Supplementary Materials: Connecting Main-Group Metals (Al, Ga, In) and Tungsten(0) Carbonyls via the N_2S_2 Metallo-Ligand Strategy

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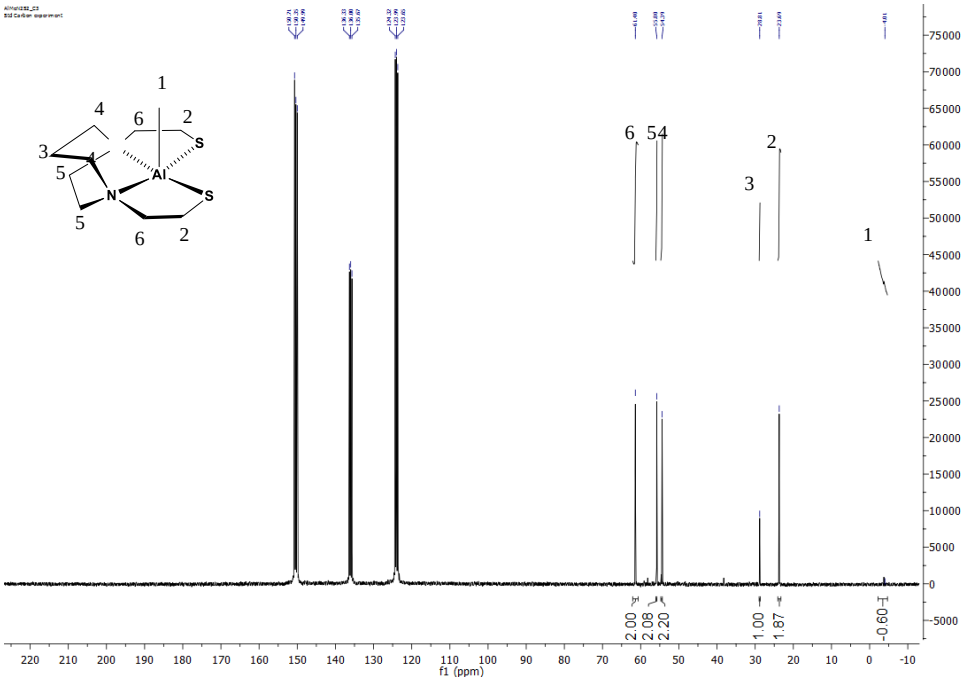

Figure S1. ^{1}H-NMR (up) and ^{13}C-NMR Spectrum of **MeAlN$_2$S$_2$** complex in pyridine-d$_5$ at 23.2 °C using a 300 MHz NMR spectrometer referenced to residual pyridine.

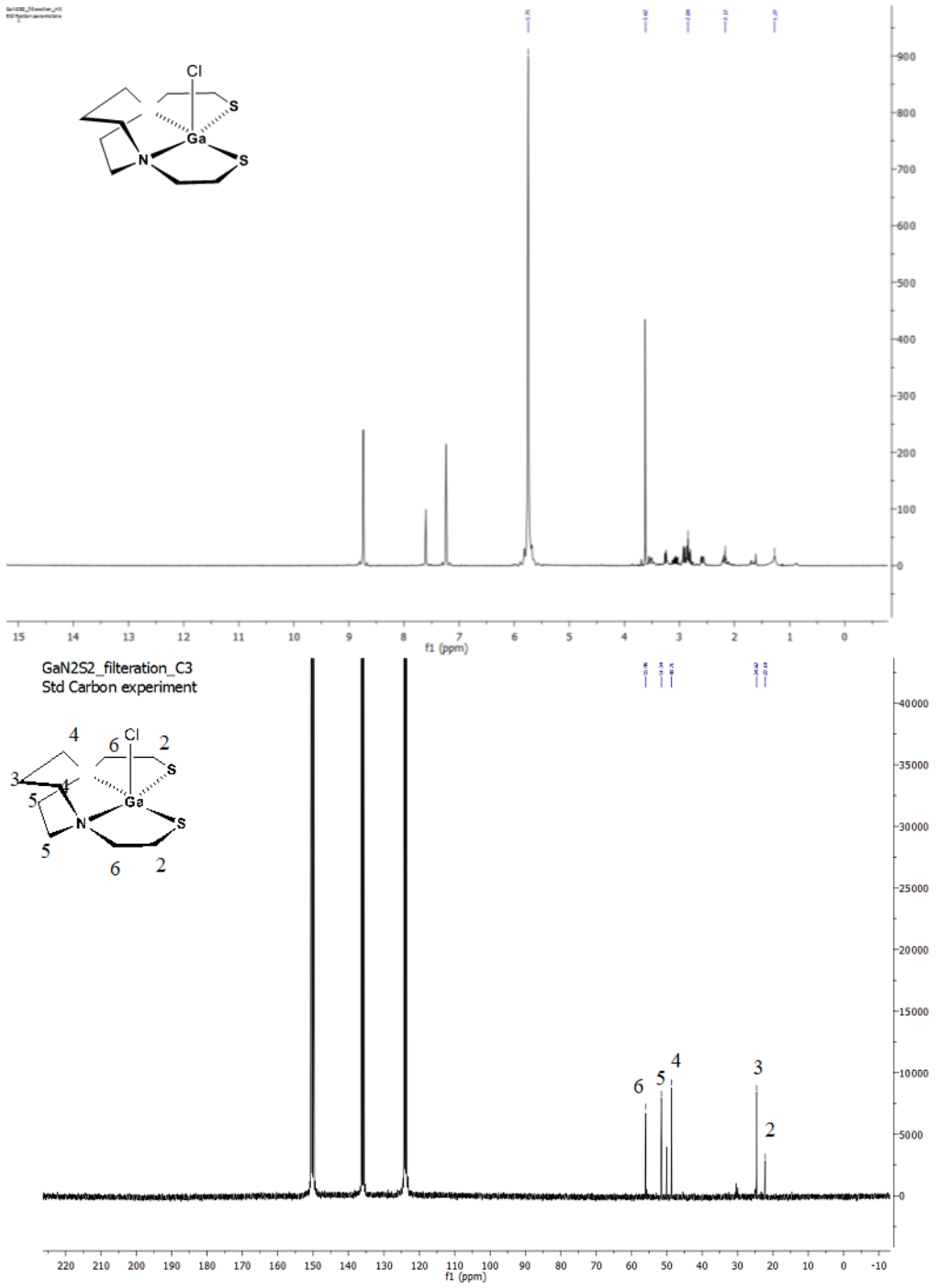

Figure S2. ^{1}H-NMR (up) and ^{13}C-NMR Spectrum of **ClGaN$_2$S$_2$** complex in pyridine-d$_5$ at 23.2 °C using a 300 MHz NMR spectrometer referenced to residual pyridine.

