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# A Novel Reactivity of Phosphanylalumane (>P–AI<): Reversible Addition of a Saturated Interelement Bond to Olefins

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**Abstract:** The reversible addition reactions of olefins with a phosphanylalumane, P–AI single bond species, were investigated. The P–AI bond added to ethylene and relatively small terminal alkenes (propylene and hex-1-ene) at room temperature to give the corresponding alkene-adducts. Heating of the terminal alkene-adducts released the corresponding alkenes and regenerated the P–AI bond, but no release of ethylene was observed even under vacuum conditions. The reactivity of ethylene-adduct as a new saturated  $C_{2}$ -*vicinal* P/AI-based FLP was also investigated. The ethylene-adduct was found to undergo complexation with nitriles to give the corresponding nitrile adducts to the AI center, which retained the ethylene-tether as in the case of the corresponding P/B-based FLP. However, the reactivity of ethylene-adduct toward CO<sub>2</sub> and benzaldehyde differed from that of the P/B-system giving the corresponding adducts.

Reversible behavior (oxidative addition and reductive elimination) of main group element compounds toward small molecules has been emphasized from the viewpoint of alternatives to transition metal complexes.<sup>[1]</sup> Reversible reactions of various main group element compounds with small molecules have been reported so far.<sup>[2]</sup> In the case of olefins, a variety of main group element compounds, such as a distannyne (-Sn=Sn-),<sup>[3]</sup> digermynes (-Ge=Ge-),<sup>[4]</sup> digallenes (\_ Ga=Ga-),<sup>[5]</sup> silvlenes (>Si:),<sup>[6]</sup> germylenes (>Ge:),<sup>[7]</sup> Mg(I) reagents,<sup>[8]</sup> and a diazadiborinine,<sup>[9]</sup> have been known to undergo reversible reactions. Most recently, it has also been found in Al(I) species (Scheme 1a).<sup>[10]</sup> In addition, reversible additions of B/P-FLP to alkene or alkyne are known.<sup>[11]</sup> Thus, the reversible addition/elimination behavior with olefins has currently been limited to low-coordinated species and FLPs. Their electron-deficient moiety (the highly reactive  $\pi^*$  or vacant p orbitals) plays a major role on the interaction with olefins. Especially, the orbital interaction between dimetallynes and ethylene is like the transition metal-ethylene interaction interpreted with the Dewar-Chatt-Duncanson model.<sup>[12]</sup> Taking into account of the synergistic orbital interactions with olefins mentioned above, a direct bond between Lewis acid (LA) and Lewis base (LB) can work similarly (Figure 1b). However, it is easy to imagine that electronic perturbations between LA and LB can inactivate each function. Actually, regarding the addition reaction to olefin, there is no report on >N-B< bond, and only irreversible 1,2-addition reaction of >P–B< bond to a terminal allene by rhodium catalyst is known.<sup>[13]</sup>

On the other hand, phosphanylboranes, >P–B< bond compounds, are known to react with various small molecules, including H<sub>2</sub>, without catalyst due to their weak P→B π interactions.<sup>[13,14]</sup> Based on this background, we made a working hypothesis that >P–AI< single-bond compounds (phosphanyl-alumanes) having a long σ-bond between the third-row elements would show decrease of the π-interaction, acquire effective interaction with olefins, and are suitable for the investigation of the reversible behavior with olefins (Scheme 1b). Thus, further exploration of the reactivity of phosphanylalumanes can develop not only transition metal-mimicking reactivity of main group compounds but also unprecedented small molecule activation by saturated interelement species.



Scheme 1. (a) Examples of reversible addition reactions of ethylene with distannyne and Al(I) compounds. (b) Postulated interaction of LA–LB bond with ethylene.

Furthermore, such alkene conversions are important in forming C–E (E = main group element) bond(s), which will introduce LA (AI) and LB (P) onto the resulting alkanes in the case of phosphanylalumanes. The LA/LB-substituted alkanes will be of worth as new reactive compounds like frustrated Lewis pairs (FLPs). For example, Erker and Stephan *et al.* obtained ethylene-bridged P/B-based FLP **A** by the hydroboration reaction of dimesitylvinylphosphane (Mes<sub>2</sub>PCH=CH<sub>2</sub>) with HB(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub> (Scheme 2).<sup>[15]</sup>

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Scheme 2. Synthesis of P/B-based FLP A by Erker and Stephan et al.

