Supporting Information

INSERTION REACTION OF CHALCOGENS INTO AN Al–P BOND

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1. Spectroscopic data

Figure S1. ^{1}H NMR spectrum of **2** (600 MHz, C_6D_6, 298 K).

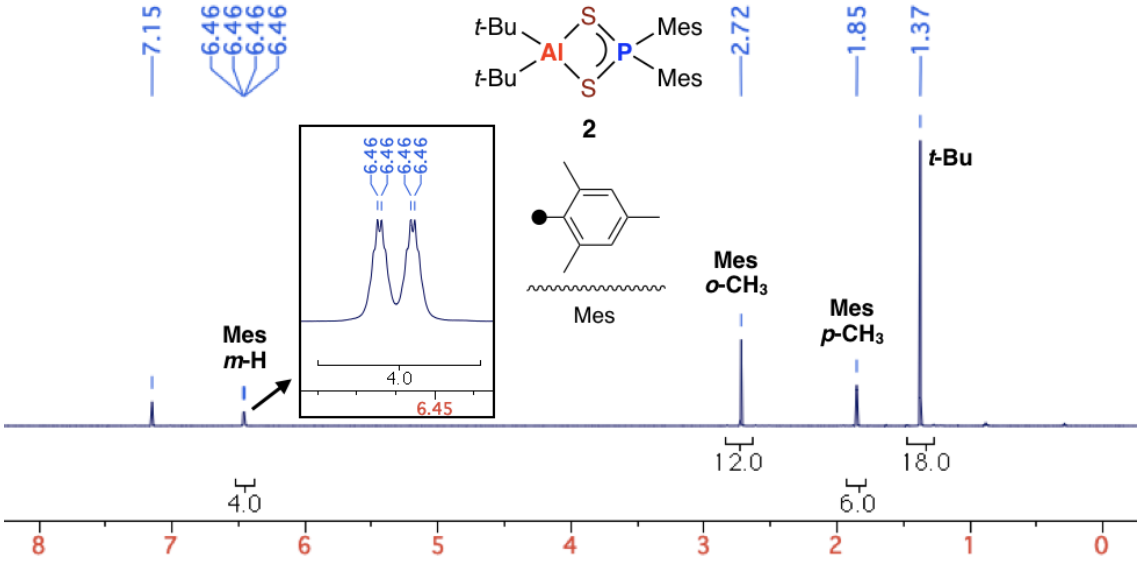


Figure S2. ^{13}C{^{1}H} NMR spectrum of **2** (151 MHz, C_6D_6, 298 K).

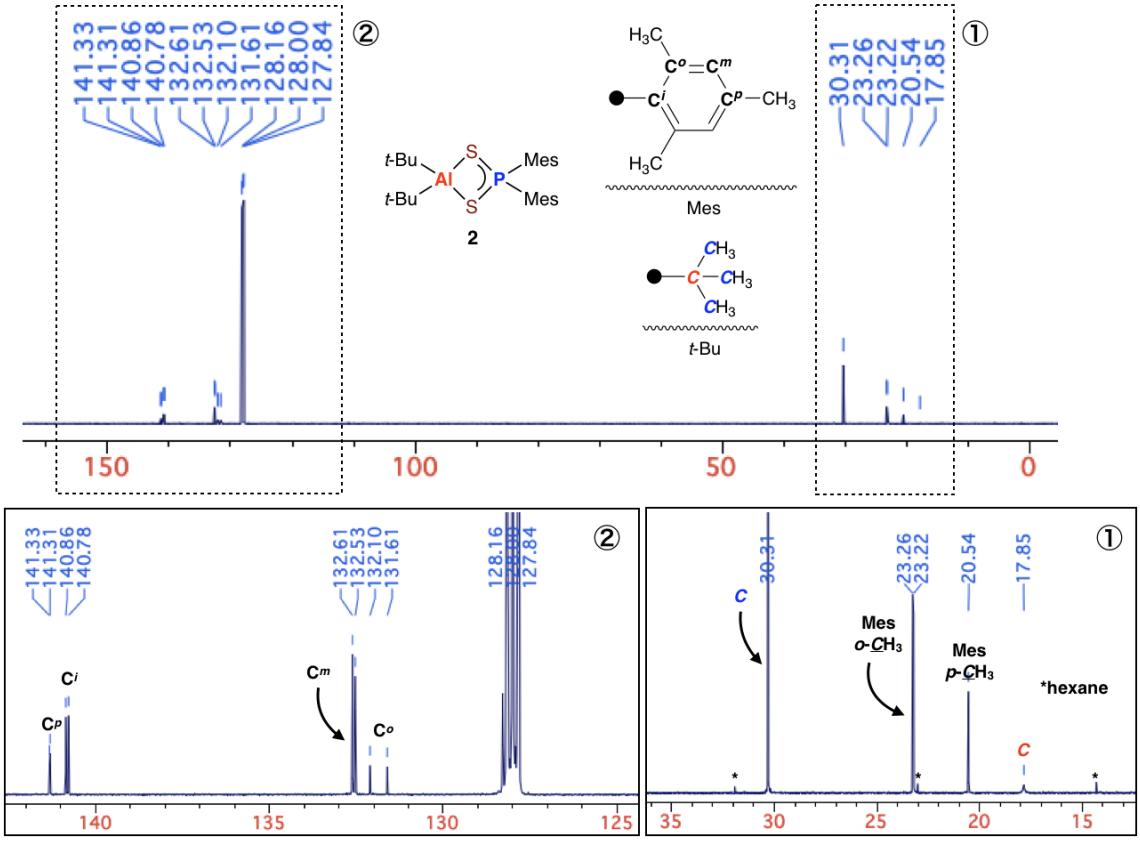


Figure S3. $^{27}Al\{^{1}H\}$ NMR spectrum of **2** (156 MHz, C_6D_6, 298 K).

