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INSERTION REACTION OF CHALCOGENS INTO AN Al–P BOND

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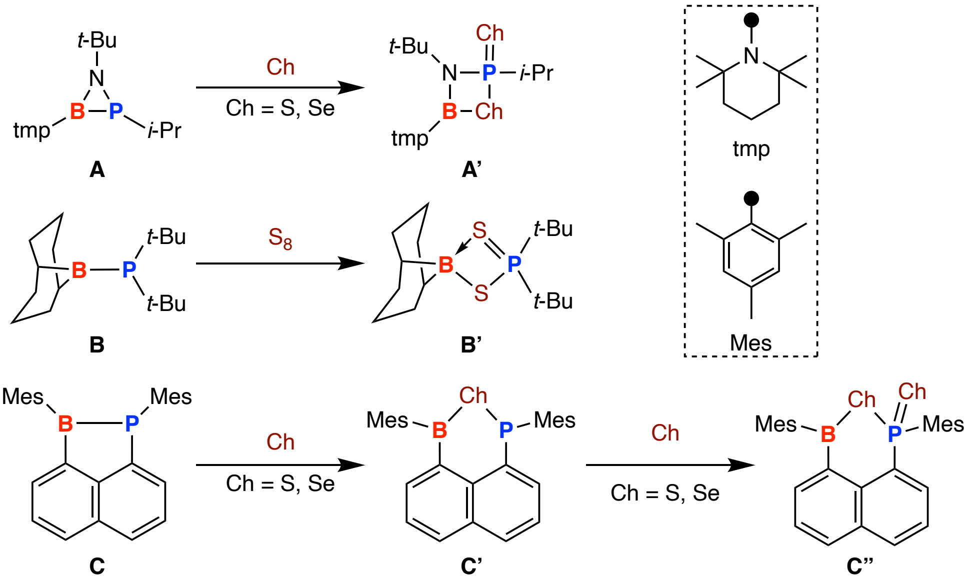
Abstract – We examined the reactions of a phosphanylalumane (>Al–P<) with chalcogen sources as a part of our investigation of the reactivity of the Al–P bonds. In the case of sulfur source, two S atoms were inserted into the Al–P bond to afford an [Al–S–P–S] heterocycle. Structural analysis and theoretical calculations revealed a charge-separated structure between the $[Al]^+$ and $[S_2P]^-$ moieties of the [Al–S–P–S] 4-membered ring, which is different from the [B–S–P–S] ring having concrete B–S σ-bonds in the 4-membered ring.

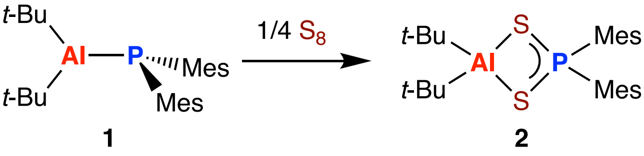
Recent progress building the bonding between "heavy" group 13 and group 15 elements (E–E': E = Al, Ga, and In, E' = P, As, and Sb) enables us to enhance the well-established chemistry of aminoboranes (>B–N<), which are attractive from the viewpoint of materials science.[1]



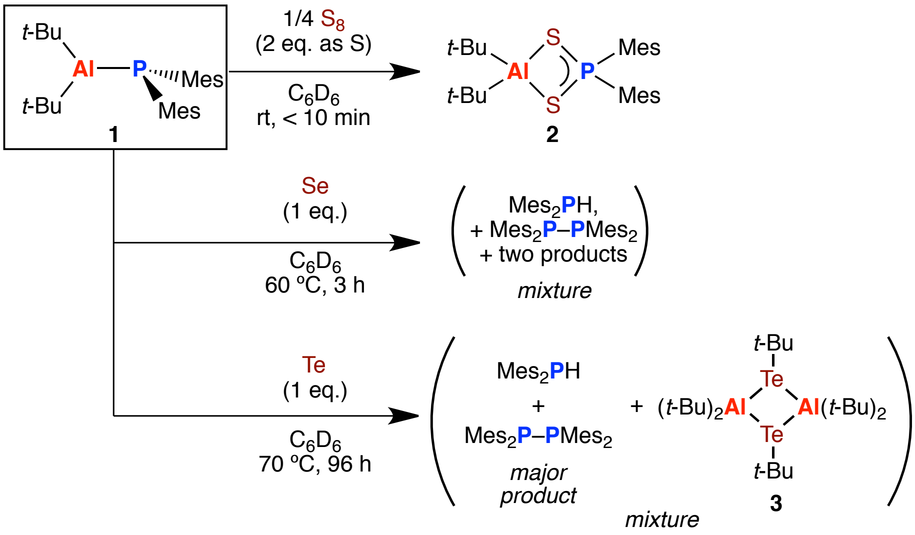
Scheme 1. Chalcogenation reactions of phosphanylboranes tmp = 2,2,6,6-tetramethylpiperidyl. Mes = 2,4,6-trimethylphenyl