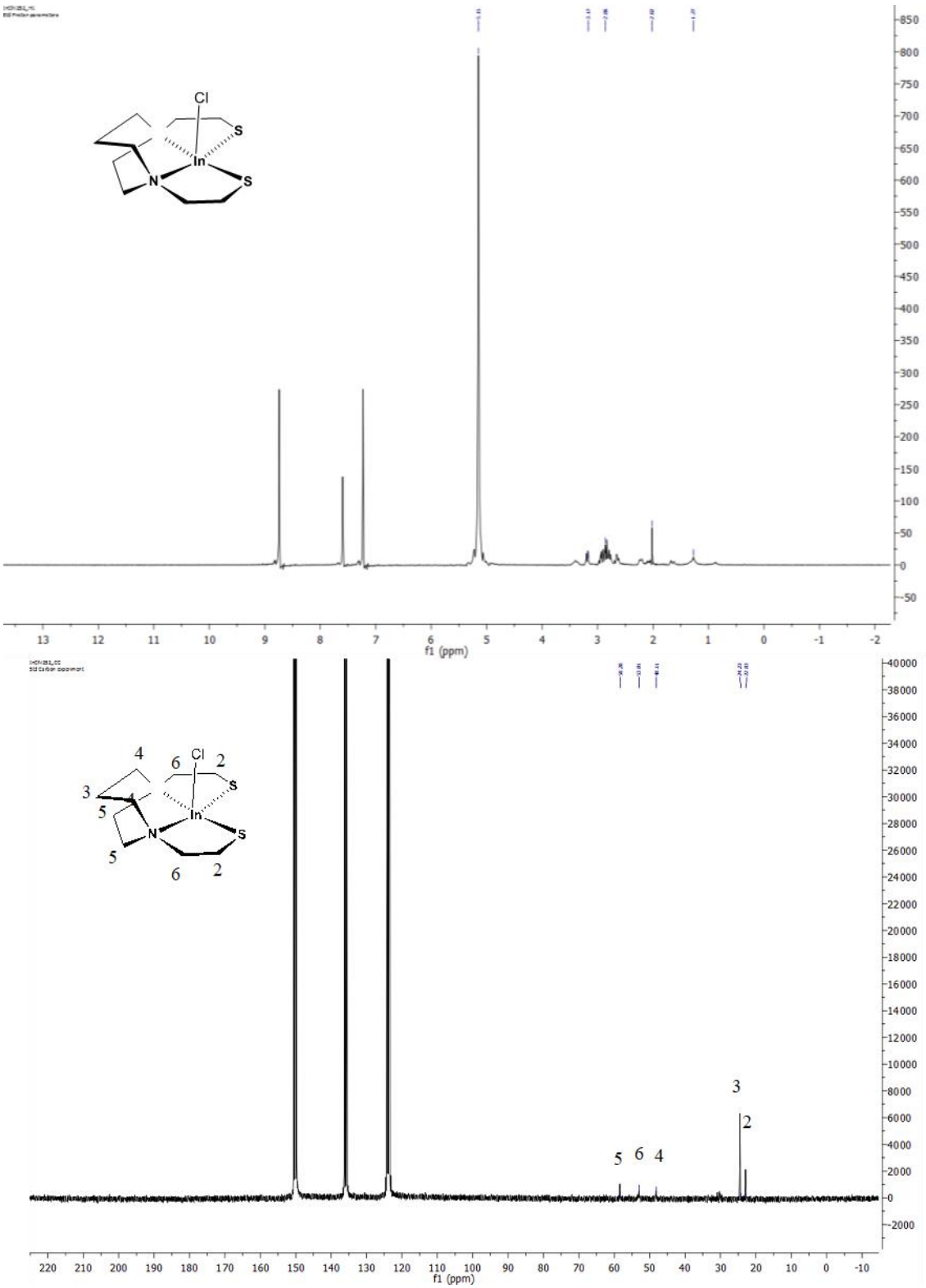

Figure S3. ^{1}H-NMR (up) and ^{13}C-NMR Spectrum of **ClInN$_2$S$_2$** complex in pyridine-d$_5$ at 23.2 °C using a 300 MHz NMR spectrometer referenced to residual pyridine.

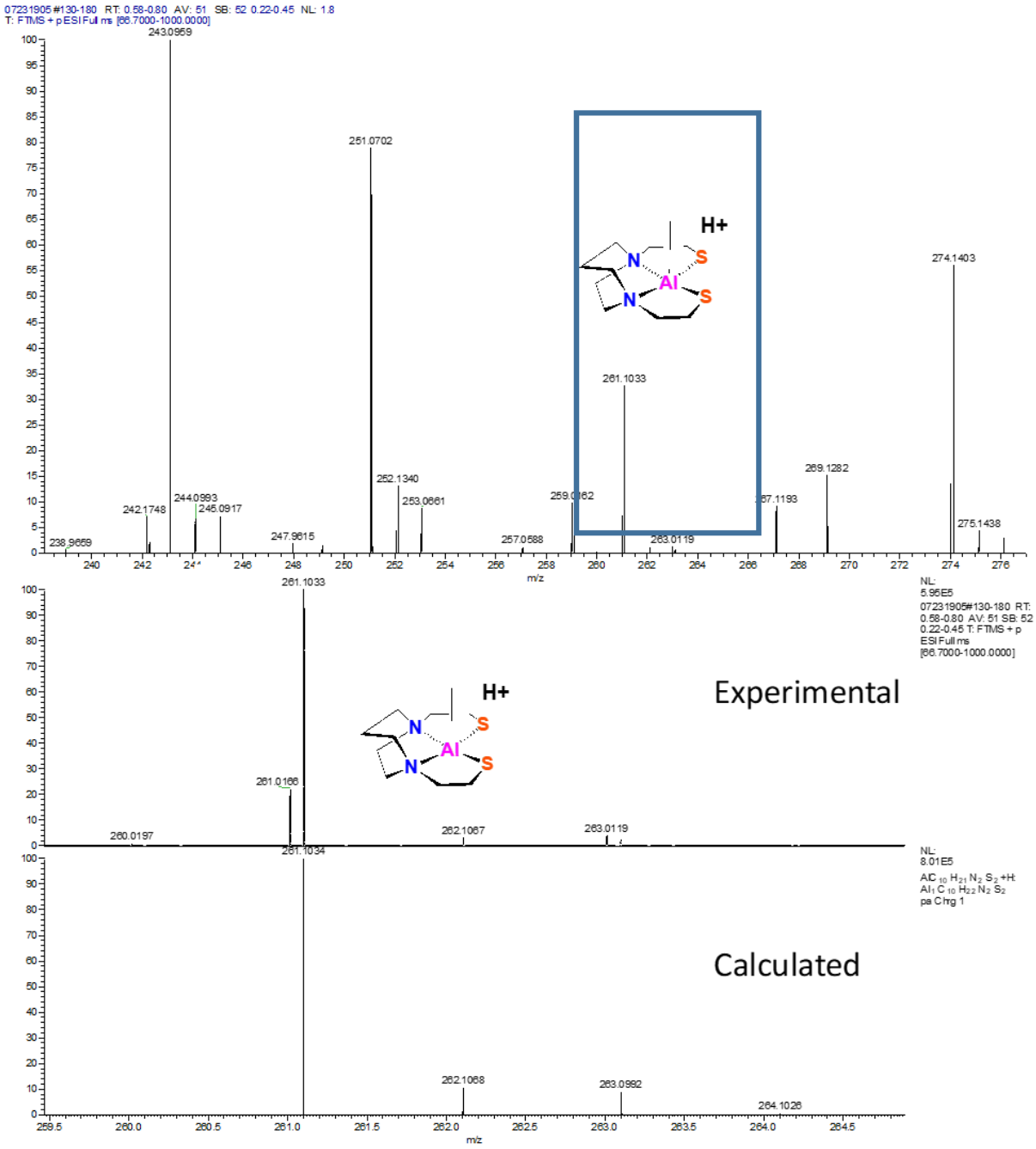

Figure S4. High resolution $^{+}$ESI-MS of **MeAlN$_2$S$_2$** in MeCN/MeOH with isotope bundle for the parent ion (Calculated isotope bundle shows below).