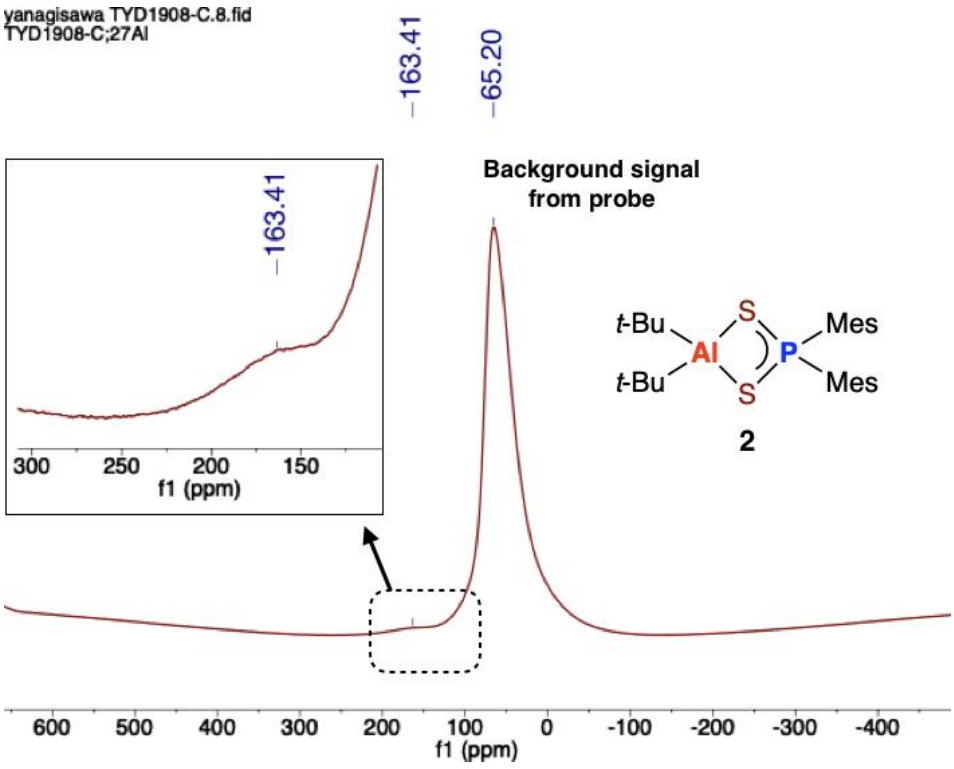


Figure S4. $^{31}P\{^{1}H\}$ NMR spectrum of **2** (243 MHz, C_6D_6, 298K).

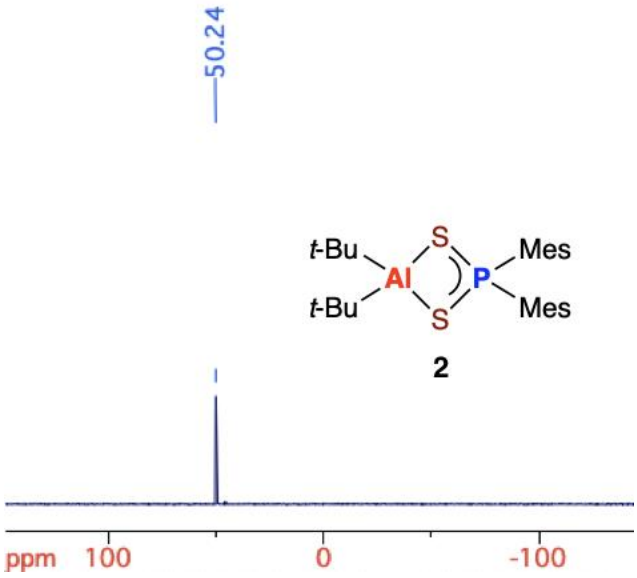


Figure S5. ^{1}H NMR spectrum of the mixture of **1** and Se heated at 60 ºC for 3 h (300 MHz, C_6D_6, 298 K).

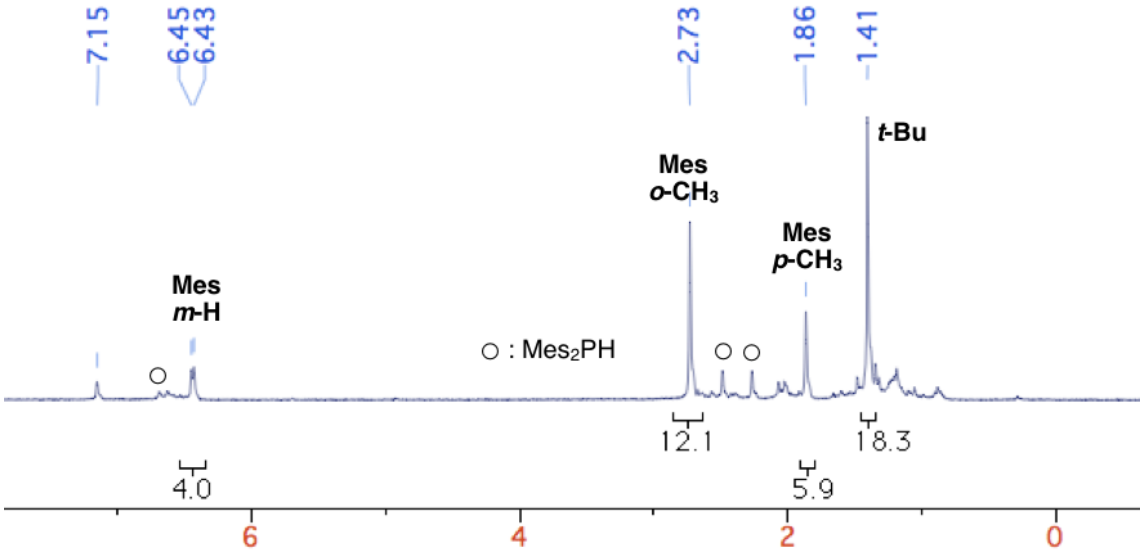


Figure S6. ^{31}P{^{1}H} NMR spectrum of the mixture of **1** and Se heated at 60 ºC for 3 h (121 MHz, C_6D_6, 298 K).

