618000
H	1.41461000	-3.71442900	-2.22961200
H	1.39084300	-3.74192500	2.11289200
H	3.63312400	-2.51815600	1.30378300
H	3.65312000	-2.50299400	-1.37793100
H	-4.12929400	-1.22317100	1.82788400
H	-4.10888900	-2.20104700	-0.66782300
H	-4.06993900	-0.12846700	-2.36988900
H	-4.10513200	2.13124700	-0.92386700
H	-4.12381500	1.45451000	1.66928800
H	0.04298500	4.49014200	-0.06886700
H	1.41345100	3.73362700	2.11476300
H	3.64807700	2.50180900	1.29666700
H	3.65921600	2.49013300	-1.38511800
H	1.42306700	3.71211300	-2.22783700

Figure S19. Optimized geometry of **3**

Total energy = -19965.21468030 a.u.

Cartesian coordinates for the calculated structure **3** (in Å)

C	-1.52932300	-1.56850100	3.53610900
C	-0.22318300	-1.33674300	4.02858100
C	0.59507000	-2.42628700	3.64410900
C	-0.20674100	-3.33597500	2.91544300
C	-1.52035000	-2.80634700	2.84840200
C	1.22342400	3.95832100	0.00000000
C	1.96748600	3.58286500	-1.14475100
C	3.16246700	2.96481300	-0.70796200
Se	2.09822500	0.11922600	1.95325700
Se	-0.64099900	1.43463200	1.84805700
Se	-2.80014100	2.26283900	1.20358600
Se	1.21230900	-2.83857600	0.00000000
Se	-2.11065800	-1.27660900	0.00000000
Ta	1.29365600	1.49303800	0.00000000
Ta	-0.08594600	-1.28293700	1.54072300
C	1.96748600	3.58286500	1.14475100
C	3.16246700	2.96481300	0.70796200
Se	-0.64099900	1.43463200	-1.84805700
Se	-2.80014100	2.26283900	-1.20358600
C	-1.52932300	-1.56850100	-3.53610900
C	-0.22318300	-1.33674300	-4.02858100

C	0.59507000	-2.42628700	-3.64410900
C	-0.20674100	-3.33597500	-2.91544300
C	-1.52035000	-2.80634700	-2.84840200
Se	2.09822500	0.11922600	-1.95325700
Ta	-0.08594600	-1.28293700	-1.54072300
H	3.93442600	2.56217200	1.34151700
H	1.66289600	3.71670100	2.16876400
H	0.25550700	4.43384500	0.00000000
H	1.66289600	3.71670100	-2.16876400
H	3.93442600	2.56217200	-1.34151700
H	1.64471400	-2.53860700	-3.85925100
H	0.11847700	-4.27144100	-2.49436300
H	-2.36364200	-3.26685200	-2.36334700
H	-2.37952800	-0.91667800	-3.65313200
H	0.09868800	-0.47115600	-4.58346500
H	-2.37952800	-0.91667800	3.65313200
H	-2.36364200	-3.26685200	2.36334700
H	0.11847700	-4.27144100	2.49436300
H	1.64471400	-2.53860700	3.85925100
H	0.09868800	-0.47115600	4.58346500

Notes and references:

1   Due to poor data quality, hydrogens on methyl units not locatedand bond distances and angles are not provided.

2   ^{11}B{^{1}H} spectra were processed with a backward linear prediction algorithm to remove the broad ^{11}B background signal of the NMR tube. For references see (*a*) J. J. Led and H. Gesmar, *Chem. Rev.*, 1991, **91**, 1413−1426; (*b*) L. Yang, R. Simionescu, A. Lough and H. Yan, *Dyes Pigm.*, 2011, **91**, 264−267; (*c*) R. Weiss and R. N. Grimes, *J. Am. Chem. Soc.*, 1978, **100**, 1401−1405.