Systematic investigation of their characters and reactivities has just begun, and very little study has been done for the reactions of such bonds with a chalcogen source (S, Se, and Te = Ch). To date, three chalcogenation reactions of phosphanylboranes (>B–P<: **A**, **B** and **C**) have been reported.[2] In either case, chalcogen atoms are inserted into the B–P bond to give the corresponding cyclic (**A'**: [B–Ch–P–N], **B'**: [B–S–P–S]) or bridged (**C'**: B–Ch–P) products having characteristic structures (Scheme 1).

Recently, we have succeeded in the synthesis of a new phosphanylalumane (>Al–P<: **1**) and revealed the weak π-type interaction between the Al and P atoms and the high Lewis acidity/basicity of the Al/P centers, respectively.[3] We have focused on the atom insertion reactions of phosphanylalumanes giving reactive and functional products. In this paper, we investigated the reactions of **1** with several Ch sources. As a result, the insertion of two S atoms into the Al–P bond was found to afford a novel 4-membered ring [Al–S–P–S] with tetra-coordinated Al center **2** (Scheme 2).



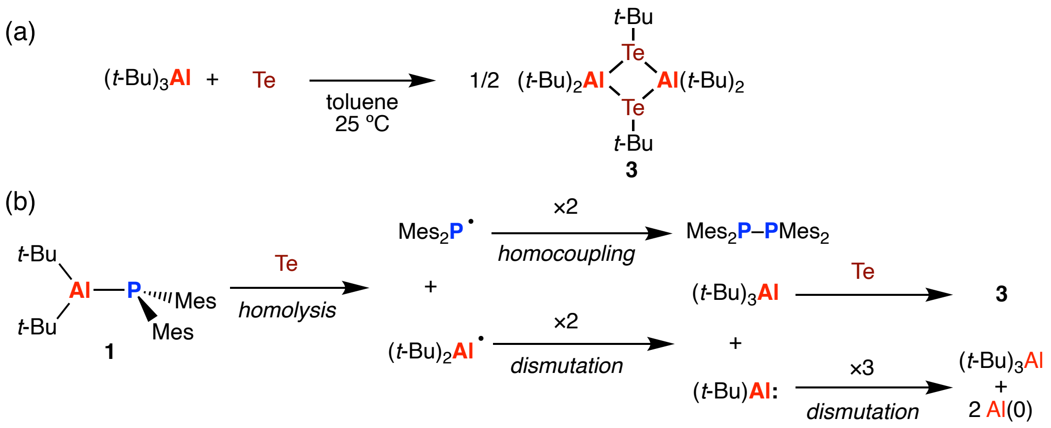
Scheme 2. This work: Chalcogenation reaction of phosphanylalumane **1**