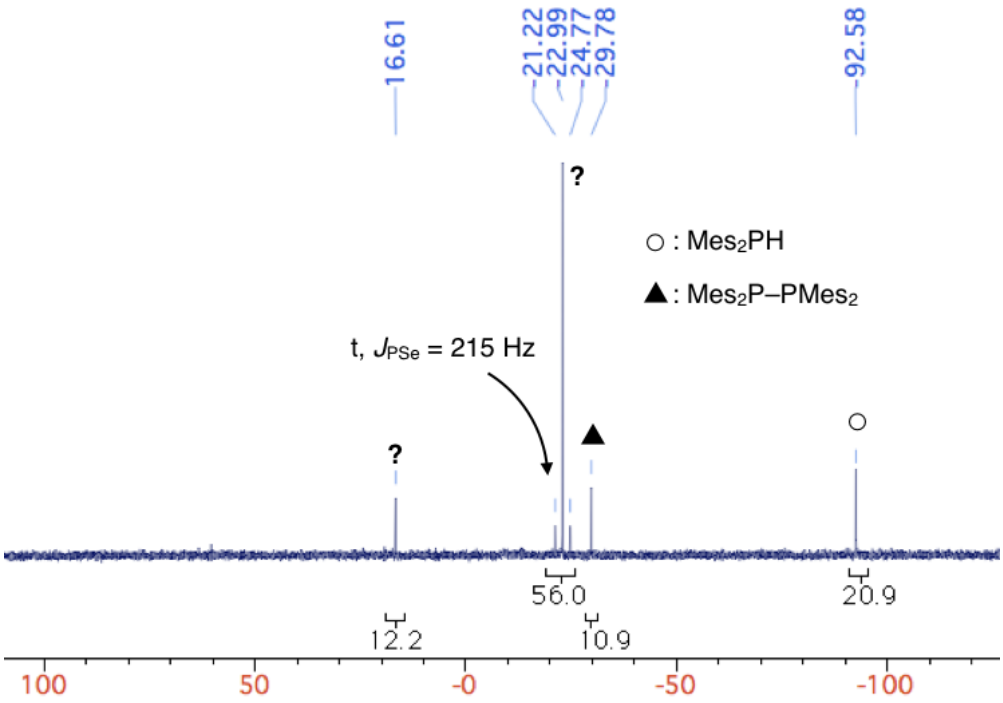


Figure S7. ^{1}H NMR spectrum of the mixture of **1** and Se heated at 70 ºC for 96 h (300 MHz, C_6D_6, 298 K).

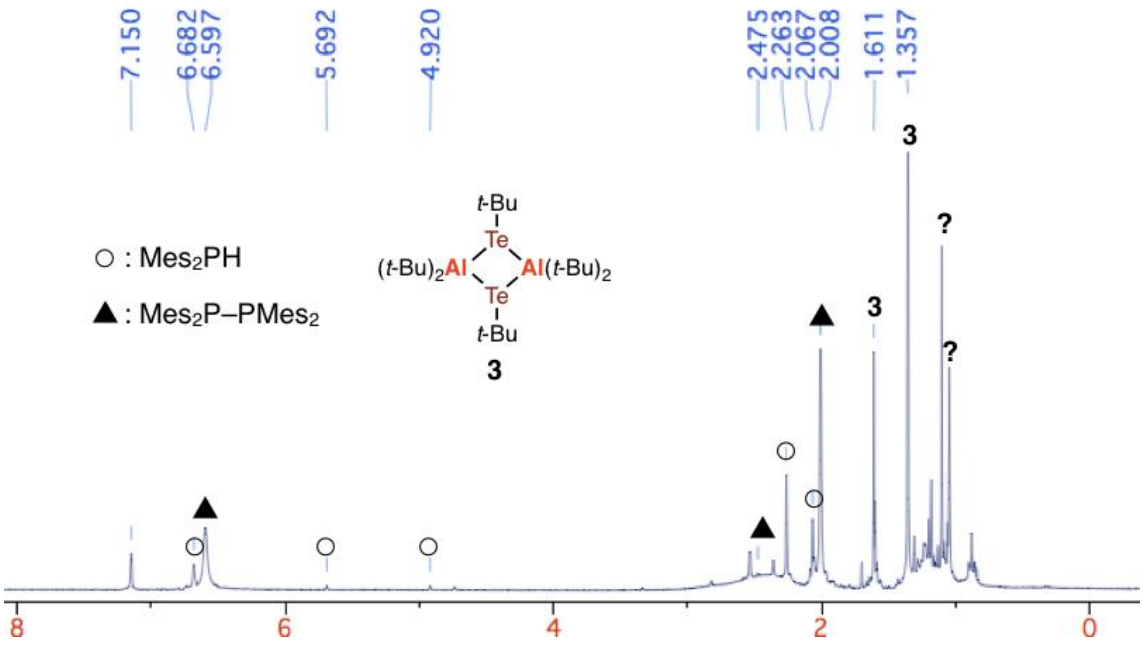


Figure S8. ^{31}P{^{1}H} NMR spectrum of the mixture of **1** and Te heated at 70 ºC for 96 h (121 MHz, C_6D_6, 298 K).

