EurJIC
European Journal of Inorganic Chemistry

Research Article
doi.org/10.1002/ejic.202500165

Chemistry Europe
European Chemical Societies Publishing

www.eurjic.org

Stabilities and Limitations in the Reactivity of Phosphorus Ylide-Based Aluminum– and Gallium–Carbon Ambiphiles: A Combined Experimental and Computational Approach

Felix Krämer, Pascal Weisenburger, Israel Fernández,* and Frank Breher*

The unexpected reactivity and stability limits of phosphorus ylide-based aluminum– and gallium–carbon ambiphiles are described. While the previously published *t*-butyl-substituted compound (2-{Al*t*Bu$_2$}-C$_6$H$_4$)Ph$_2$PCMe$_2$ (**1^{tBu}**) reacts reversibly with NH$_3$ at room temperature (RT) with cleavage of a N—H bond, the reaction with MeNH$_2$ is much less favorable and proceeds irreversibly only at 90 °C. All other title compounds **1^{R}** with R = Me, Et, Mes, and C$_6$F$_5$ decompose in the presence of NH$_3$. The decomposition of **1^{Et}** in the presence of ammonia can be well followed by nuclear magnetic resonance (NMR) spectroscopy. All title compounds remain stable in the presence of *t*-BuNH$_2$ and Et$_2$NH. In addition, an unexpected reactivity is found in the reaction of **1^{R}** and the gallium analogues **2^{R}** with isocyanates. Instead of yielding the expected ring-expansion products, the title compounds catalyze the trimerization of isocyanates. Also the reactivity toward MeOH and H$_2$O is presented. Quantum chemical calculations show that activation of the O—H bonds should be feasible at RT. Experimental findings, however, only show the decomposition of **1^{tBu}** in the corresponding reactions. Nevertheless, the cleavage of the O—H bond is feasible and affords the activation products **7** and **8** starting from the ammonia activation product **3**.

1. Introduction

Frustrated Lewis pairs (FLPs) have gained increasing attention over the last few years.[1] While the initial systems consist of boron-containing Lewis acids, a number of aluminum-based FLPs have been described in recent years.[2] In addition to a variety of small molecule activation reactions, mostly leading to the formation of stable adducts, Al-based FLPs have been used in some catalytic transformations such as the activation of C—F bonds,[3] dimerization of alkynes,[4] hydrogenation of unsaturated C—C[5] and C—N[6] bonds, dehydrogenation of aminoborane,[7] transfer of ammonia,[8] CO_2 reduction,[9] and as initiators of polymerization reactions.[10]

Clear limits regarding the stability or reactivity of such systems are much more difficult to find in the literature. In the field of small molecule activation, it is common practice to investigate the reactivity of a potentially reactive molecule with a broad range of substrates. However, only successful reactions or those that yield "publishable" results are typically reported. Consequently, questions regarding the limitations and scope of these transformations often remain open. Do certain systems not react with certain substrates or has this never been attempted? Do some systems catalyze certain reactions, but with less activity than systems known from literature? These are questions that often remain unanswered when searching for literature reports to classify the reactivity of your own compounds. The readership will surely agree with us that a large proportion of experimentally produced scientific results probably disappear into laboratory journals and shelves, never to be considered again. However, we can learn a lot from "failed" reactions or reactions that produce unexpected results.

Another driving force to publish failed experiments, catalyst studies with low activity or reactions with low yields is the growing importance of machine learning in science and also in preparative chemistry.[11] Glorius and co-workers showed, for example, that the use of data from experiments with low output significantly increases the predictive performance of data-driven models.[12] However, it is independent of whether we want to analyze data with a computer-based prediction model or with the human mind. Whatever observations (i.e., whichever data points) are helpful for an artificial or natural intelligence to better understand the underlying relationships to make more meaningful predictions.[13]

With this in mind, we hereby present the results of our detailed investigation of the reactivity and stability of our recently published phosphorus ylide-based aluminum– and gallium–carbon ambiphiles entitled aluminum- and gallium-carbon ambiphiles entitled (*o*-AlCPs and *o*-GaCPs): (2-{ER$_2$}-C$_6$H$_4$)Ph$_2$PCMe$_2$ (E = Al and R = Me (**1^{Me}**), Et (**1^{Et}**), *t*-Bu (**1^{tBu}**), Mes (**1^{Mes}**), and C$_6$F$_5$ (**1^{C6F5}**); E = Ga and R = Et (**2^{Et}**), *t*-Bu (**2^{tBu}**), and C$_6$F$_5$ (**2^{C6F5}**)).

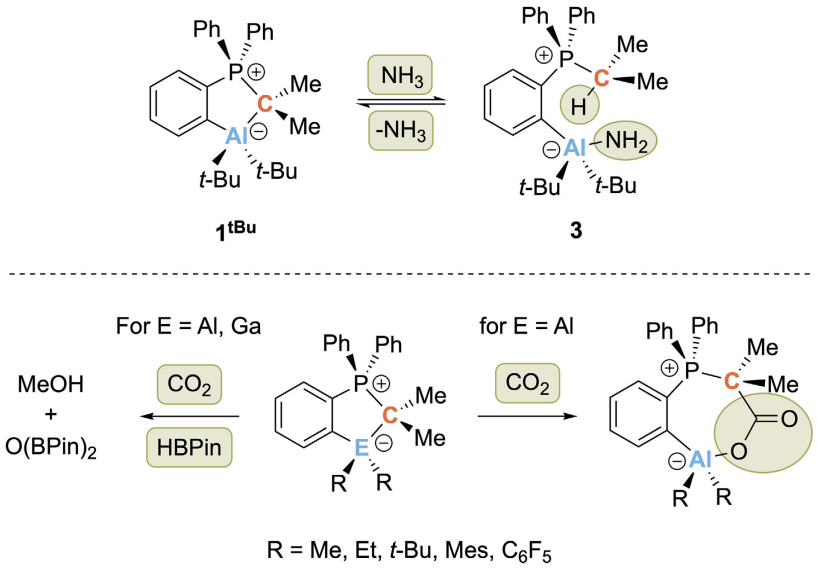
F. Krämer, P. Weisenburger, F. Breher
Institute of Inorganic Chemistry
Karlsruhe Institute of Technology (KIT)
Engesserstraße 15, 76131 Karlsruhe, Germany
E-mail: breher@kit.edu

I. Fernández
Departamento de Química Orgánica I
Facultad de Ciencias Químicas and Centro de Innovación en Química Avanzada (ORFEO-CINQA)
Universidad Complutense de Madrid
28040 Madrid, Spain
E-mail: israel@quim.ucm.es

Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejic.202500165

Research Article
doi.org/10.1002/ejic.202500165

Chemistry Europe
European Chemical Societies Publishing



Scheme 1. Reactivity of the aluminum– and gallium–carbon ambiphiles $\mathbf{1}^{R}$ and $\mathbf{2}^{R}$ toward ammonia and CO_2. R = Me, Et, *t*-Bu, Mes, and C_6F_5.