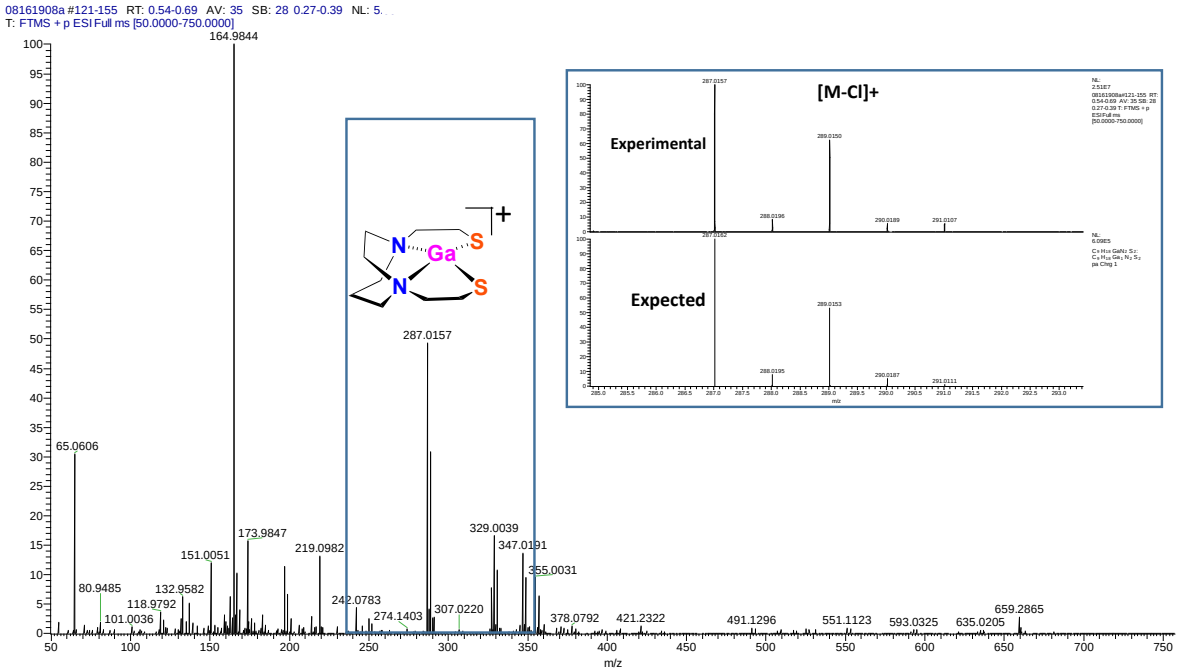

Figure S5. High resolution $^{+}$ESI-MS of **ClGaN$_2$S$_2$** in MeCN/MeOH with isotope bundle for the parent ion (Experimental and expected isotope bundle shows in box).

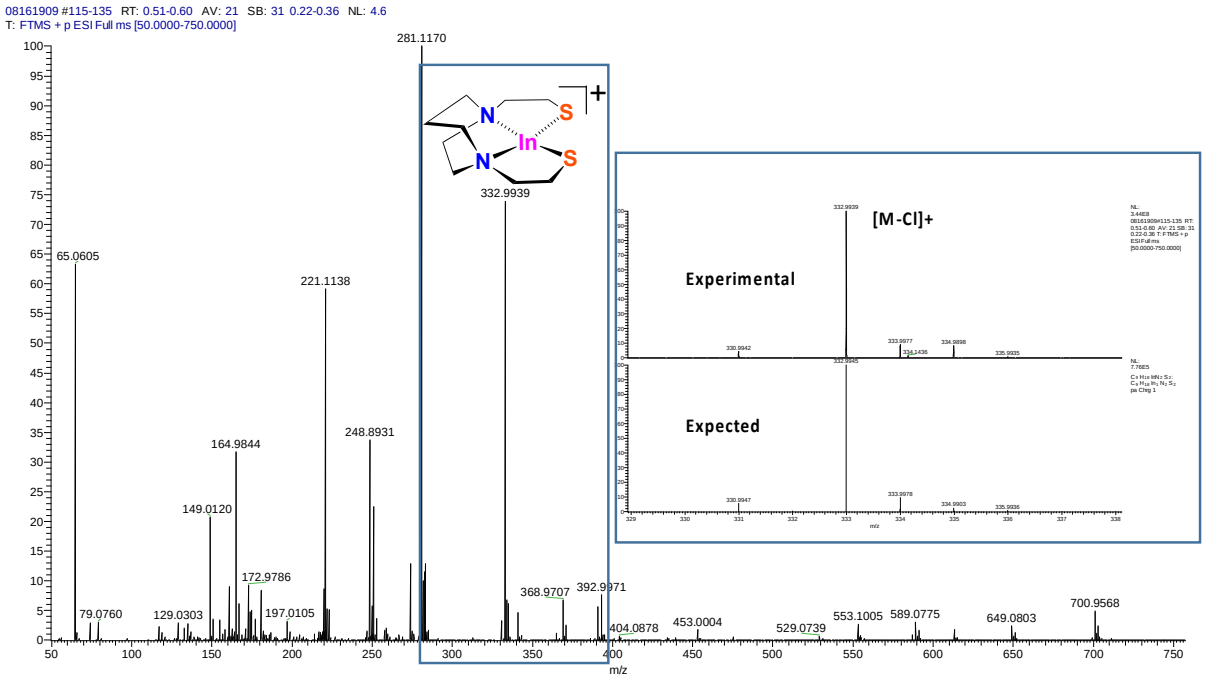

Figure S6. High resolution $^{+}$ESI-MS of **ClInN$_2$S$_2$** in MeCN/MeOH with isotope bundle for the parent ion (Experimental and expected isotope bundle shows in box).