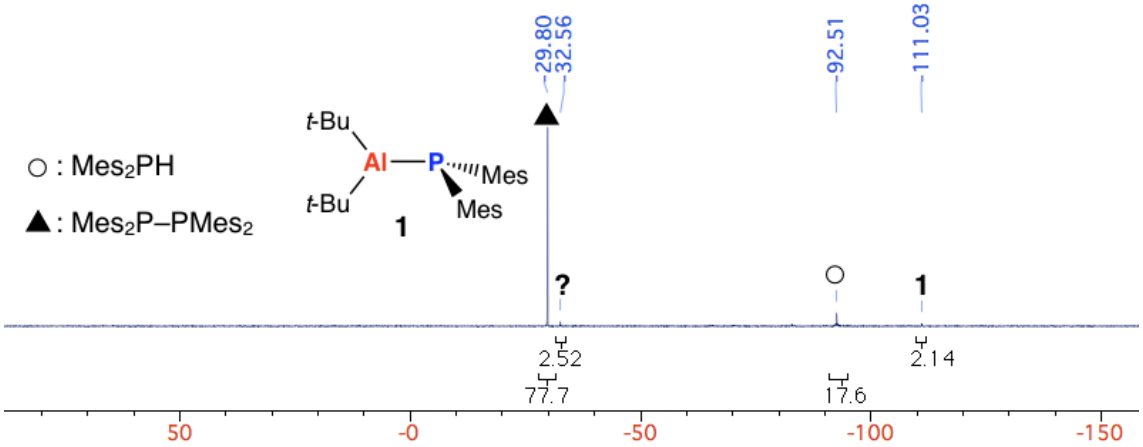


Figure S9. ^{1}H NMR spectrum of the mixture of **1** and $Ph_3P{=}S$ (300 MHz, C_6D_6, 298 K).

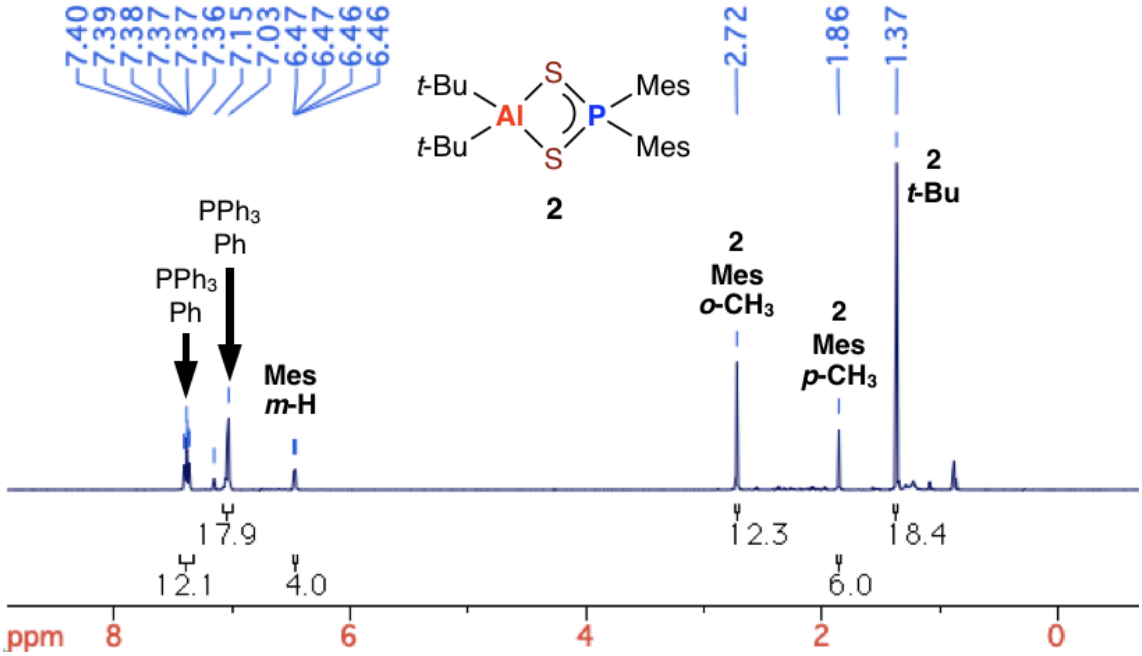


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of the mixture of **1** and $Ph_3P{=}S$ (121 MHz, C_6D_6, 298 K).

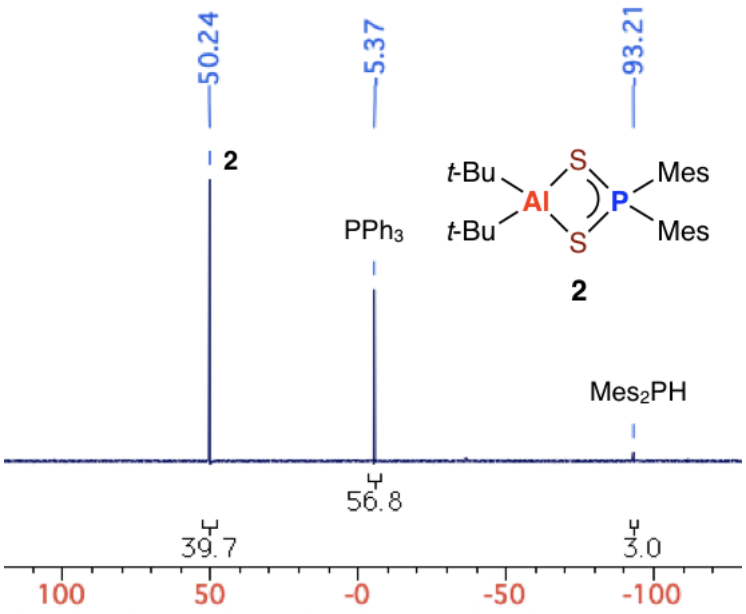


Figure S11. ^{1}H NMR spectrum of the mixture of **1** and $Ph_3P{=}Se$ (300 MHz, C_6D_6, 298 K).