Recently, we have succeeded in the synthesis and isolation of novel phosphanylalumane 1 with carbon-based protecting groups on the P and AI atoms.<sup>[16]</sup> With this new class of stale E-E' bond compounds, phosphanylalumanes, new research for the addition reactions to olefins and the synthesis of reactive species, possibly acting as the saturated P/AI-based intramolecular FLPs, should be opened for discussion. Here, we found the reversible addition reaction to alkenes by the P-AI  $\sigma$ -bond species for the first time (Scheme 3). In other words, the P–Al  $\sigma$ -bond of **1**, an P(III)-Al(III) compound, was weakened by the addition to terminal alkenes (RCH=CH<sub>2</sub>) in the case of the relatively small substituents (R = H, Me, and *n*-Bu) to afford alkene-adducts **2**R, and the P-Al bond of 1 is regenerated by the elimination of the alkenes on heating in the case of R = Me (2Me) and *n*-Bu (2Bu). To ensure the generation of ethylene-adducts 2H, a variety of reactions were also examined.



 $\label{eq:scheme 1} \begin{array}{l} \mbox{Scheme 3. Reversible addition reactions of 1 with alkenes described in this work.} \end{array}$ 

A degassed solution of **1** in  $C_6D_6$  was instantly exposed to an excess amount of ethylene gas (ca. 1 atm) at -196 °C. After warming to room temperature, the pale-yellow solution of **1** turned into colorless within 5 minutes (Scheme 4). The <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR and their two-dimensional NMR spectroscopic studies suggested the formation of the corresponding *cis*-1,2-adduct **2H**. This compound is the first example of a saturated C<sub>2</sub>-bridged P/AI analogue of P/B system **A**.<sup>[15]</sup>

In the <sup>1</sup>H NMR spectrum, the quartet signal corresponding to the P-bound CH<sub>2</sub> moiety of **2H** appeared at 2.78 ppm (q, <sup>2</sup>*J*<sub>PH</sub> = 8 Hz and <sup>3</sup>*J*<sub>HH</sub> = 8 Hz), which is comparable to that of the P/B system **A** [2.87 ppm (q, <sup>2</sup>*J*<sub>PH</sub> = 8 Hz and <sup>3</sup>*J*<sub>HH</sub> = 8 Hz)].<sup>[15]</sup> On the other hand, the double-triplet signal corresponding to the Albound CH<sub>2</sub> moiety of **2H** appeared at 0.99 ppm (dt, <sup>3</sup>*J*<sub>PH</sub> = 36 Hz and <sup>2</sup>*J*<sub>HH</sub> = 16 Hz), which is considerably up-field shifted than that of **A** [2.29 ppm (dt, <sup>3</sup>*J*<sub>PH</sub> = 42 Hz and <sup>2</sup>*J*<sub>HH</sub> = 8 Hz)], reflecting the lower electronegativity of Al than B (Al: 1.47 < B: 2.01).<sup>[17]</sup> In addition, the <sup>31</sup>P{<sup>1</sup>H} NMR signal of **2H** (0.4 ppm) appeared in higher magnetic field than that of **A** (20.6 ppm). This result indicated that the interaction between the P and Al atoms in **2H** was weaker than that between the P and B atoms in **A** due to the elongation of bonds containing the Al atom in **2H**.



Scheme 4. Reaction of 1 with ethylene.

Unfortunately, as with the P/B system **A**, no crystals suitable for X-ray crystallography have been obtained for **2H**. Therefore, the structural optimization for **2H** was performed at the B3LYP-D3/6-31G(d) level of theory. The <sup>31</sup>P NMR chemical shift of the optimized structure was in good agreement with the observed one (Figure S34, Table S3), suggesting that the DFT-optimized structure (gas phase) is well matched to that in solution. The optimized P····Al distance (2.663 Å) was much longer compared to that of **1** (2.348 Å) and the sum of the covalent bond radii ( $r_{AI}$ +  $r_{P}$  = 2.37 Å),<sup>[18]</sup> and the natural bond orbital corresponding to the P–Al  $\sigma$ -bond was not found (Table S4). Therefore, the P–AI  $\sigma$ -bond of **1** seems to be weakened by addition to ethylene.



Figure 1. Scope of alkenes. [a] Estimated by  $^1H$  and  $^{31}P\{^1H\}$  NMR measurement of the reaction mixture (in %). [b] Isolated yield.