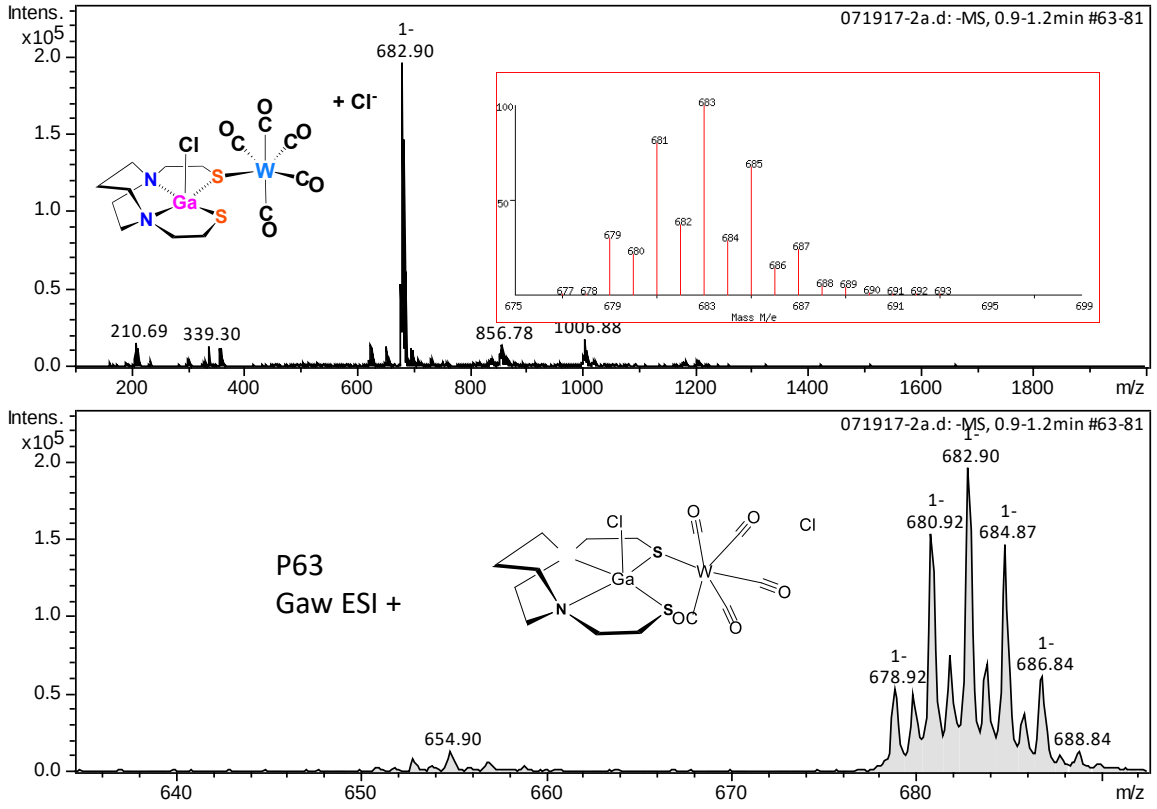

Figure S7. Low Resolution of $^{+}$ESI-MS of **ClGaW(CO)$_5$** in THF with isotope bundle for the parent ion (Calculated isotope bundle shows in red bracket).

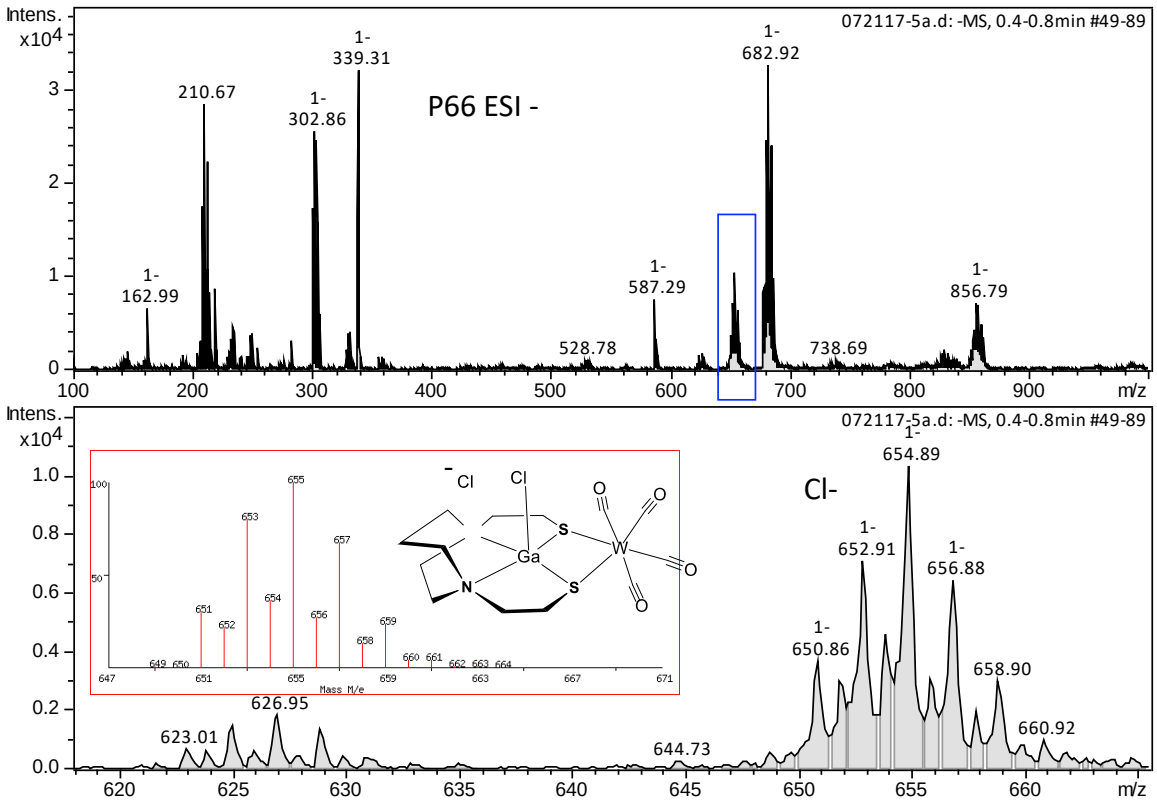

Figure S8. Low Resolution of $^{+}$ESI-MS of **ClGaW(CO)$_4$** in THF with isotope bundle for the parent ion (Calculated isotope bundle shows in red bracket).