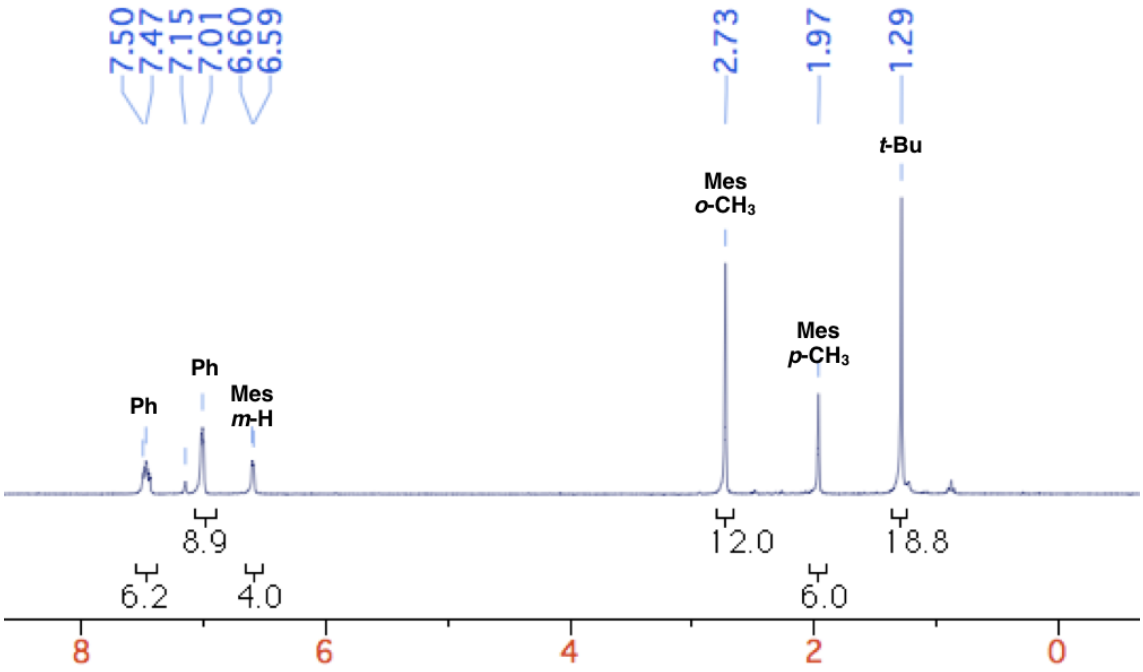


Figure S12. $^{31}P\{^{1}H\}$ NMR spectrum of the mixture of **1** and $Ph_3P{=}Se$ (121 MHz, C_6D_6, 298 K).

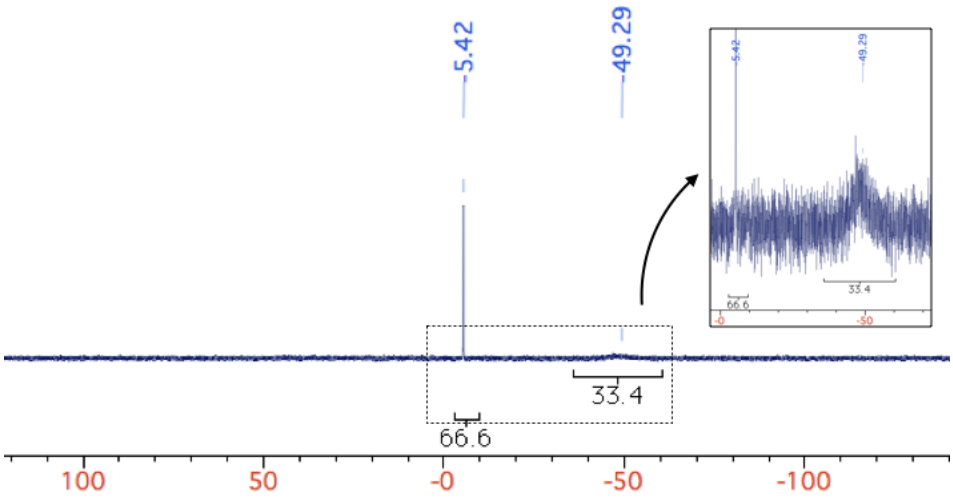


Figure S13. ^{1}H NMR spectrum of the mixture of **1** and (n-Bu)$_3$P=Te (400 MHz, C_6D_6, 298 K).

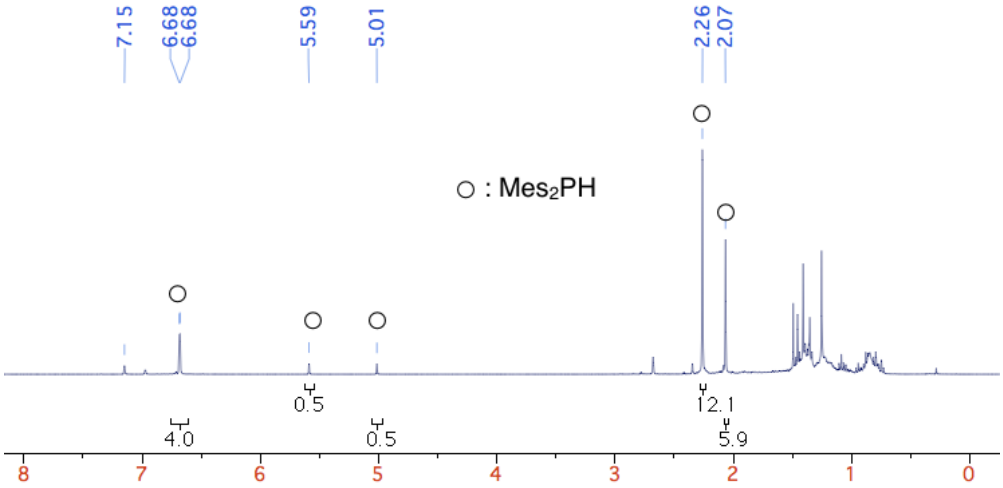
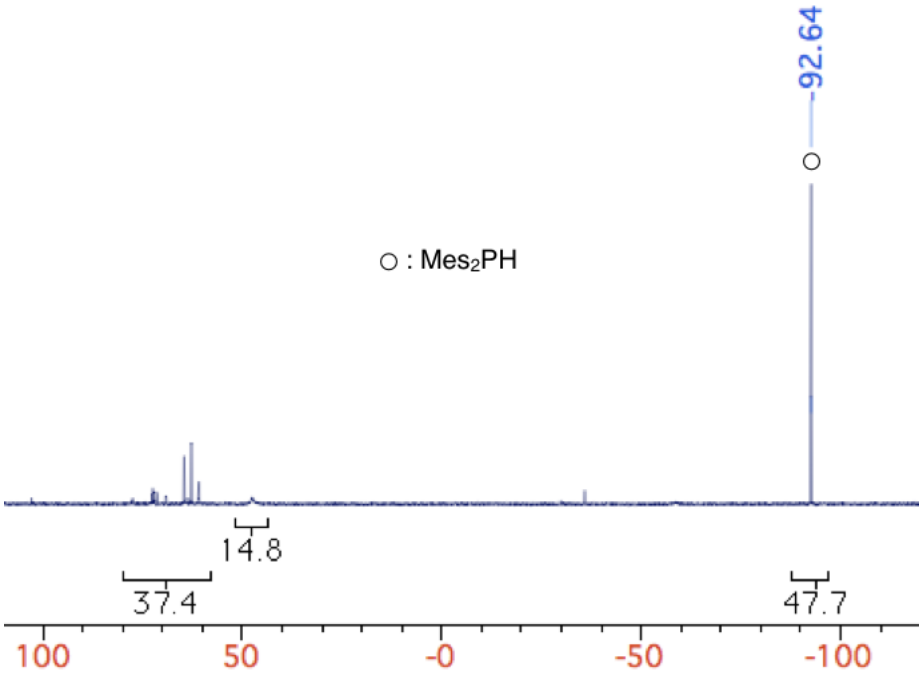