Next, the scope of alkenes was examined, and the results are summarized in Figure 1. The reaction of 1 with propylene was not completed within 5 min even with the exposure to an excess amount of propylene gas (ca. 1 atm), unlike ethylene case. NMR spectra after 24 h at room temperature showed the formation of propylene-adduct 2Me (65%) and the partial decomposition (probably hydrolysis) of 1, giving Mes<sub>2</sub>PH (30%). Therefore, 2Me could not be isolated by any means. In the case of hex-1-ene, the reaction was slow even in the presence of an excess amount of hex-1-ene. The ratio of 1 to hex-1-ene-adduct 2Bu reached a static state (about 4:1) after leaving it for several days. Further investigation revealed that the static state was attained 21 hours after the treatment of 1 with two equivalents of hex-1-ene at room temperature. This result suggests the reversibility of the reactions at room temperature (Table S1, Figure S1). When more amount of the alkene was used (e.g., neat condition of hex-1-ene), only the decomposition giving Mes<sub>2</sub>PH was promoted. Terminal alkenes having a relatively large substituent and internal alkenes were found to be unreactive.

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The position of methyl substituent of 2Me was determined by the measurement of <sup>1</sup>H, <sup>1</sup>H{<sup>31</sup>P}, and <sup>1</sup>H-<sup>1</sup>H COSY NMR spectra (Figures S10-S12). The relatively large coupling (16.8 Hz) was observed between the methyl protons and the P atom, strongly suggesting that the methyl group should be placed on the C atom adjacent to the P atom  $({}^{3}J_{HP})$ . In this model, the  ${}^{2}J_{HP}$  of the methine proton (<8 Hz) was smaller than the  ${}^{3}J_{HP}$  of the methylene proton (61 Hz), showing the tendency same as 2H and A. Although the low occurrence of 2Bu relative to the 1 and hex-1-ene prevented complete assignment of the protons, the <sup>31</sup>P NMR chemical shift (15.9 ppm) and the  ${}^{3}J_{PH}$  value (63 Hz) of 2Bu were quite similar to those of 2Me (16.4 ppm and 61 Hz, respectively), suggesting that hex-1ene added to 1 in the direction same as 2Me. Therefore, the alkyl-substituted C atom of terminal alkenes selectivity connected to the P atom of 1, due to its small electron density.

No elimination of ethylene from **2H** was observed even on heating up to 105 °C in the solid state under high vacuum condition (<10<sup>-1</sup> Pa) or in a toluene solution. When a  $C_6D_6$  solution of **2Me** was heated at 60 °C for 1.5 h, the <sup>1</sup>H NMR signals corresponding to **2Me** disappeared and the signals for **1** and propylene were observed. Similarly, heating of the reaction mixture containing **2Bu** at 50 °C for 1.5 h resulted in the disappearance of **2Bu** and the increasing of **1** and hex-1-ene.



Scheme 5. Calculated reaction pathways for the reactions of 1 with alkenes. Relative Gibbs energies ( $\Delta G$  in kcal mol<sup>-1</sup>) were calculated at the TPSSTPSS-D3/6-311+G(2d,p)<AI,P>,6-31G(d,p)<C,H>//B3LYP-D3/6-31G(d) level of theory, and are shown in parentheses.

We estimated the energy profile for the reactions of **1** with alkenes by theoretical calculations to investigate the reversible behavior. Scheme 5 shows the calculated reaction pathways for the addition of alkenes (ethylene, propylene, and hex-1-ene) to **1** with the values of relative energies. The reactions should proceed via the interaction with the 3p(Al) orbital of **1** and the  $\pi$  orbital of the alkene to form the  $\pi$ -complex intermediate (**INT3**),<sup>[19]</sup> and then pass through the transition state **TS4**. This *syn*-type addition differs from *anti*-addition proposed in the B/P

intermolecular FLPs.<sup>[20]</sup> Ethylene-adduct **2H** was found to be extremely more stable than other thermodynamically unfavourable alkene-adducts (**2Me** and **2Bu**) (**2H**: -72.1 kcal mol<sup>-1</sup> < **2Me**: 2.2 kcal mol<sup>-1</sup> and **2Bu**: 2.9 kcal mol<sup>-1</sup>). Correspondingly, the barrier for alkene elimination (**2R**→**TS4**) was the largest for the case of **2H** (**2H**: 23.2 kcal mol<sup>-1</sup> > **2Me**: 20.1 kcal mol<sup>-1</sup> and **2Bu**: 19.9 kcal mol<sup>-1</sup>). These results well explained the experimental results that the alkene was eliminated on heating in the cases of **2Me** and **2Bu**.

Since crystals suitable for X-ray crystallographic analysis have not been obtained for ethylene-adduct **2H** at this stage, capturing of **2H** by further reactions was attempted. In the P/B system **A**, pivalonitrile is known to act as a LB to give nitrileadduct.<sup>[21]</sup> Similarly, the reaction of P/AI system **2H** with pivalonitrile gave the corresponding nitrile-adduct **5Bu** as judged by NMR spectroscopy (Scheme 6a). However, **5Bu** was an oily product, and hence it was difficult to isolate and obtain single crystals suitable for X-ray crystallographic analysis. The use of benzonitrile instead of pivalonitrile afforded **5Ph** as a crystalline compound, and the structural analysis revealed the retainment of the ethylene bridge (Scheme 6b).<sup>[22]</sup> This result clearly supports the structure of **2H**.