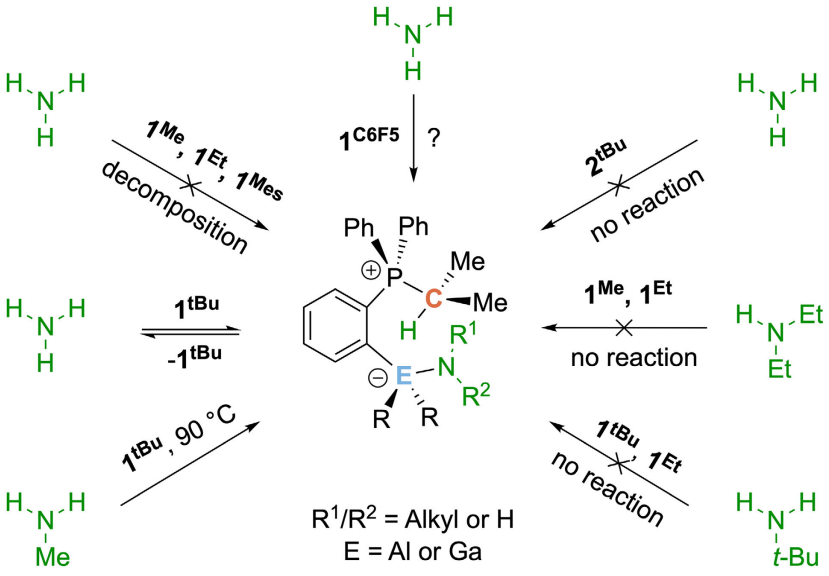
We were able to use these successfully in the activation and catalytic transfer of ammonia as well as in the catalytic reduction of CO_2 to methanol (**Scheme 1**).[8,9] Due to the low stability of $\mathbf{2}^{Et}$ under ambient conditions (decomposition within a few days at room temperature under argon), this species was not included in the reactivity studies so far.

2. Results and Discussion

2.1. Reactions Toward NH_3 and Amines

To investigate whether $\mathbf{1}^{tBu}$ also reacts with primary amines by cleaving a N—H bond, the title compound was mixed with $MeNH_2$ and *t*-$BuNH_2$, respectively, in benzene-d_6 on NMR tube scale (**Scheme 2**). No reaction was observed with the sterically demanding *t*-$BuNH_2$, even after several days of heating at 90 °C. With $MeNH_2$, $\mathbf{1}^{tBu}$ reacts very slowly with cleavage of one N—H bond. After 3 days of heating to 60 °C, hardly any reaction is recognizable. After a further 10 days of heating to 90 °C, the reaction was complete.

The more drastic reaction conditions compared to the reaction with ammonia are most likely due to the higher steric pressure in the transition state leading to a significantly higher reaction barrier. Indeed, our calculations (at the PCM-M062X/def2-TZVPP//PCM-M062X/def2-SVP level) confirm that the barrier associated with the key initial step involving $\mathbf{1}^{tBu}$ (i.e., addition of the nucleophile to the Al center with concomitant Al—C ring-opening) dramatically increases from NH_3 to *t*-$BuNH_2$ ($\Delta G^{\neq} = 24.2$ kcal mol^{-1} < 39.4 kcal mol^{-1}, respectively, **Figure 1**)



Scheme 2. Reactivity of $\mathbf{1}^{R}$ and $\mathbf{2}^{R}$ toward amines.

Research Article
doi.org/10.1002/ejic.202500165

Chemistry Europe
European Chemical Societies Publishing

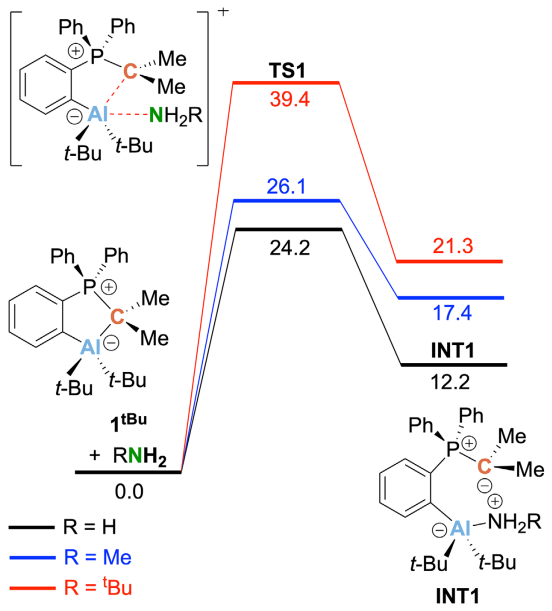


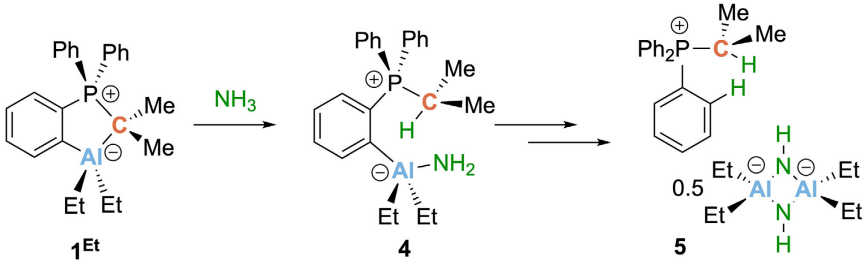
Figure 1. Computed reaction profile for the key addition of NH_3, $MeNH_2$, and *t*-$BuNH_2$ to $\mathbf{1}^{tBu}$. Relative free energies (ΔG, at 298 K) are given in kcal mol^{-1}. All data have been computed at the PCM-M06-2X/def2-TZVPP// PCM-M06-2X/def2-SVP level.