Figure S14. ^{31}P{^{1}H} NMR spectrum of the mixture of **1** and (n-Bu)$_3$P=Te (162 MHz, C_6D_6, 298 K).



2. X-Ray crystallographic analysis

The intensity data were collected on a Rigaku/MSC Mercury CCD diffractometer (Rigaku Corp., Tokyo, Japan) with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) (for **2**), or a Rigaku Saturn 70 CCD diffractometer (Rigaku Corp., Tokyo, Japan) with a VariMax Mo optic system using Mo Kα radiation (λ = 0.71073 Å) (for **4**). An empirical absorption correction was applied to the diffraction data using ABSPACK[1] for **2** and **4**. The structure was solved by a direct method (SHELXT)[2] and refined by full-matrix least-squares method on F^2 for all reflections (SHELXL-2016/4).[3] All hydrogen atoms were placed using AFIX instructions, while all other atoms were refined anisotropically.

2.1 Crystal structure of 4

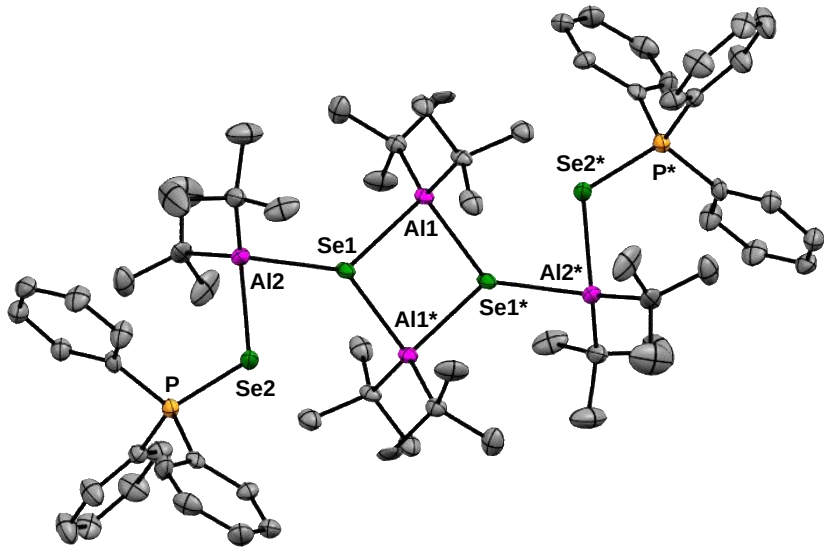


Figure S15. Crystal structure of **4** (thermal ellipsoids at the 50% probability level). Hydrogen atoms and disordered molecules are omitted for clarity.

Table S1. Crystallographic data for **2** and **4**.

	2	**4**
Empirical formula	$C_{26}H_{40}AlPS_2$	$C_{68}H_{102}Al_4P_2Se_4$
Formula weight	474.65	1405.19
Temperature (K)	143(2)	103(2)
Crystal system	Triclinic	Monoclinic
Crystal size (mm)	0.180×0.130×0.100	0.080×0.060×0.040
Space group	*P*–1 (#2)	$P2_1/n$ (#14)
a (Å)	10.9804(2)	16.5625(13)
b (Å)	14.0136(3)	12.6866(8)
c (Å)	18.6664(3)	17.8040(13)
α (º)	74.130(2)	90
b (º)	89.877(2)	107.472(8)
γ (º)	82.132(2)	90
V (Å^3)	2734.93(9)	3568.4(5)
Z	4	2
$D_{calcd.}$ (g•cm^{-3})	1.153	1.308
μ (mm^{-1})	0.296	2.187
F(000)	1024	1456
θ range (º)	1.874 to 25.249	2.007 to 25.248
Reflections collected	30483	40451
Independent reflections	9854 [R_{int} = 0.0343]	6456 [R_{int} = 0.1948]
Completeness to θ_{max}	99.6%	99.9%
Data/restraints/parameters	9854/0/565	6456/0/373
Goodness of fit	1.034	1.013
R_1 [$I>2\sigma(I)$]	0.0369	0.0628
wR_2 [$I>2\sigma(I)$]	0.0857	0.0913
R_1 (all data)	0.0550	0.1296
wR_2 (all data)	0.0942	0.1101
Largest diff. peak (e•Å)	0.458	0.514
Largest diff. hole (e•Å)	–0.194	–0.588
CCDC number	1992857	1992858

3. Computational studies

DFT calculations were performed using the Gaussian 16 (Rev. B. 01)[4] program package with B3LYP functional[5] including Grimme dispersion correction (D3)[6] along with a combined basis sets: 6-31G(d) level. All the geometry optimizations have been performed until the residual mean force is smaller than 1.0×10^{-5} a.u. (tight threshold in Gaussian). The frequency calculations were carried out for each optimized structure to confirm the absence of any imaginary frequencies. Natural bond orbital (NBO) analysis have been carried with the with the NBO 6.0 program package,[7] linked to single-point calculations using Gaussian 16 (Rev. D. 01)

3.1 Coordinates (xyz) for the calculated structures

Table S2. Compound **2**.