Scheme 3. Reactions of **1** with elemental chalcogens

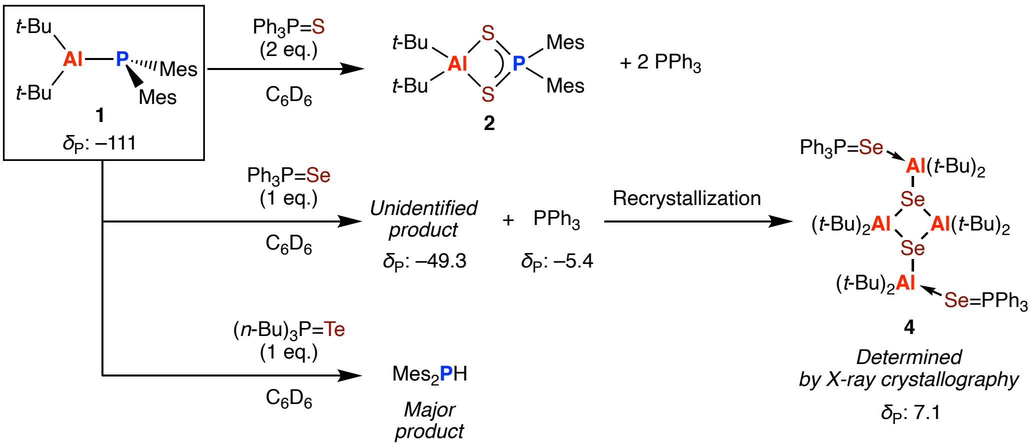
Treatment of **1** with S_8 (1 eq. as S) at room temperature gave a mixture of **1** and the product in a ratio of approximately 1:1. Recrystallization of the mixture from benzene gave **2** (45%) in which two S atoms were inserted into the Al–P bond of **1**. Thus, when the amount of S_8 was increased to two equivalents as S in the reaction of **1**, **2** was formed almost quantitatively (Scheme 3). Single crystals of **2** suitable for

X-ray crystallography were isolated in high yield (83%) by the recrystallization from benzene at room temperature. The detailed reaction mechanism of the reaction is not clear at present, as is the case with the reactions of other B–P compounds with elemental sulfur. Judging from the results of the reactions of the B–P compound (especially **C**) with elemental chalcogens, the insertion of one S atom into the Al–P bond of **1** occurred initially, and the reaction with the second S atom afforded the corresponding phosphine sulfide forming a four-membered ring with intramolecular coordination. In addition, an attempt to desulfurize **2** by adding the electron-rich phosphine [$P(NMe_2)_3$] showed no reaction. When elemental selenium was applied to the chalcogenation instead of S_8, heating at 60 ºC for 3 h afforded four products containing Mes_2PH and $Mes_2P–PMes_2$ as judged by the $^{31}P\{^1H\}$ NMR spectrum. Isolation of the major product from the mixture was not successful. In the case of the reaction with elemental tellurium, the reaction was very slow. When the mixture was heated for a long time (70 ºC, 96 h), $Mes_2P–PMes_2$ was isolated as a major product after the recrystallization of the mixture from hexane. Further treatment of the residual mother liquor gave single crystals of alkylated telluride **3**. Alkylated telluride **3** is known to be derived from the insertion of Te into Al–C bonds of (t-Bu)$_3$Al (Scheme 4a).[4] Therefore, in the case of **1**, the presence of tellurium promoted the homolysis of **1** by a radical mechanism to produce (t-Bu)$_3$Al by the dismutation, which is supported by the formation of $Mes_2P–PMes_2$ by the corresponding homocoupling (Scheme 4b). Phosphanylalumane **1** self-decomposes with prolonged exposure to high temperatures, giving large amounts of Mes_2PH and $Mes_2P–PMes_2$. However, in the presence of elemental Se and Te, the decomposition was promoted by a different mechanism to give different products. As a result, the reaction system became more complicated by elemental Se and Te.



Scheme 4. (a) Synthesis of alkylated telluride **3**[4]; (b) Possible mechanism for the formation of **3** from **1**.

Reactions with elemental selenium and tellurium resulted in the decomposition of **1** probably because of the homolytic cleavage of the Al–P bond. Therefore, the reactions of **1** with phosphine chalcogenides were next investigated as another type of chalcogen sources (Scheme 5).