Scheme 6. (a) Nitrile-coordination to 2H to give the corresponding adduct 5. (b) Thermal ellipsoid plot (50% probability) of 5Ph. Hydrogen atoms and solvent molecules are omitted for clarity.

P/B system A is known to bind CO<sub>2</sub> in the presence of an excess amount of CO2 to give CO2-adduct under -20 °C, and it liberates CO2 above -20 °C in CH2CI2, regenerating A.[23] In addition, the groups of Uhl and Lammertsma have successfully captured CO2 using C1-geminal P/AI-FLP at room temperature.<sup>[24]</sup> Binding of CO<sub>2</sub> is useful in terms of CO<sub>2</sub> reduction, and intermolecular P/AI-FLP based CO<sub>2</sub> capture and stoichiometric reduction have been reported by Stephan et al.[25] However, we found that the reactivity of 2H with CO<sub>2</sub> was completely different from those of **A** and C<sub>1</sub>-geminal P/AI-FLP. The exposure of **2H** to a CO<sub>2</sub> atmosphere afforded compound **6**<sub>2</sub>. In this case, contrary to our expectation, CO<sub>2</sub>-trapping product 7 was not obtained. Compound 62 was the dimeric form of the CO2inserted product into the P-Al bond of 1. (Scheme 7). Compound  $6_2$  can be obtained directly by exposing 1 to a CO<sub>2</sub> atmosphere. The CO<sub>2</sub> insertion into the P-Al bond of **1** was much faster than the previously reported insertion in the case of (Me<sub>3</sub>Si)<sub>2</sub>P-Al(tmp)<sub>2</sub> (tmp = 2,2,6,6-tetramethylpiperidino).<sup>[26]</sup>

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Scheme 8. Calculated reaction mechanisms for the reaction of 2H with CO<sub>2</sub> and ethylene-release from 2H (a) and the reaction of 1 with CO<sub>2</sub> (b). Relative Gibbs free energies ( $\Delta G$  in kcal mol<sup>-1</sup>) were calculated at the B3LYP-D3/6-31G(d) level of theory and are shown in parentheses.



Scheme 7. Reactions of  $CO_2$  with 1 and 2H. [a] One step from 1. [b] Two steps via 2H.

The structure of **6**<sub>2</sub> was established by X-ray crystallography to confirm the dimeric, 8-membered ring form in the solid state, in which the two Al atoms were bridged with a phosphanyl-carbonate ligand (Mes<sub>2</sub>PCO<sub>2</sub>)<sup>-</sup> (Figure S32).<sup>[22]</sup> The (Mes<sub>2</sub>PCO<sub>2</sub>)<sup>-</sup> acts as the bidentate chelating ligand sandwiching the (*t*-Bu)<sub>2</sub>Al cation, [(*t*-Bu)<sub>2</sub>Al]<sup>+</sup>.

The factors of ethylene elimination were clarified by theoretical calculations (Scheme 8, Figure S35). The barrier to release ethylene from **2H** ( $\Delta\Delta G^{\pm} = 25.5$  kcal mol<sup>-1</sup>: **2H** $\rightarrow$ **TS4H**) was larger than that of the reaction of **2H** with CO<sub>2</sub> giving the corresponding CO<sub>2</sub> adduct **9** via **INT8** and **TS9** ( $\Delta\Delta G^{\pm} = 7.4$  kcal mol<sup>-1</sup>: **2H** $\rightarrow$ **TS9**). The release of ethylene from **7** was found to proceed with the barrier ( $\Delta\Delta G^{\pm} = 17.8$  kcal mol<sup>-1</sup>: **7** $\rightarrow$ **TS10**) lower than that in the case of **2H**. Therefore, ethylene is eliminated not from **2H** directly, but from **7**. The barrier for the reaction of **2H** with CO<sub>2</sub> ( $\Delta\Delta G^{\pm} = 7.4$  kcal mol<sup>-1</sup>: **2H** $\rightarrow$ **TS9**) did not differ greatly

from that for the reaction of **1** with  $CO_2 (\Delta \Delta G^{\ddagger} = 7.1 \text{ kcal mol}^{-1}: 1 \rightarrow TS12)$ .



Scheme 9. (a) Reactions of phenylacetylene with 1 and 2H. (b) Reactions of diphenylacetylene with 1 and 2H. [a] Judged by NMR spectra. [b] Ref. 28.