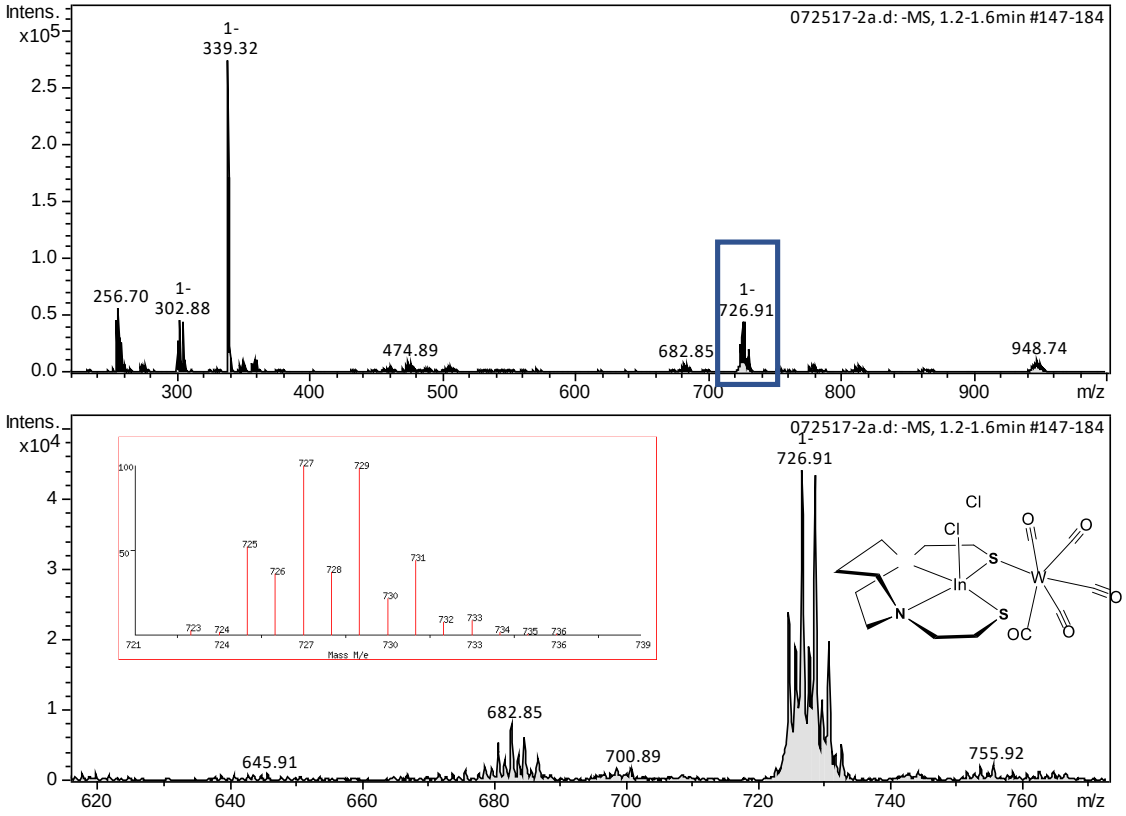

Figure S9. Low Resolution of $^{+}$ESI-MS of **ClInW(CO)$_5$** in THF with isotope bundle for the parent ion (Calculated isotope bundle shows in red bracket).

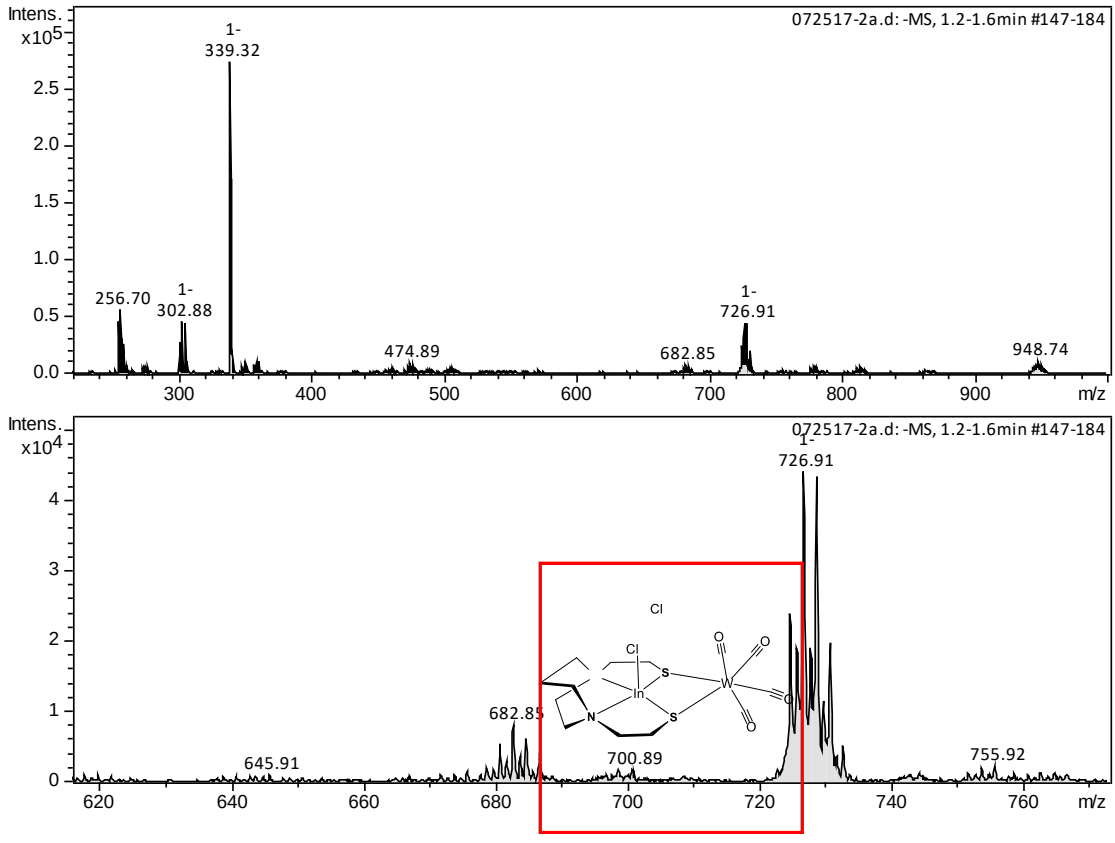

Figure S10. Low Resolution of $^{+}$ESI-MS of **ClInW(CO)$_4$** in THF with isotope bundle for the parent ion.