Scheme 5. Reactions of **1** with phosphine chalcogenides

As a new sulfur source, phosphine sulfide ($Ph_3P=S$) was selected to react with **1**. When **1** (δ_P = –111 ppm) was treated with two equivalents of $Ph_3P=S$ (δ_P = 42.7 ppm) at room temperature, compound **2** (δ_P = 50.2 ppm) and two equivalents of PPh_3 (δ_P = –5.4 ppm) generated. On the other hand, the treatment of **1** with one equivalent of phosphine selenide ($Ph_3P=Se$) (δ_P = 36.0 ppm) showed a clean reaction to give one set of ^{1}H NMR signals corresponding to the substituents. A sharp singlet assignable to PPh_3 (δ_P = –5.4 ppm) and a broadened signal (δ_P = –49.3 ppm), which was not observed in the reaction with the elemental selenium, appeared in the ^{31}P{^{1}H} NMR spectrum. At present, we assume that the insertion of one Se atom into the Al–P bond of **1** occurred. However, recrystallization of the reaction mixture from benzene gave a trace amount of an unexpected compound **4** (δ_P = 7.1 ppm).[5] The reaction of **1** with phosphine telluride [$(n\text{-Bu})_3P=Te$] afforded Mes_2PH as a major product. We assumed that these decompositions are due to the instability of transient reactive products. Although the selenium and tellurium systems did not give expected results even using both elemental chalcogens and phosphine chalcogenides, we demonstrated the chalcogenation reactions of the Al–P single-bond for the first time.

The structure of **2** was elucidated by X-ray crystallography to show two crystallographically independent molecules in the unit cell, which exhibit structural parameters almost identical to each other (Figure 1). The sum of the internal bond angles of their [Al–S–P–S] 4-membered rings were approximately 360º (Molecule A: 359.47º and Molecule B: 359.32º), indicating that the [Al–S–P–S] moiety of **2** is a nearly planar 4-membered ring. To date, such [Al–S–P–S] 4-membered ring has been found only in the distorted-octahedral Al(III) complex [$(Ph_2PS_2)_3Al$] **D** having a hexa-coordinated Al center.[6] Complex **D** was reported to have a delocalized 4-membered [Al–S–P–S] ring consisting of dithiophosphinate ligand $[PS_2]^-$ and a cationic Al moiety. The Al–S bonds of **2** [Molecule A: 2.3466(8), 2.358(1) Å and Molecule B: 2.3499(9), 2.3574(9) Å] were slightly shorter than those of **D** [2.396(3)-2.457(3) Å]. The two P–S bond lengths of **2** [Molecule A: 2.0412(9), 2.0411(8) Å and Molecule B: 2.0428(8), 2.0390(9) Å] were almost identical to each other, slightly longer than those of **D** [1.999(3)-2.019(2) Å], and slightly shorter than that of singly-bonded **C’** [2.1204(11) Å]. These values indicated that the equivalent, multiple-bond character of the two P–S bonds of **2**. Since the bulkiness of the substituents on the P atom has no significant effect on the P–S bond lengths,[7] the difference in the coordination number of the Al atom between **2** and **D** probably resulted in the small change of Al–S and P–S bond lengths.

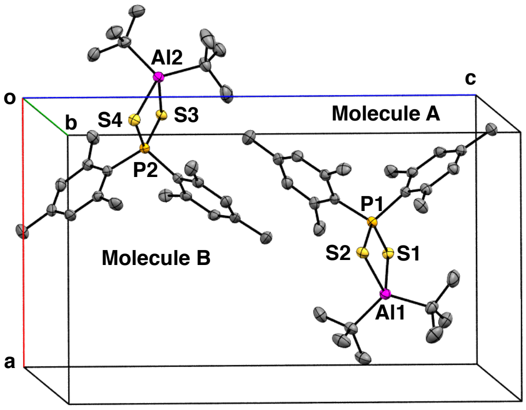
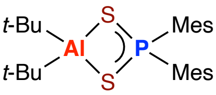
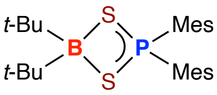
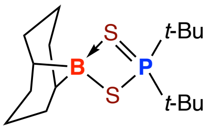
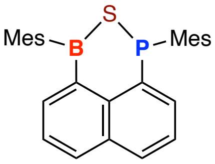


Figure 1. Crystal packing of **2** (thermal ellipsoids at the 50% probability level). Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg.): (Molecule A) P1–S1 2.0412(9), P1–S2 2.0411(8), Al1–S1 2.3466(8), Al1–S2 2.358(1), S2–P1–S1 103.12(3), P1–S1–Al1 85.52(3), S1–Al1–S2 85.62(3), Al1–S2–P1 85.21(3). (Molecule B) P2–S3 2.0428(8), P2–S4 2.0390(9), Al2–S3 2.3499(9), Al2–S4 2.3574(9), S4–P2–S3 103.29(3), P2–S3–Al2 85.24(3), S3–Al2–S4 85.80(3), Al2–S4–P2 84.99(3).