and the process becomes much more endergonic ($\Delta\Delta G_R = 9.1$ kcal mol^{-1}), which is consistent with the lack of reactivity observed in the process involving *t*-$BuNH_2$. At variance, the barrier computed for the analogous process involving $MeNH_2$ ($\Delta G^{\neq} = 26.1$ kcal mol^{-1}) indicates that this process should be feasible. However, as compared to the process involving NH_3, the reaction is clearly much more endergonic ($\Delta\Delta G_R = 5.2$ kcal mol^{-1}), which might be the reason behind the need for the required more drastic conditions for the reaction to occur.

On this basis, the reactivity of the other *o*-AlCPs and *o*-GaCPs toward NH_3 and the primary amines $MeNH_2$ and *t*–$BuNH_2$ was investigated (Scheme 2). For this purpose, solutions of $\mathbf{1}^{R}$ or $\mathbf{2}^{R}$ were degassed in benzene-d_6 and then gassed with NH_3 (1.1 bar). The reaction of $\mathbf{1}^{Me}$ and $\mathbf{1}^{Mes}$ in benzene-d_6 with NH_3 yielded only decomposition products as detected by NMR spectroscopy. And, $\mathbf{1}^{C6F5}$, which is substituted with electron-withdrawing C_6F_5 groups, reacted with ammonia to form a colorless solid, which was found to be insoluble in benzene-d_6, CH_2Cl_2, and THF. Only the decomposition product Ph_3P could be detected in solution. With $MeNH_2$ and *t*-$BuNH_2$, all other title compounds remain stable and unreacted according to the ^1H NMR spectra. The *o*-GaCP $\mathbf{2}^{tBu}$ showed even higher stability and no reactivity toward primary amines and NH_3.

Our density-functional theory (DFT) calculations of the reaction involving the ethyl-substituted *o*-AlCP $\mathbf{1}^{Et}$ with NH_3 show a rather similar profile to that computed for $\mathbf{1}^{tBu}$ (see previous sections). In this particular case, the activation barrier of the initial key step reaction is, as expected based on steric grounds, 6.2 kcal mol^{-1} lower than the analogous process involving $\mathbf{1}^{tBu}$ and the formation of corresponding reaction product **4** is only slightly endergonic ($\Delta G_R = 2.3$ kcal mol^{-1}), therefore suggesting a similar reversible reaction. Despite that, the investigation of the reaction of $\mathbf{1}^{Et}$ with NH_3 in solution using ^1H and ^{31}P NMR spectroscopy shows that although **4** is indeed formed (**Scheme 3**), it does not appear to be stable. When vacuum is applied or the reaction mixture is left to stand for 2 days, decomposition is observed. The observations of the reaction on a preparative scale also support this thesis. Initially, the reaction mixture turns orange when gassed with ammonia and a colorless solid is formed. Within 2 days, the mixture discolors completely. One can only speculate as to whether and how exactly the reaction product (**5**) depicted in Scheme 3 is formed. We assume a proton shift from the NH_2 to the phenyl moiety providing $[Ph_3PCHMe_2]^+$ and 0.5 equivalents of the dimer $[Et_2AlNH]_2^{2-}$.

In the ^1H NMR spectra of the reaction of $\mathbf{1}^{Et}$ with ammonia (**Figure 2**A–D), the decomposition after the formation of **4** can be easily traced. Plot B, i.e., the ^1H NMR spectrum after gassing $\mathbf{1}^{Et}$ with NH_3, shows that the desired product **4** is formed. The doublet for the methyl groups on the ylidic carbon atom (label CMe_2) at $\delta_{1H} = 1.5$ ppm disappears and a new signal with a chemical shift of $\delta_{1H} = 0.87$ ppm is formed (label $CHMe_2$). The splitting pattern (doublet of doublet with $^1J_{PH} = 16.9$ Hz and $^1J_{HH} = 7.1$ Hz) is very similar to the signal in **3** and suggests protonation of the ylidic carbon atom.[8] Unlike in compound **3**, a septet of small intensity was detected at $\delta_{1H} = 2.3$ ppm, which can be assigned to the proton at C_{ylide} (label $CHMe_2$). The subsequent formation of a new species can be clearly seen in plot C, which was measured after applying vacuum and redissolving the crude product in benzene-d_6. After 1 day, spectra were recorded again and the ^1H NMR spectrum D was obtained. This shows the complete decomposition of **4**, not regenerating the initial reactant $\mathbf{1}^{Et}$, as expected due to the computed reversible nature of the reaction, but providing the phosphonium salt **5**. The characteristic chemical shifts of the observed signals at $\delta_{1H} = 1.00$ ppm (dd, $^1J_{PH} = 16.6$ Hz and $^1J_{HH} = 7.1$ Hz) and $\delta_{1H} = 2.61$ ppm (sept, $^1J_{HH} = 7.1$ Hz) confirm these findings. These are supported by the characteristic signals of the aromatic protons for a Ph_3P



Scheme 3. Possible decomposition of **4** to product **5**.