Similar elimination of ethylene from **2H** is also observed in the case of the reaction with phenylacetylene.<sup>[27]</sup> When **2H** was treated with phenylacetylene, **2H** was quantitatively converted into Mes<sub>2</sub>PH and [PhC=CAl(*t*-Bu)<sub>2</sub>]<sub>2</sub> in accompany with the elimination of ethylene (Scheme 9). This is the same combination of products for the reaction of **1** with phenylacetylene.<sup>[28]</sup> Considering the results of theoretical calculations for the reaction of **2H** with CO<sub>2</sub>, the reaction of **2H** 

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with phenylacetylene passed through the intermediate **INT13**, leading to the elimination of ethylene to give Mes<sub>2</sub>PH and [PhC=CAl(*t*-Bu)<sub>2</sub>]<sub>2</sub>. On the other hand, **1** and **2H** showed different reactivity toward diphenylacetylene (Scheme 9b). Phosphanyl-alumane **1** underwent *cis*-addition to diphenylacetylene under heating conditions to give **14**,<sup>[28]</sup> whereas **2H** did not react with diphenylacetylene under heating.

These experimental and theoretical results suggested that the addition reactions of 1 with  $CO_2$  and phenylacetylene should pass through characteristic ethylene-bridged intermediates, 7 and **INT13**, respectively. Therefore, we expected that the transformation of small molecules, which could not be achieved by 1 due to the decomposition or no reactivity, could be achieved by using **2H**.



Scheme 10. (a) Reactions of 1 and 2H with benzaldehyde. (b) Plausible mechanism for the generation of 15 and 16.

While benzaldehyde is also known to form the cyclic adducts with the P/B-system  $A^{[21]}$  and  $C_1$ -geminal P/AI-system,<sup>[29]</sup> the reaction of **1** with benzaldehyde afforded a complicated mixture probably via the generation of a radical species arisen from the carbonyl moiety (Scheme 10a, top). On the other hand, a  $C_6D_6$  solution of **2H** was treated with an excess amount of benzaldehyde to give one set of signals corresponding to *t*·Bu moieties (Scheme 10a, bottom). X-Ray crystallographic analysis revealed the formation of benzyloxy(di-*t*-Bu)aluminum dimer **15** (Figure S33).<sup>[22]</sup> The corresponding P-containing moieties turned into acylphosphine **16**<sup>[30]</sup> as a major product. The reaction mechanism can be explained as an intramolecular Tishchenko-type reaction (Scheme 10b).<sup>[31]</sup>

Reaction of **2H** with benzaldehyde gave a cyclic intermediate **17**, which is similar to the intermediate **7** postulated in the reaction with  $CO_2$ . Elimination of ethylene from **17** was accompanied by the addition of further benzaldehyde to give the cyclic product **19**. Intramolecular 1,3-hydride shift formed **15** and

**16**. As the result, two molecules of benzaldehyde were converted into two different products. In our system, the AI moiety of **2H** can be greatly involved in the capture of the oxygen atoms of benzaldehyde as a LA.

To conclude, we found the reversible addition reactions of olefins with phosphanylalumane 1 as the first case for singlebond compounds of main group elements. Although the substrate scopes of alkenes are limited to terminal alkenes (R-CH=CH<sub>2</sub>) having relatively small substituents (R = H, Me, and n-Bu), the corresponding alkene-adducts 2 were obtained. In the case of R = Me and n-Bu, the P-AI bond of the alkene-adducts (2Me and 2Bu) was recombined in accompany with the liberation of corresponding alkene on heating. On the other hand, ethylene was not liberated from 2H even under heating conditions. We demonstrated the reactivity of 2H as a new C2-vicinal P/AI-based FLP. In the reaction of 2H with nitriles, nitriles were coordinated to AI as linear LBs, bringing the retention of ethylene-bridge like the case of P/B-system. However, reactions of 2H with CO<sub>2</sub>, phenylacetylene, and benzaldehyde gave characteristic products that involved elimination of ethylene from the initial intermediates.

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#### **Conflict of interest**

The authors declare no conflict of interest.

**Keywords:** addition reaction • aluminum • olefin • phosphanylalumane • reversible behavior

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Phosphanylalumane (P–Al single-bond compound) was reacted with relatively small terminal olefins (ethylene, propylene, and hex-1-ene) at room temperature. Heating of propylene- and hex-1-ene-adducts gave the regeneration of the P–Al bond with liberation the corresponding olefins. An unprecedented reactivity of the ethylene-adduct with the release of ethylene was demonstrated, in sharp contrast to the conventional P/Bsystem.

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