Table 1. Summary of structural and NBO analysis on **2**, **2BP**, **B'**, and **C'**

Compound		 **2**	 **2BP**	 **B'**	 **C'**
P–S/Å	obsd.	2.0412(9), 2.0411(8)[d] 2.0428(8), 2.0390(9)[e]	–	–	2.1204(11)
	calcd.	2.072	2.061	2.046	2.168
E–S/Å[a]	obsd.	2.3466(8), 2.358(1)[d] 2.3499(9), 2.3574(9)[e]	-	-	1.802(4)
	calcd.	2.384	2.099	2.091, 2.093	1.799
WBI (P–S)[b]		1.11	1.09	1.09	0.922
WBI (E–S)[a,b]		0.466	0.805	0.820, 0.822	1.36
Q_E[a,c]		1.70	0.510	0.416	0.530
Q_P[c]		1.22	1.24	1.26	0.762
Q_S[c]		–0.572	–0.269	–0.280, –0.281	–0.142

[a] E = B or Al. [b] WBI: Wiberg bond indices. [c] Q: Natural population analysis (NPA) charge. [d] Molecule A. [e] Molecule B.

We clarified the structural features of the "heavy" 4-membered ring of **2** by theoretical calculations. For comparisons, the hypothetical B-analogue of **2** (**2BP**), and the real model of **B'** (the structure was not reported) and **C'** were also calculated. The DFT calculations at the B3LYP-D3/6-31G(d) level reproduced the experimentally observed structural parameters of **2** and **C'**. The results of theoretical calculations are summarized in Table 1. Although **2** displayed slightly longer P–S bonds than those of **2BP** and **B′** (**2**: 2.072 Å > **2BP**: 2.061 Å and **B'**: 2.046 Å), the Wiberg bond indices (WBIs) (P–S) of **2** was the largest. This character was clearly caused by the introduction of the Al atom instead of the B atom. The natural bond orbitals (NBOs) corresponding to the B–S bonds were found in **2BP**, **B'**, and **C'**. However, the NBOs relevant to Al–S bonds were not found in **2**. Instead, the large values of orbital interactions between the Al atom and the S atoms (Lone pair [S] → Lone vacancy [Al]: 70.3 kcal mol^{-1}) were found in **2** by the second-order perturbation analysis. These results clearly showed that the bonding situation of the Al–S bonds different from those of the B–S bonds. Compound **2** showed a very large Q_E compared to Q_P (Q_E: 1.70 > Q_P: 1.22). On the other hand, in **2BP** and **B′**, Q_P was unexpectedly larger than Q_E (Q_E: 0.510 < Q_P: 1.24 for **2BP**, Q_E: 0.416 < Q_P: 1.26 for **B'**), indicating that their P atoms were more electropositive than B atoms. In addition, the charge of the S atom (Q_S) of **2** showed more negative charge (–0.572) compared to those of **2BP** (–0.269) and **B'** (–0.281). Given above discussion, compound **2** has a large contribution of charge separation between the $[(t\text{-Bu})_2\text{Al}]^+$ and $[\text{Mes}_2\text{PS}_2]^-$ moieties. In other words, $[\text{Mes}_2\text{PS}_2]^-$ can be regarded as a bidentate ligand to sandwich the Al cation. From these inferences, one can expect the use of **2** as the dimesityldithiophosphinate ligand $[\text{Mes}_2\text{PS}_2]^-$. We investigated the transmetallation by the reaction of **2** and *t*-BuLi in the hope of promoting the reaction by the elimination of $(t\text{-Bu})_3\text{Al}$, but the reaction resulted in the cleavage of the P–S bonds to give Mes_2PH.