Research Article
doi.org/10.1002/ejic.202500165

Chemistry Europe
European Chemical Societies Publishing

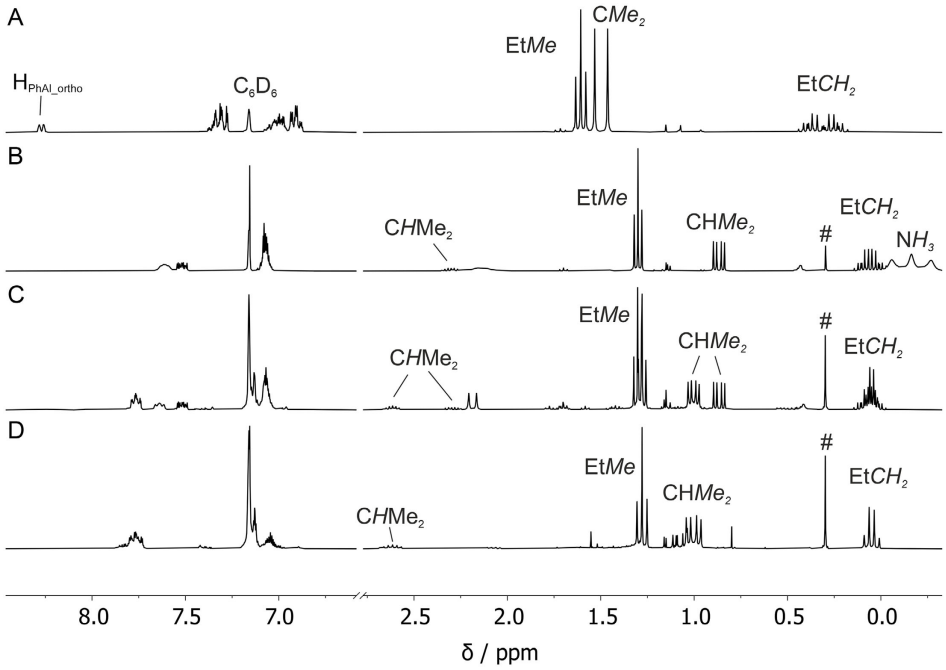
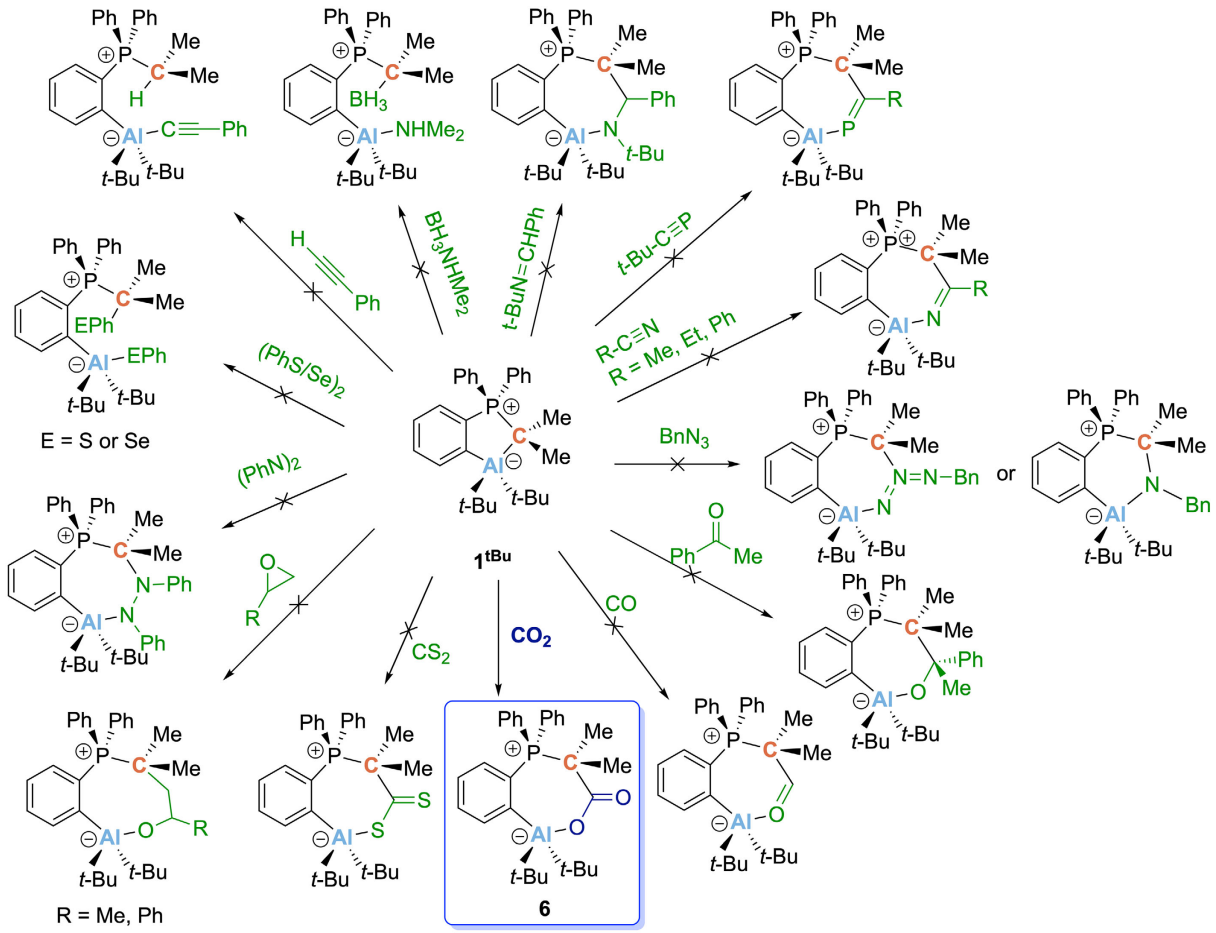


Figure 2. ^{1}H NMR spectra of the reaction of $\mathbf{1}^{Et}$ with NH_3 in C_6D_6. A) ^{1}H NMR spectrum of $\mathbf{1}^{Et}$; B) ^{1}H NMR spectrum after gassing $\mathbf{1}^{Et}$ with NH_3; C) ^{1}H NMR spectrum after applying vacuum and redissolving in C_6D_6; and D) ^{1}H NMR spectrum C measured again after 1 day. #: silicone grease.



Scheme 4. Possible reaction products of substrates that showed no reaction with $\mathbf{1}^{tBu}$ in benzene-d_6 at 90 °C.