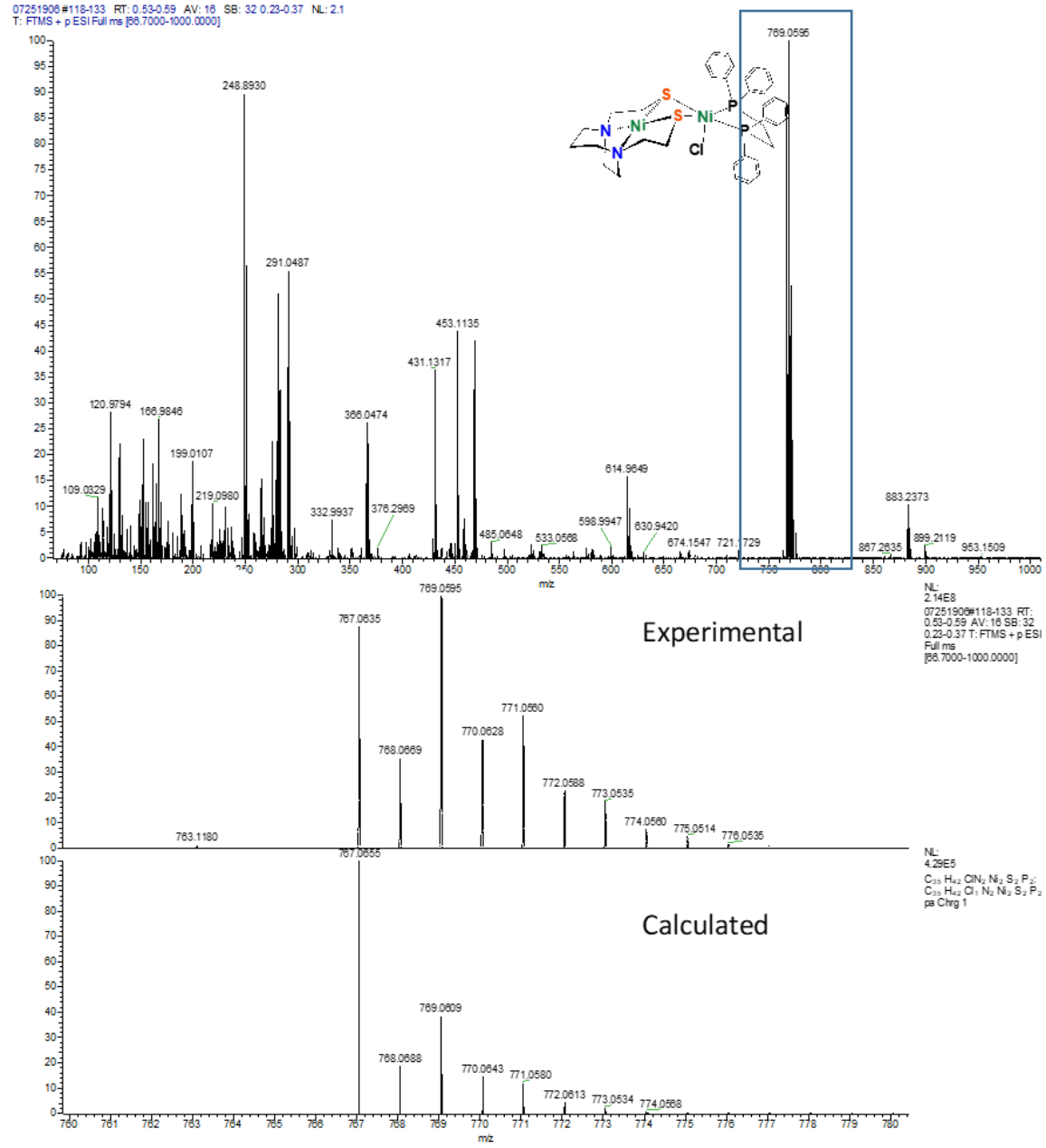

Figure S11. High Resolution of $^{+}$ESI-MS of the products from the reaction of **InClN$_2$S$_2$** with NidppeCl$_2$ in MeOH with isotope bundle for the parent ion (Experimental and calculated isotope bundle shows below).

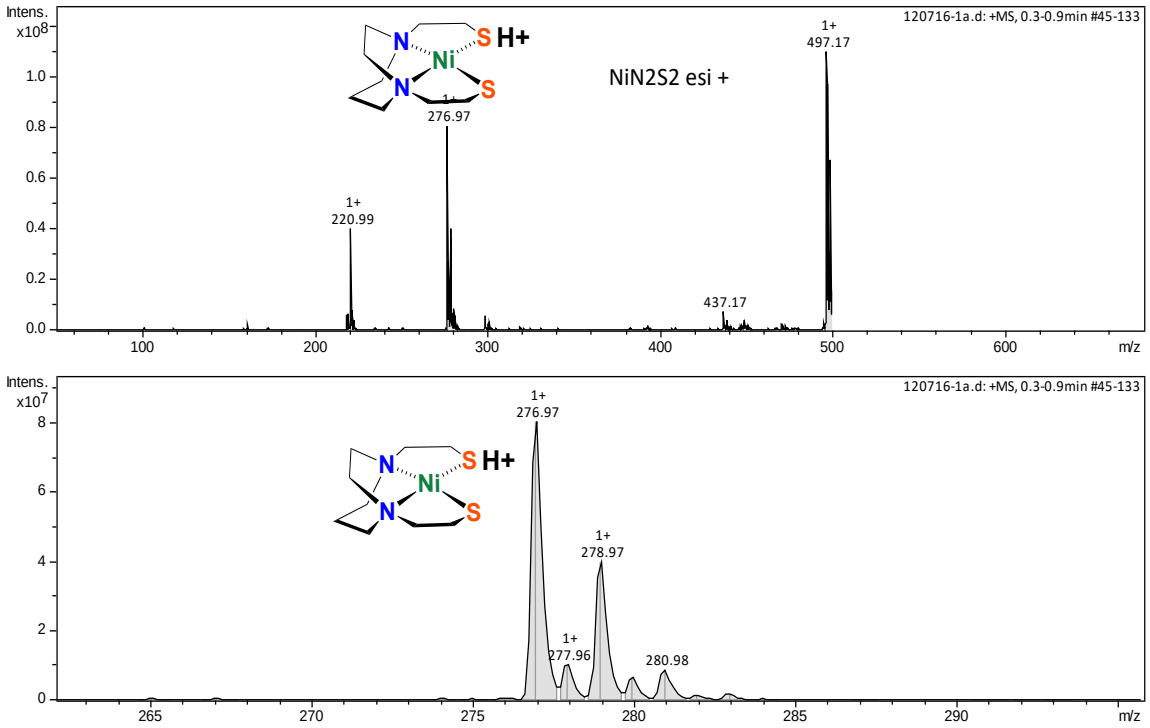

Figure S12. Low resolution of $^{+}$ESI-MS of the products from the reaction of **AlMeN$_2$S$_2$** with Ni(BF$_4$)$_2$ in MeOH with isotope bundle for the parent ion.

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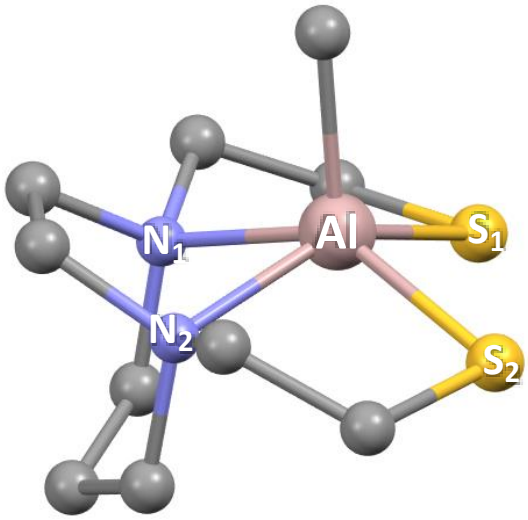


Figure S13. Crystal structure of **MeAlN$_2$S$_2$**.

Table S1. Data and structure refinement for **MeAlN$_2$S$_2$**.

Identification Code	**mo AlMe 0m**
Empirical formula	$C_{10}H_{21}N_2AlS_2$
Formula weight	260.39
Temperature/K	100.15
Crystal system	triclinic
Space group	P-1
a/Å	7.354(4)
b/Å	7.723(4)
c/Å	12.601(6)
α/°	94.767(7)
β/°	98.204(7)
γ/°	115.566(6)
Volume/Å^3	630.6(5)
Z	2
ϱ_{calc}g/cm^3	1.371
μ/mm^{-1}	0.463
F(000)	280.0
Crystal size/mm^3	0.05 × 0.02 × 0.02
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.31 to 50.99
Index ranges	$-8 \le h \le 8$, $-9 \le k \le 9$, $-15 \le l \le 15$
Reflections collected	6296
Independent reflections	2333 [R_{int} = 0.0971, R_{sigma} = 0.1270]
Data/restraints/parameters	2333/0/138
Goodness-of-fit on F^2	1.250
Final R indexes [I >= 2σ (I)]	R_1 = 0.0733, wR_2 = 0.1248
Final R indexes [all data]	R_1 = 0.1185, wR_2 = 0.1386
Largest diff. peak/hole / e Å^{-3}	0.63/−0.44

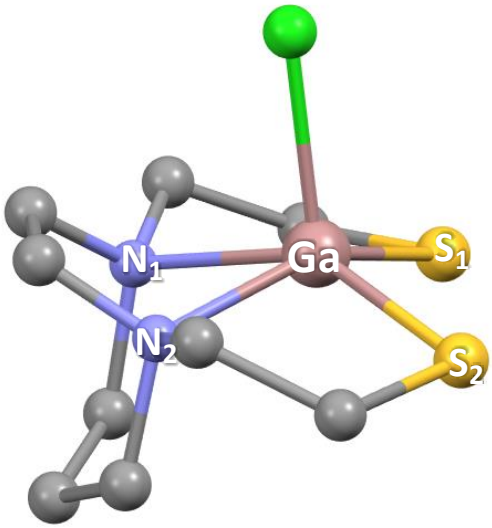


Figure S14. Crystal structure of **ClGaN$_2$S$_2$**.