To conclude, we demonstrated the insertion reaction of sulfur atoms toward Al–P bond of **1**. Two sulfur atoms easily inserted into the Al–P bond to give the corresponding [Al–S–P–S] 4-membered ring compound **2**. Two P–S bonds in **2** are equivalent to each other and shorter than the known P–S single-bond, indicating a slight multiple-bond character. We aim at the functionalization of the dithiophosphinate ligand $[\text{Mes}_2\text{PS}_2]^-$, and clarified that the [Al–S–P–S] ring of **2** consists of the 4-membered ring with charge separation into $[(t\text{-Bu})_2\text{Al}]^+$ and $[\text{Mes}_2\text{PS}_2]^-$. These results were supported by the structural analysis and theoretical calculations. Further efforts to verify the reactivity of **2** and its utilization as a new $[\text{PS}_2]^-$ ligand is now in progress.

EXPERIMENTAL

GENERAL

All the manipulations were performed under a dry argon atmosphere using standard Schlenk techniques or gloveboxes. Solvents were purified by the Ultimate Solvent System, Glass Contour Company (hexane)[7] or by trap-to-trap distillation from a potassium mirror prior to use (C_6D_6). ^{1}H, ^{13}C, ^{27}Al, and ^{31}P NMR spectra were measured on a JEOL JMM-ECA600 (^{1}H: 600 MHz, ^{13}C: 151 MHz, ^{27}Al: 156 MHz, ^{31}P: MHz) in the Joint Usage/Research Center (JURC, Institute for Chemical Research, Kyoto University), on a JEOL AL-300 spectrometer (^{1}H: 300 MHz, ^{13}C: 75 MHz, ^{27}Al: 156 MHz, ^{31}P: MHz), or on a JEOL AL-300 spectrometer. For the ^{1}H NMR spectra, signals arising from residual partially hydrogenated C_6D_5H (7.15 ppm for ^{1}H), C_6D_6 (128.0 ppm for ^{13}C), and $Al(NO_3)_3$ in D_2O (0 ppm for ^{27}Al) were used as references. ^{1}H and ^{13}C NMR signals were assigned with the aids of the ^{1}H-^{1}H COSY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC spectra. Melting points were determined on a Yanaco micro melting point apparatus and uncorrected. Elemental analyses were carried out at the Microanalytical Laboratory, Institute for Chemical Research, Kyoto University. Sulfur (FUJIFILM Wako Pure Chemical Industries, Ltd., Tokyo, Japan) was purified by the recrystallization from benzene in the dark. Phosphine sulfide ($Ph_3P{=}S$),[8] phosphine selenide ($Ph_3P{=}Se$),[9] and phosphine telluride [$(n\text{-Bu})_3P{=}Te$][10] were prepared according to the literatures.

EXPERIMENTAL PROCEDURE

Reaction of 1 with elemental sulfur (1 eq. as S)

In a *J.* Young NMR tube, S_8 (0.9 mg, 0.003 mmol, 1 eq. as S) was added to a solution of **1** (19.9 mg, 0.0274 mmol) in C_6D_6 (0.5 mL) at room temperature. After the removal of solvent, the residual solid was washed with hexane and recrystallized from benzene at room temperature to afford **2** as colorless crystals (5.9 mg, 0.012 mmol, 45%).

Reaction of 1 with elemental sulfur (2 eq. as S)