Research Article
doi.org/10.1002/ejic.202500165

Chemistry Europe
European Chemical Societies Publishing

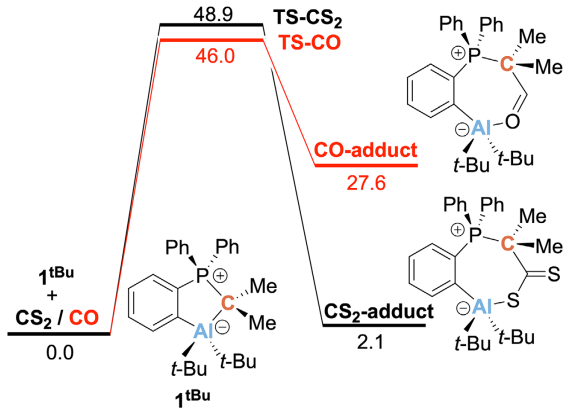


Figure 3. Computed reaction profile for the reactions of $\mathbf{1}^{tBu}$ with CS_2 (black lines) and CO (red lines). Relative free energies (ΔG, at 298 K) are given in kcal mol^{-1}. All data have been computed at the PCM-M06-2X/def2-TZVPP//PCM-M06-2X/def2-SVP level.

fragment and the disappearance of the signal for the *ortho*-Ph proton (label H_{PhAl_ortho}). The course of the reaction can also be followed in the $^{31}P\{^1H\}$ NMR spectra (see Figure S5, Supporting Information).

A similar reactivity was observed in the reaction of $\mathbf{1}^{Et}$ with $MeNH_2$. However, the decomposition is less selective, and three species are formed. No reaction can be detected in the ^1H and ^{31}P NMR spectra with the sterically demanding *t*-BuNH_2. To avoid decomposition by protonation of the phenyl ring, an attempt was made to react $\mathbf{1}^{Et}$ with the secondary amine Et_2NH. The increased steric bulk of the ethyl groups compared to NH_3 makes coordination to the aluminum atom more difficult and no reaction takes place.

2.2. Reactivity Toward Element—Element (Multiple) Bonds

As previously reported, we found that $\mathbf{1}^{tBu}$ and its methyl and ethyl and mesityl counterparts readily react with CO_2 to afford the corresponding CO_2 adduct **6** (Scheme 1 and **4**).[9a] The process occurs in a concerted manner with a computed barrier of ≈36 kcal mol^{-1}, which is compatible with the harsh reaction conditions used experimentally (typically heating at 90 °C for 4–17 days). To further investigate the reactivity of *o*-AlCPs, $\mathbf{1}^{tBu}$ was reacted with related small molecules providing element—carbon or element—element single or multiple bonds.

For instance, the reactions with CS_2 and CO were fruitless even when heated at 90 °C during prolonged reaction times. This is consistent with our calculations, which indicate unfeasible barriers for both concerted processes ($\Delta G^{\neq}$ = 48.9 and 46.1 kcal mol^{-1}, respectively, **Figure 3**). In addition, the reactions become endergonic (ΔG_R = 2.1 and 27.6 kcal mol^{-1}, respectively), which sharply contrasts with the high exergonicity computed for the analogous process involving CO_2 (ΔG_R = −13.2 kcal mol^{-1}). These results therefore suggest that compounds $\mathbf{1}^{R}$ are reluctant to react with weaker nucleophiles, which is also confirmed by the unsuccessful reactions involving acetophenone, epoxides, and alkynes (Scheme 4).

We then moved to related unsaturated systems having a nucleophilic center (i.e., a lone pair of electrons) in their structures. Thus, we attempted the reactions of $\mathbf{1}^{tBu}$ with nitriles R—C≡N (R = Me, Et, Ph), the phosphaalkyne *t*-Bu—C≡P, azobenzene, *t*-BuN = C(H)Ph, and BzN_3. Unfortunately, $\mathbf{1}^{tBu}$ showed no reactivity with all these substrates in benzene-d_6, even when heated to 90 °C.

We also computed the parent process involving acetonitrile and found, not surprisingly, that the reaction occurs stepwise where the initial step is associated with the Al—N≡C—Me adduct formation with concomitant Al—C ring-opening, which is followed by a ring-closure involving the formation of the new C_{ylide}—C(nitrile) bond (**Figure 4**). From the computed free energy value shown in Figure 4, it becomes clear that, although the transformation seems kinetically feasible ($\Delta G^{\neq}$ = 32.6 kcal mol^{-1}), the endergonicity of the overall process (ΔG_R = 5.2 kcal mol^{-1}) and, particularly, of the initial step (ΔG_R = 25.6 kcal mol^{-1}), renders the process thermodynamically difficult. Moreover, the calculations involving the related phosphaalkyne Me—C≡P indicate an

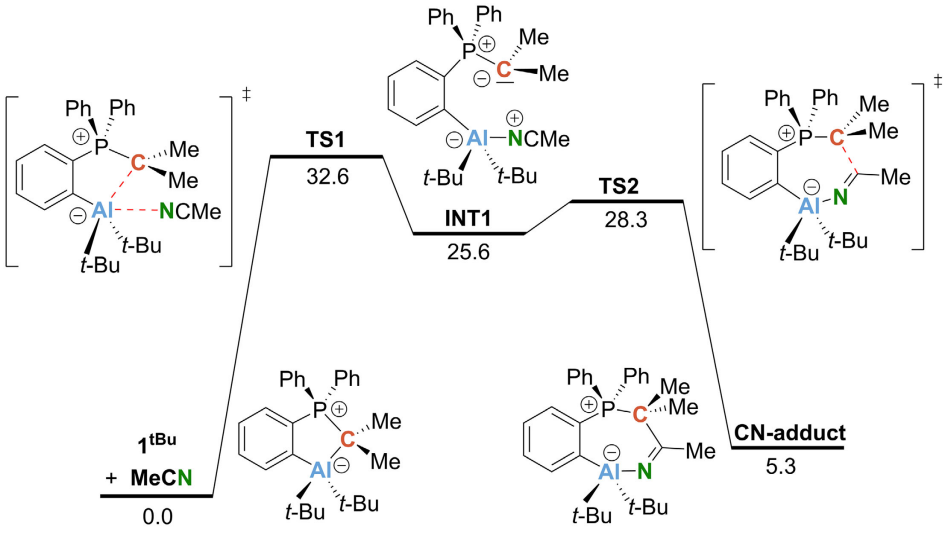
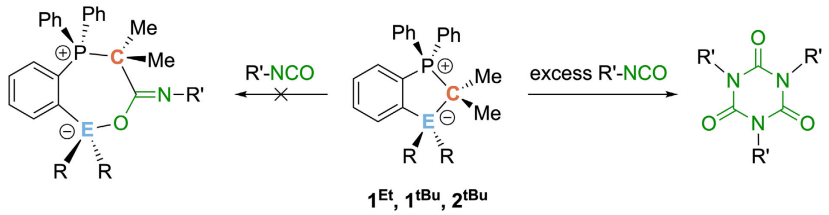


Figure 4. Computed reaction profile for the reaction of $\mathbf{1}^{tBu}$ with acetonitrile. Relative free energies (ΔG, at 298 K) are given in kcal mol^{-1}. All data have been computed at the PCM-M06-2X/def2-TZVPP//PCM-M06-2X/def2-SVP level.