Table S2. Crystal data and structure refinement for **ClGaN$_2$S$_2$**.

Identification Code	**cu 062517**
Empirical formula	$C_9H_{18}ClGaN_2S_2$
Formula weight	323.54
Temperature/K	100.0
Crystal system	triclinic
Space group	P-1
a/Å	7.3341(5)
b/Å	7.6637(5)
c/Å	12.6658(9)
α/°	94.557(2)
β/°	98.228(2)
γ/°	114.796(2)
Volume/Å^3	631.86(8)
Z	2
ϱ_{calc}g/cm^3	1.701
μ/mm^{-1}	7.767
F(000)	332.0
Crystal size/mm^3	0.1 × 0.01 × 0.01
Radiation	CuK*α* (*λ* = 1.54178)
2*θ* range for data collection/°	7.138 to 122.514
Index ranges	$-8 \le h \le 8$, $-8 \le k \le 8$, $-14 \le l \le 14$
Reflections collected	11060
Independent reflections	1862 [R_{int} = 0.0270, R_{sigma} = 0.0232]
Data/restraints/parameters	1862/0/136
Goodness-of-fit on F^2	1.040
Final R indexes [I >= 2*σ* (I)]	R_1 = 0.0498, wR_2 = 0.1389
Final R indexes [all data]	R_1 = 0.0500, wR_2 = 0.1392
Largest diff. peak/hole / e Å^{-3}	1.42/−0.51

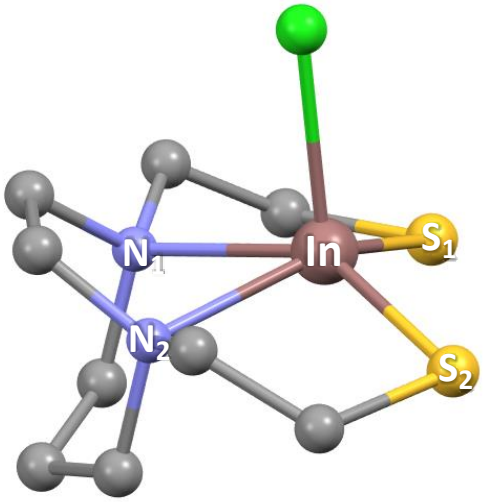


Figure S15. Crystal structure of **ClInN$_2$S$_2$**.

Table S3. Crystal data and structure refinement for **ClInN$_2$S$_2$**.

Identification Code	AlET 0m-auto
Empirical formula	$C_9H_{18}ClInN_2S_2$
Formula weight	368.66
Temperature/K	143.19
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	12.7424(6)
b/Å	7.3373(3)
c/Å	15.3561(7)
α/°	90
β/°	114.107(1)
γ/°	90
Volume/Å^3	1310.5(1)
Z	4
ϱ_{calc}g/cm^3	1.8684
μ/mm^{-1}	19.029
F(000)	742.1
Crystal size/mm^3	0.1 × 0.1 × 0.2
Radiation	Cu K*α* (*λ* = 1.54178)
2*θ* range for data collection/°	7.6 to 144.84
Index ranges	−15 ≤ *h* ≤ 15, -9 ≤ *k* ≤ 9, −18 ≤ *l* ≤ 18
Reflections collected	18017
Independent reflections	2567 [R_{int} = 0.0540, R_{sigma} = 0.0333]
Data/restraints/parameters	2567/0/135
Goodness-of-fit on F^2	1.000
Final R indexes [I >= 2*σ* (I)]	R_1 = 0.0305, wR_2 = 0.0840
Final R indexes [all data]	R_1 = 0.0307, wR_2 = 0.0844
Largest diff. peak/hole / e Å^{-3}	0.72/−1.88

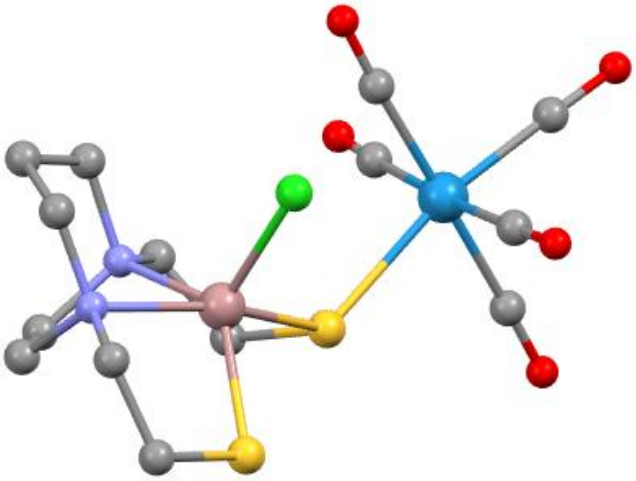
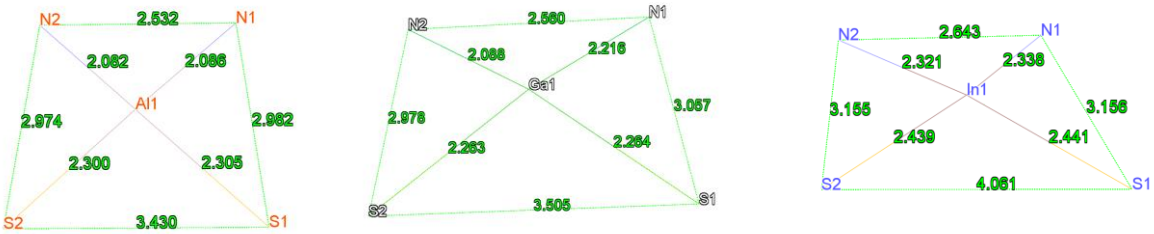


Figure S16. Crystal structure of **ClGaW(CO)$_5$**.

Table S4. Crystal data and structure refinement for gawco5.