2	G = −1502705.5 kcal mol^{-1}										
Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
P	0.3738	0	0	H	-3.3502	2.0252	2.1939	H	2.9523	-0.4752	1.83
Al	-2.6633	0	0	C	-4.8718	1.7131	-0.928	H	3.2105	0.8036	3.0198
S	-0.9165	0.1853	1.6112	H	-4.5663	1.5625	-1.9724	C	0.5899	-2.6419	2.0862
S	-0.9165	-0.1853	-1.6112	H	-5.5867	0.9202	-0.6764	H	-0.4672	-2.5998	1.8278
C	1.5045	1.4754	0.0643	H	-5.4249	2.667	-0.8892	H	0.7739	-3.5889	2.6017
C	2.4173	1.5236	1.1575	C	-2.7689	2.933	-0.3481	H	0.775	-1.8345	2.799
C	1.4816	2.5473	-0.8678	H	-1.8542	2.9761	0.2572	C	4.1844	4.8665	0.5573
C	3.2744	2.6205	1.2803	H	-2.4736	2.8907	-1.4036	H	3.7193	5.6205	1.206
C	2.3691	3.6154	-0.6828	H	-3.3025	3.8877	-0.2029	H	5.1315	4.5755	1.024
C	3.2701	3.6802	0.3762	C	-3.6639	-1.7407	-0.0305	H	4.4079	5.3513	-0.3987
H	3.9677	2.6433	2.118	C	-4.1754	-1.9523	-1.4728	C	0.5899	2.6419	-2.0862
H	2.3484	4.4287	-1.4043	H	-3.3502	-2.0252	-2.1939	H	0.775	1.8345	-2.799
C	1.5045	-1.4754	-0.0643	H	-4.7499	-2.8911	-1.5491	H	-0.4672	2.5998	-1.8278
C	2.4173	-1.5236	-1.1575	H	-4.8401	-1.1441	-1.8048	H	0.7739	3.5889	-2.6017
C	1.4816	-2.5473	0.8678	C	-2.7689	-2.933	0.3481	C	4.1844	-4.8665	-0.5573
C	3.2744	-2.6205	-1.2803	H	-2.4736	-2.8907	1.4036	H	5.1316	-4.5754	-1.0238
C	2.3691	-3.6154	0.6828	H	-3.3025	-3.8877	0.2029	H	4.4077	-5.3515	0.3986
C	3.2701	-3.6802	-0.3762	H	-1.8542	-2.9761	-0.2572	H	3.7195	-5.6204	-1.2062
H	3.9677	-2.6433	-2.118	C	-4.8718	-1.7131	0.928	C	2.542	-0.4579	-2.2267
H	2.3484	-4.4287	1.4043	H	-4.5662	-1.5625	1.9724	H	1.5806	-0.2274	-2.6933
C	-3.6639	1.7407	0.0305	H	-5.5866	-0.9202	0.6765	H	2.9523	0.4752	-1.83
C	-4.1754	1.9523	1.4728	H	-5.4249	-2.667	0.8892	H	3.2105	-0.8036	-3.0198
H	-4.7499	2.8911	1.5492	C	2.542	0.4579	2.2267				
H	-4.8401	1.1441	1.8048	H	1.5806	0.2274	2.6933				

Table S3. Compound **2BP**.

2BP	G = −1366131.6 kcal mol^{-1}										
Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
P	0.2004	0	0	H	-0.4541	-2.6269	2.099	C	-4.5764	1.4916	-0.9917
B	-2.624	0	0	H	0.9596	-3.3424	2.8777	H	-4.2316	1.2732	-2.01
S	-1.1835	0.0824	1.5251	H	0.7412	-1.5949	2.8507	H	-5.3755	0.7859	-0.7468
S	-1.1835	-0.0824	-1.5251	C	3.9108	4.9573	0.5457	H	-5.0251	2.4952	-1.0086
C	2.1365	1.6336	1.2129	H	3.3826	5.7387	1.1077	C	-2.5008	2.6463	-0.3184
C	1.3858	2.4887	-0.9599	H	4.8215	4.7149	1.104	H	-1.5701	2.6466	0.2586
C	2.9657	2.7502	1.3399	H	4.2035	5.3884	-0.4173	H	-2.2465	2.6488	-1.3819
C	2.2437	3.581	-0.7679	C	0.6154	2.5047	-2.2643	H	-3.0205	3.5915	-0.1082
C	3.0336	3.7433	0.3659	H	0.7412	1.5949	-2.8507	C	-3.4119	-1.4466	-0.0252
H	3.5785	2.8414	2.2338	H	-0.4541	2.6269	-2.099	C	-3.995	-1.7365	-1.4337
H	2.289	4.3371	-1.5479	H	0.9596	3.3424	-2.8777	H	-3.2021	-1.8388	-2.1837
C	1.3234	-1.4886	-0.0522	C	3.9109	-4.9573	-0.5457	H	-4.5471	-2.6869	-1.4189
C	2.1366	-1.6336	-1.213	H	4.8216	-4.7149	-1.104	H	-4.6874	-0.9671	-1.7799
C	1.3858	-2.4887	0.9599	H	4.2036	-5.3883	0.4173	C	-2.5007	-2.6463	0.3184
C	2.9658	-2.7501	-1.3399	H	3.3827	-5.7387	-1.1077	H	-2.2464	-2.6489	1.3819
C	2.2438	-3.581	0.7679	C	2.1717	-0.6416	-2.3529	H	-3.0204	-3.5916	0.1082
C	3.0337	-3.7433	-0.3659	H	1.187	-0.5194	-2.8146	H	-1.57	-2.6467	-0.2586
H	3.5786	-2.8414	-2.2338	H	2.5182	0.3425	-2.0255	C	-4.5764	-1.4916	0.9917
H	2.2891	-4.3371	1.5479	H	2.8547	-0.9877	-3.1334	H	-4.2316	-1.2733	2.01
C	2.1717	0.6416	2.3529	C	-3.4119	1.4466	0.0252	H	-5.3754	-0.786	0.7469
H	1.187	0.5194	2.8146	C	-3.995	1.7365	1.4337	H	-5.0251	-2.4952	1.0086
H	2.5182	-0.3425	2.0255	H	-4.5471	2.6869	1.4189	C	1.3233	1.4886	0.0522
H	2.8547	0.9877	3.1334	H	-4.6874	0.9671	1.7799				
C	0.6155	-2.5047	2.2643	H	-3.2021	1.8388	2.1837				

Table S4. Compound **B'**.