Research Article
doi.org/10.1002/ejic.202500165

Chemistry Europe
European Chemical Societies Publishing



Scheme 5. Reaction scheme for the reaction of $\mathbf{1}^{Et}$, $\mathbf{1}^{tBu}$, and $\mathbf{2}^{tBu}$ with Ph—NCO and *p*-(CF_3)—C_6H_4—NCO at RT (R′ = Ph, *p*–(CF_3) —Ph).

Table 1. Conversions (^{19}F NMR against Ph—CF_3 as internal standard) from the catalytic reactions of $\mathbf{1}^{R}$ and $\mathbf{2}^{R}$ (5 mol%) with *p*-(CF_3)—C_6H_4—NCO at 75 °C after 14.5 h in THF-d_8 to the trimerization product.

Compound	$\mathbf{1}^{Me}$	$\mathbf{1}^{Et}$	$\mathbf{1}^{tBu}$	$\mathbf{1}^{Mes}$	$\mathbf{1}^{C6F5}$	$\mathbf{2}^{tBu}$	$\mathbf{2}^{C6F5}$
Conv. [%]	83	76	>99	74	55	21	0

unfeasible higher barrier of 44.8 kcal mol^{-1} for the initial nucleophilic addition step, which is also consistent with the experimental findings. Finally, related saturated systems such as N-(*tert*-butyl)-1-phenylmethanimine, BH_3NHMe_2, and the dichalcogenides $(PhS)_2$ and $(PhSe)_2$ were also unproductive (Scheme 4).

An unexpected reaction occurred when $\mathbf{1}^{Et}$, $\mathbf{1}^{tBu}$, and $\mathbf{2}^{tBu}$ were reacted with Ph—NCO. Contrary to expectations, the reactions do not produce the adduct (**Scheme 5**, left), but the triphenyl isocyanuranate (Scheme 5, right, trimerization product of Ph—NCO). This was verified by X-ray structure analysis and ^1H NMR spectroscopy. According to the ^1H NMR experiments, the reaction is very fast, even with a high excess of Ph—NCO, and only the trimerization product can be detected. As recently summarized in a review article,[14] isocyanates can be trimerized by amines,[15] phosphines,[16] *N*-heterocyclic carbenes,[17] inorganic salts,[18] phosphides,[19] as well as main group and transition metal complexes.[20] To the best of our knowledge, this reactivity has not been reported for Al-based FLPs to date.[2]

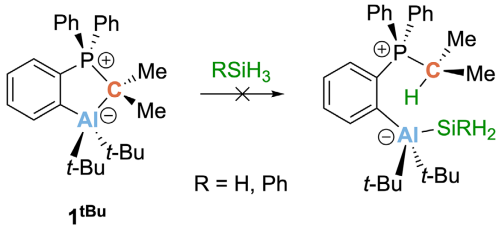
In 2019, Ward et al. presented an Al-based complex that selectively trimerizes a series of isocyanates catalytically (2 mol%) under mild conditions.[21] To investigate the catalytic activity of *o*-AlCPs $\mathbf{1}^{R}$ and *o*-GaCPs $\mathbf{2}^{R}$ in more detail, 5 mol% in THF-d_8 was mixed with *p*-(CF_3)—C_6H_4—NCO and heated to 75 °C for 14.5 h. The conversions shown in **Table 1** were determined by ^{19}F NMR spectroscopy with Ph—CF_3 as internal standard.

As can be clearly seen, $\mathbf{1}^{tBu}$ is the most active species in the trimerization of *p*-(CF_3)—C_6H_4—NCO with a conversion of >99%. In contrast to the reduction of CO_2, the Al derivatives are significantly more active in this case than the Ga derivatives, which show only small (21% conversion for $\mathbf{2}^{tBu}$) or no activity ($\mathbf{2}^{C6F5}$).[9a] Nevertheless, the activity of the title compounds is relatively low compared to the aforementioned systems known from the literature, which act in lower concentrations and at lower temperatures.

2.3. Si—H Bond Activation Studies

With regard to the possible application in hydrosilylation reactions, which has been extensively investigated for Lewis acidic compounds and FLPs, we also explored whether $\mathbf{1}^{tBu}$ reacts with SiH_4 and $PhSiH_3$ analogously to NH_3 with cleavage of the Si—H bond (**Scheme 6**).[22]

For this purpose, SiH_4 was prepared in situ from $SiCl_4$ and $LiAlH_4$ in Et_2O and a solution of $\mathbf{1}^{tBu}$ in benzene-d_6 was gassed with it. No reaction was detected in the ^1H NMR spectrum after heating to 90 °C for several hours. The same behavior was observed with $PhSiH_3$. Since it is known for FLPs that the activation of H_2 at RT cannot be detected spectroscopically, but that they are nevertheless very active catalytically, acetophenone was added to the reaction of $\mathbf{1}^{tBu}$ and $PhSiH_3$.[23] This mixture showed no reactivity either and the compounds remained unchanged in solution. This is in good agreement with the calculated prohibitive high barrier for the reaction of $\mathbf{1}^{Me}$ with SiH_4 of $\Delta G^{\neq} = 48.9$ kcal mol^{-1}.[24]



Scheme 6. Reaction of $\mathbf{1}^{tBu}$ toward silanes in benzene 90 °C.