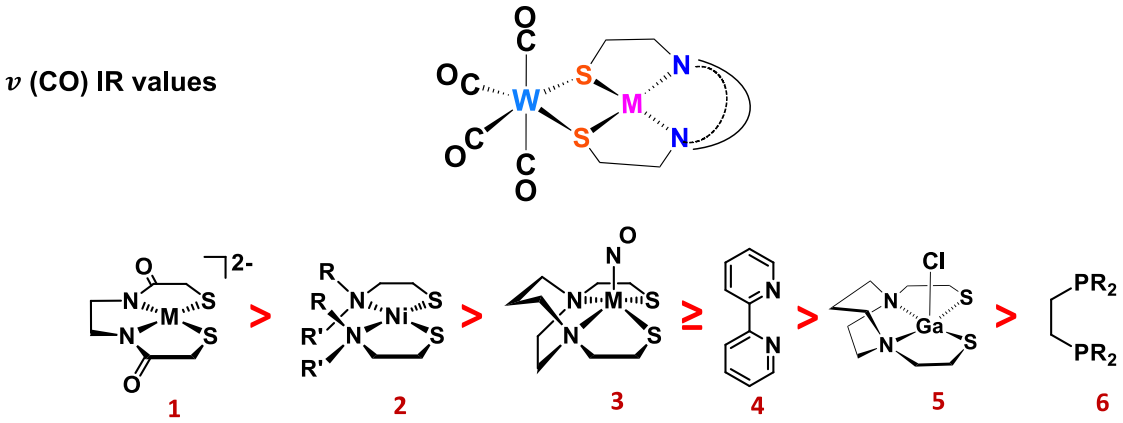
Identification Code	**gawco5**
Empirical formula	$C_{14}H_{18}ClGaN_2O_5S_2W$
Formula weight	647.44
Temperature/K	100
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.2266(11)
b/Å	19.245(2)
c/Å	12.8581(18)
α/°	90
β/°	95.932(8)
γ/°	90
Volume/Å^3	2024.8(5)
Z	4
ϱ_{calc}g/cm^3	2.124
μ/mm^{-1}	15.370
F(000)	1240.0
Crystal size/mm^3	0.1 × 0.01 × 0.01
Radiation	CuKα (λ = 1.54184)
2θ range for data collection/°	8.3 to 122.524
Index ranges	$-9 \le h \le 9$, $-21 \le k \le 21$, $-14 \le l \le 14$
Reflections collected	21370
Independent reflections	3117 [R_{int} = 0.0442, R_{sigma} = 0.0267]
Data/restraints/parameters	3117/0/239
Goodness-of-fit on F^2	1.026
Final R indexes [I >= 2σ (I)]	R_1 = 0.0320, wR_2 = 0.0781
Final R indexes [all data]	R_1 = 0.0344, wR_2 = 0.0800
Largest diff. peak/hole / e Å^{-3}	0.85/−0.52

Table S5. The ratio of M–N/M–S in **XMN$_2$S$_2$**.



	AlN2S2	GaN2S2	InN2S2
M-N/M-S	0.905	0.950	0.955

Table S6. The ν(CO) values in different **MW(CO)$_4$** complexes.



Compound	ν (A_1^1)	ν (B_1)	ν (A_1^2)	ν (B_2)
1, Ni(ema)W(CO)$_4$	1986	1853	1837	1791
2, Ni(bme-Me$_2$PDA) W(CO)$_4$	1993	1876	1843	1826
3, Fe(NO)W(CO)$_4$	1998	1880	1854	1827
4, (bipy)W(CO)$_4$	2006	1886	1870	1830
5, GaClW(CO)$_4$	2007	1926	1893	1849
6, (dppe)W(CO)$_4$	2015	1900	1900	1870

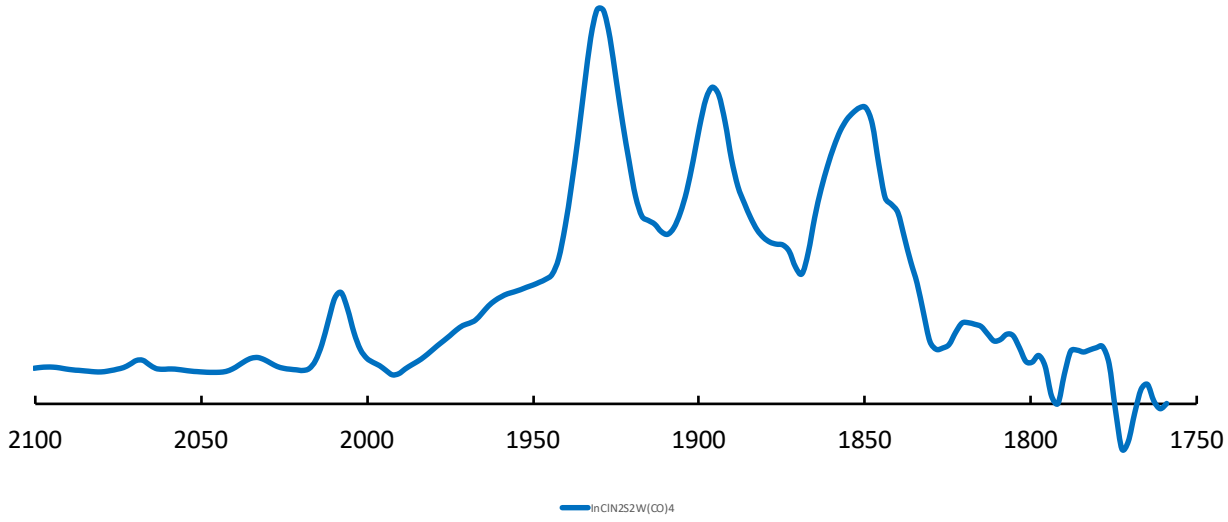


Figure S17. The IR spectra of **ClInW(CO)$_4$** resulting from **ClInW(CO)$_5$** under UV light.

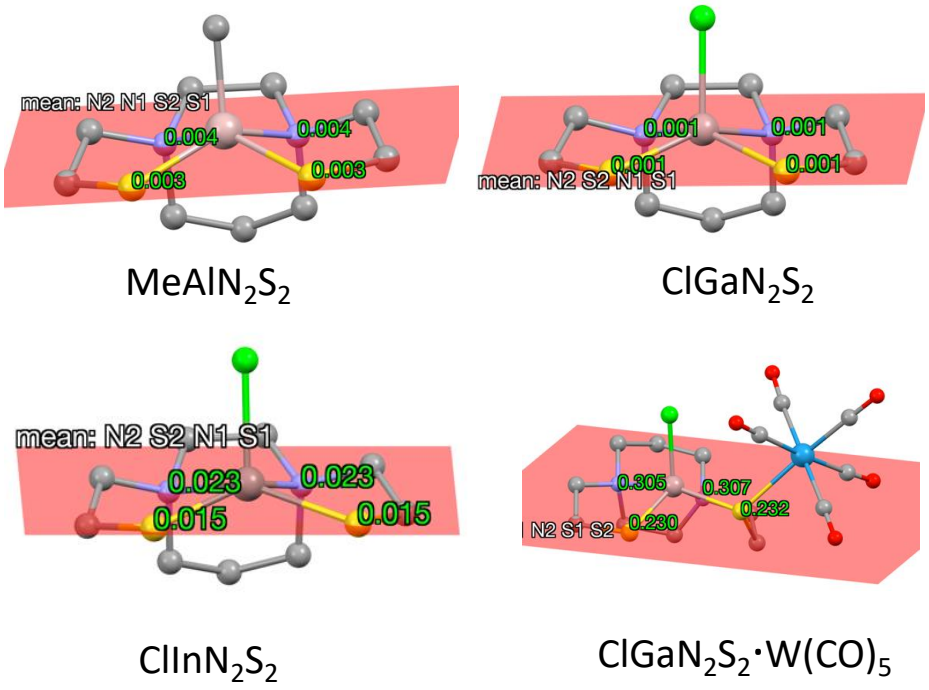


Figure S18. The deviations of Nitrogen and Sulfur atoms from N_2S_2 plane, which is calculated by Mercury Program.