B'	G = –1123998.4 kcal mol^{-1}										
Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
P	-1.3263	-0.0266	0.0066	H	1.9619	1.8065	-2.0556	H	-3.7514	-2.681	-1.2126
B	1.4213	-0.2027	0.0192	H	3.6915	1.9303	-1.6973	H	-3.7848	-0.9643	-1.6207
S	0.008	-0.316	-1.5174	C	2.5787	0.9341	-0.098	H	-2.3679	-1.9486	-2.0395
S	0.0132	0.0075	1.5533	H	3.4812	0.3301	-0.0384	C	-2.1873	1.6635	-0.114
C	3.0409	0.309	2.1844	C	3.0333	-0.1371	-2.2102	C	-1.0903	2.689	-0.474
C	3.2122	-1.1093	1.4635	C	3.2086	-1.3812	-1.2195	H	-0.2712	2.6775	0.2512
H	2.2078	-0.3581	-2.8957	C	2.8081	1.5871	1.2617	H	-0.6702	2.5044	-1.4657
H	4.2758	-1.4847	-0.9789	C	2.3701	-1.4467	0.1434	H	-1.5396	3.6897	-0.4682
H	1.9724	2.1845	1.6477	C	-2.5113	-1.5067	0.1033	C	-2.7956	2.0499	1.249
H	2.2172	0.2312	2.9025	C	-1.658	-2.7285	0.5063	H	-3.1971	3.0679	1.1728
H	3.9274	-0.1131	-2.8453	H	-0.8207	-2.8802	-0.1813	H	-3.6166	1.3964	1.5515
H	2.9555	-2.2678	-1.8138	H	-1.2552	-2.6271	1.5169	H	-2.0379	2.0476	2.0386
H	3.7	2.2295	1.263	H	-2.2962	-3.6201	0.474	C	-3.2629	1.6594	-1.2137
H	1.9374	-2.4507	0.2461	C	-3.6047	-1.2767	1.1609	H	-4.1295	1.0481	-0.9452
H	3.9369	0.459	2.7994	H	-4.3214	-0.5083	0.8571	H	-3.6202	2.6858	-1.3616
H	2.9595	-1.8577	2.2246	H	-4.1644	-2.2101	1.297	H	-2.865	1.3073	-2.1719
H	4.2786	-1.2607	1.2461	H	-3.1822	-1.0007	2.1333				
C	2.801	1.3001	-1.5624	C	-3.1368	-1.7749	-1.2805				

Table S4. Compound **C'**.

C'	*G* = –1159629.2 kcal mol^{-1}										
Atom	x	y	z	Atom	x	y	z	Atom	x	y	z
P	-1.5204	0.0722	-1.4351	C	3.8151	-0.7848	-1.1586	H	-3.9238	-0.434	-3.0931
B	1.4669	-0.004	-0.3779	C	3.1517	-1.2702	1.1326	H	-3.0228	-1.9427	-3.0686
S	0.2163	-1.1445	-0.9861	C	5.0421	-1.4094	-0.9166	H	-4.7887	-1.9756	-2.9975
C	-0.0321	3.5841	0.3817	C	4.3875	-1.8889	1.3408	C	-6.0849	-2.7296	1.6825
C	1.1728	4.208	0.8056	C	5.3481	-1.9677	0.328	H	-6.8794	-2.0066	1.9113
C	2.3653	3.5298	0.7878	H	5.777	-1.462	-1.7182	H	-6.534	-3.5284	1.0829
H	3.3273	1.6467	0.4023	H	4.6069	-2.3198	2.3164	H	-5.7555	-3.1611	2.634
C	-1.2542	1.6728	-0.552	C	-2.8321	-0.7532	-0.4079	C	3.5185	-0.1906	-2.5186
C	-1.2452	4.3157	0.4368	C	-3.8661	-1.3951	-1.1357	H	2.676	-0.7022	-2.9996
H	1.127	5.2405	1.1448	C	-2.8529	-0.7887	1.0104	H	3.2417	0.8685	-2.4383
H	3.284	4.0126	1.1093	C	-4.899	-2.0329	-0.4411	H	4.383	-0.2616	-3.1864
C	-2.4249	3.7458	0.0217	C	-3.9081	-1.4429	1.6544	C	2.1339	-1.2108	2.2511
C	-2.4166	2.4331	-0.4826	C	-4.9433	-2.0636	0.9529	H	1.7881	-0.1832	2.4209
H	-1.222	5.3363	0.8108	H	-5.6877	-2.5243	-1.0071	H	1.2462	-1.8092	2.0115
H	-3.3578	4.3004	0.0683	H	-3.9172	-1.4716	2.7424	H	2.5475	-1.5861	3.1927
H	-3.3555	2.0006	-0.8209	C	-1.7973	-0.1447	1.8813	C	6.6924	-2.6092	0.5817
C	2.385	2.1845	0.3704	H	-0.7865	-0.3206	1.5086	H	7.4188	-1.8743	0.9546
C	1.2466	1.5055	-0.0646	H	-1.935	0.9406	1.9353	H	6.6225	-3.4049	1.3315
C	-0.0101	2.2237	-0.0986	H	-1.8521	-0.5399	2.9005	H	7.11	-3.042	-0.3339
C	2.8543	-0.709	-0.1278	C	-3.9009	-1.4363	-2.6524				

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