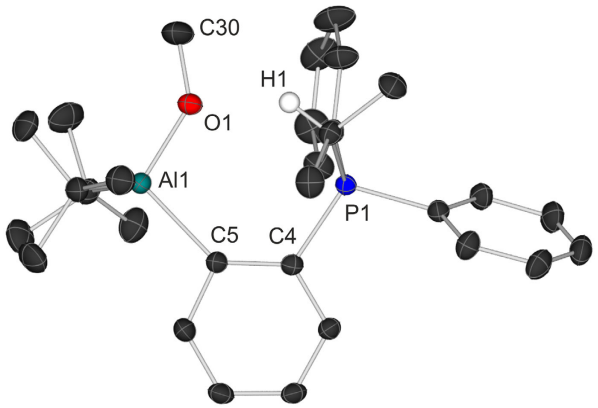


Figure 5. Molecular structure of **7** in the solid state (ellipsoids with 30% probability). The hydrogen atoms are not shown for a better overview. Selected bond lengths (Å) and angles (°): P1—C1 = 1.8273(16); Al1—O1 = 1.7498(12); Al1—C5 = 2.0627(16); C5—C4—P1 = 121.94(11); and C4—C5—Al1 = 135.53(11).

Research Article
doi.org/10.1002/ejic.202500165

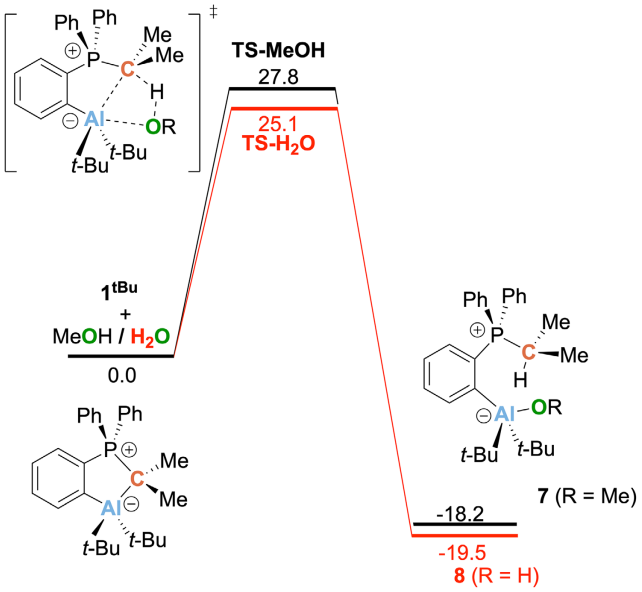
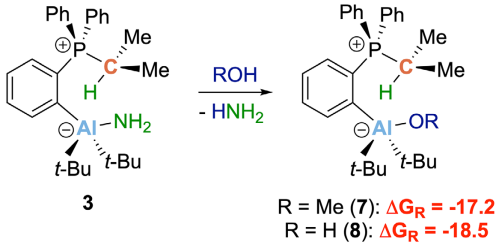


Figure 6. Computed reaction profile for the reactions of $\mathbf{1}^{tBu}$ with MeOH (black lines) and H_2O (red lines). Relative free energies (ΔG, at 298 K) are given in kcal mol^{-1}. All data have been computed at the PCM-M06-2X/def2-TZVPP//PCM-M06-2X/def2-SVP level.

2.4. Stability of $\mathbf{1}^{tBu}$ Toward MeOH and H_2O

The surprisingly high stability of $\mathbf{1}^{tBu}$ was revealed during the workup of the reaction mixture of the NH_3 transfer to the substrate maleimide.[8] In an attempt to obtain the product (maleamides) by recrystallization from MeOH, the product **7** was isolated. Compound **7** (space group $P\bar{1}$) crystallizes from MeOH at −30 °C in the form of colorless blocks (**Figure 5**).



Scheme 7. Formation of **7** (**8**) from **3** by displacement of NH_3 by MeOH (H_2O). Free energy values (ΔG, at 298 K) are given in kcal mol.

Contrary to initial expectations, the Al—C bonds are intact and the O—H bond of the methanol appears to be heterolytically cleaved. Compared with the CO_2 activation product **6**, the atomic distances and bond angles are very similar.[9a]

It was of interest to study how the formal MeOH activation product **7** is formed. FLP-mediated O—H bond activation has been reported by different groups. Those systems were able to cleave the O—H bond without decomposition.[25]

Our computations revealed that the activation of MeOH (or H_2O) by $\mathbf{1}^{tBu}$ occurs, in contrast to the activation of NH_3, in a concerted manner with a feasible activation barrier of $\Delta G^{\neq} = 27.8$ (25.1) kcal mol^{-1} in a highly exergonic ($\Delta G_R = -18.2$ (−19.5) kcal mol^{-1}) transformation (**Figure 6**). We were therefore confident that **7** should easily be formed in the reaction of $\mathbf{1}^{tBu}$