In a *J.* Young NMR tube, S_8 (3.9 mg, 0.015 mmol, 2.0 eq. as S) was added to a solution of **1** (25.2 mg, 0.0614 mmol) in C_6D_6 (0.5 mL) at room temperature, and the monitored NMR spectra showed the quantitative formation of **2**. The solvent was removed and the residual solid was recrystallized from benzene at room temperature to afford **2** as colorless crystals (24.2 mg, 0.0510 mmol, 83%). **2**: Colorless crystals, mp 147-148 ºC (dec.). ^{1}H NMR (600 MHz, C_6D_6, 298 K): δ = 1.37 (s, 18H, *t*-Bu C$\boldsymbol{H}_3$), 1.85 (s, 6H, Mes *p*-C$\boldsymbol{H}_3$), 2.72 (s, 12H, Mes *o*-C$\boldsymbol{H}_3$), 6.46 (dd, $^4J_{PH}$ = 3.0 Hz, 4H, Mes *m*-$\boldsymbol{H}$) ppm. ^{13}C{^{1}H} NMR (151 MHz, C_6D_6, 298 K): δ = 17.8 (br. s, Al$\boldsymbol{C}$Me$_3$), 20.5 (s, Mes *p*-$\boldsymbol{C}$H$_3$), 23.2 (d, $^3J_{PC}$ = 15.1 Hz, Mes-*o*-$\boldsymbol{C}$H$_3$), 30.3 (s, AlC($\boldsymbol{C}$H$_3$)$_3$), 131.9 (d, $^2J_{PC}$ = 75.5 Hz, Mes *o*-C), 132.6 (d, $^3J_{PC}$ = 12.1 Hz, Mes *m*-***C***), 140.8 (d, $^{1}J_{PC}$ = 12.1 Hz, Mes *ipso*-***C***), 141.3 (d, $^{4}J_{PC}$ = 3.0 Hz, Mes-*p*-***C***) ppm. ^{27}Al{^{1}H} NMR (156 MHz, C_6D_6, 298 K): δ = 163.4 ppm. ^{31}P{^{1}H} NMR (243 MHz, C_6D_6, 298 K): δ = 50.3 ppm. Anal. Calcd for $C_{26}H_{40}AlPS_2$: C, 65.79 H, 8.49. Found: C, 65.97; H, 8.45.

Reaction of 1 with selenium

In a *J.* Young NMR tube, elemental Se (2.5 mg, 0.0316 mmol, 1.0 eq.) was added to a solution of **1** (12.3 mg, 0.0316 mmol) in C_6D_6 (0.6 mL) at room temperature, and the reaction was monitored by NMR spectroscopy. After heating at 60 ºC for 3 h, **1** was completely consumed, and the formation of Mes_2PH (relative intensity: 21), $Mes_2P–PMes_2$ (rel. int.: 11), and two unidentified products (rel. int.: 12 and 56, respectively) was suggested by ^{31}P{^{1}H} NMR spectroscopy. These products could not be separated by the differences in solubility.

Reaction of 1 with tellurium

In a *J.* Young NMR tube, elemental Te (10.1 mg, 0.0792 mmol, 1.0 eq.) was added to a solution of **1** (31.6 mg, 0.0770 mmol) in C_6D_6 (0.6 mL) at room temperature, and the reaction was monitored by NMR spectroscopy. After heating at 70 ºC for 96 h, most of **1** (98%) was consumed. The solvent was removed and the residual solid was extracted with hexane. The recrystallization from hexane at –35 ºC gave the isolation of the major product, $Mes_2P–PMes_2$. The supernatant solution was cooled at –35 ºC to give a trace amount of **3** as colorless crystals suitable for X-ray crystallographic analysis.

Reaction of 1 with two equivalents of Ph_3P=S

In a *J.* Young NMR tube, Ph_3P=S (14.3 mg, 0.0486 mmol, 2.0 eq.) was added to a solution of **1** (10.2 mg, 0.0248 mmol) in C_6D_6 (0.5 mL) at room temperature, and the reaction was monitored by NMR spectroscopy. The formation of **2** and PPh_3 was suggested by ^{31}P{^{1}H} NMR spectroscopy. The separation of **2** and PPh_3 from a mixture was not successful.

Reaction of 1 with Ph_3P=Se

In a *J.* Young NMR tube, Ph_3P=Se (11.4 mg, 0.0334 mmol, 1.0 eq.) was added to a solution of **1** (14.1 mg, 0.0334 mmol) in C_6D_6 (0.5 mL) at room temperature, and the reaction was monitored by NMR spectroscopy. After the removal of solvent, the residue was extracted with hexane. The extract was concentrated under reduced pressure, and the residual materials were recrystallized from benzene at room temperature to afford a trace amount of **4**. The full isolation of **4** from a mixture was not successful.

Reaction of 1 with (n-Bu)$_3$P=Te

In a *J.* Young NMR tube, Ph$_3$P=Te (4.4 mg, 0.0529 mmol, 1.0 eq.) was added to a solution of **1** (21.4 mg, 0.0521 mmol) in C$_6$D$_6$ (0.5 mL) at room temperature, and the reaction was monitored by NMR spectroscopy showing the decomposition of **1** to give Mes$_2$PH as a major product.

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