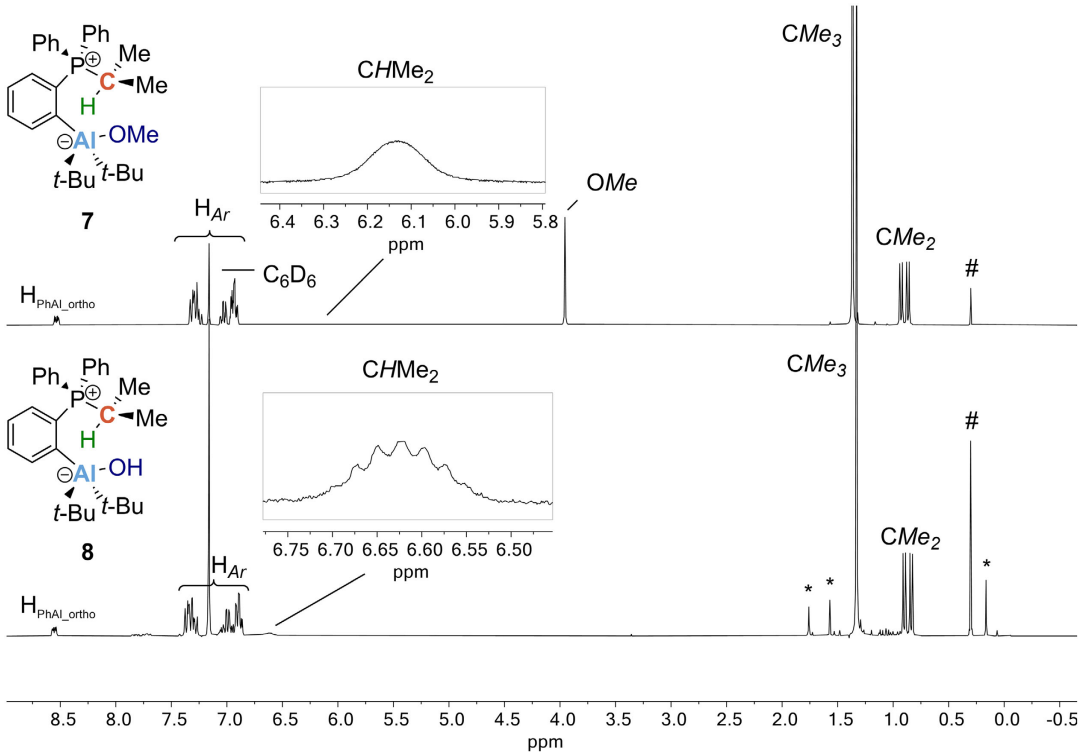


Figure 7. ^{1}H NMR spectrum of **7** (top) and of the reaction mixture of $\mathbf{1}^{tBu}$, H_2O and 2 bars of NH_3 to yield **8**, after extraction in benzene-d_6 (bottom). #: silicone grease and *: unknown impurity.

Research Article
doi.org/10.1002/ejic.202500165

with MeOH. At RT, however, no reaction was observed. Even more astonishingly, heating of the reaction mixture of $\mathbf{1^{tBu}}$ in MeOH only provided decomposition products. Similar observations were made with H_2O. While $\mathbf{1^{tBu}}$ is stable in non-dried benzene at RT, we obtained the same results as for MeOH when heating $\mathbf{1^{tBu}}$ in non-dried benzene. The cleavage of the C_{Ph}—Al bond seems to be favored over O—H bond activation in both cases. This suggests that **7** is not formed in a reaction of $\mathbf{1^{tBu}}$ with MeOH, but from replacing NH_3 from the activation product **3** in a highly exergonic reaction ($\Delta G_R = -17.2$ kcal mol^{-1}, **Scheme 7**).

To verify this hypothesis, $\mathbf{1^{tBu}}$ was dissolved in CD_2Cl_2 and 4 equivs. of dried MeOH were added. The solution was degassed and subsequently gassed with ≈2 bars of NH_3. A broad signal appeared in the ^{31}P NMR spectrum at $\delta = 33.7$ ppm. The ^{1}H NMR spectrum (**Figure 7**) gave the expected resonances for the activation product **7** with a chemical shift of $\delta_{1H} = 0.90$ ppm (dd, $^3J_{PH} = 18.6$ Hz, $^3J_{HH} = 7.0$ Hz; CH*Me*$_2$), 1.37 ppm (CMe_3), and 3.96 ppm (OMe). This spectrum was found to be identical to that for the isolated crystals.

Similar experiments were conducted with degassed water instead of MeOH. A signal in the ^{31}P NMR spectrum at $\delta = 33.5$ ppm and a similar ^{1}H NMR spectrum compared to the reaction with MeOH indicated the formation of the formal H_2O activation product **8** (Figure 7). Although several attempts were made, we were not able to isolate **8** in pure crystalline form. But based on these experimental findings, it appears reasonable to conclude that **7** and **8** are formed by ligand exchange from **3** at RT (Scheme 7) and not by O—H bond activation of MeOH and H_2O from $\mathbf{1^{tBu}}$.

3. Conclusion

Herein, we described unexpected reactivities, substrates that do not react with the title compounds, and the limits of stability of our P-ylide-substituted aluminum– and gallium–carbon ambiphiles. While $\mathbf{1^{tBu}}$ reacts reversibly with NH_3 at RT with cleavage of an N—H bond, the reaction with $MeNH_2$ is much more difficult and proceeds irreversibly only at 90 °C. While the *o*-GaCPs $\mathbf{2^R}$ show no reactivity with ammonia, the other *o*-AlCPs decompose in the presence of NH_3. No reactivity of $\mathbf{1^R}$ was observed with *t*-$BuNH_2$ and Et_2NH. The reaction with silanes such as SiH_4 and $PhSiH_3$ showed that the title compounds are not able to activate nonpolar element—hydrogen bonds. Other substrates with carbon—nitrogen, carbon—phosphorus, and nitrogen—nitrogen multiple bonds showed also no reaction. We found an unexpected reactivity in the reaction of $\mathbf{1^R}$ and $\mathbf{2^R}$ with isocyanates. Instead of yielding the ring-expansion products as expected, the title compounds catalyzed the trimerization of isocyanates with $\mathbf{1^{tBu}}$ being the most active catalyst. The reactivity toward MeOH and H_2O was found to be very interesting. Quantum chemical calculations showed that activation of the O—H bond in MeOH and H_2O should be possible at RT. Experimental findings, however, only show the decomposition of $\mathbf{1^{tBu}}$ in the corresponding reactions. We attribute this to the preferential cleavage of the C_{Ph}—Al bond when $\mathbf{1^{tBu}}$ is heated in the presence of MeOH or H_2O. Nevertheless, the cleavage of the O—H bond is feasible and affords the activation products **7** and **8** starting from the ammonia activation product **3**. We thus demonstrated the high stability and clear limits in the reactivity of our aluminum– and gallium–carbon ambiphiles. Inspired by this, the further development and investigation of new, more reactive group 13-carbon ambiphiles is part of current research in our laboratories.

4. Experimental Section

General Methods

All operations were carried out under dry argon using standard Schlenk and glove box techniques.[26] The phosphaalkine *t*-BuPC was synthesized according to literature procedures.[27] The gases NH_3 and CO were used as received from AirLiquide. All other chemicals were purchased from Sigma-Aldrich or abcr. Liquids were dried over molecular sieves or CaH_2, degassed and condensed prior to use. Methanol was dried over $NaOCH_3$ and distilled. Solids were subjected to three successive cycles of vacuum and argon. Solvents were dried over Na/K or CaH_2 and rigorously degassed before use. Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance Neo 400 or an Avance 300 spectrometer operating at ^{1}H Larmor frequencies of 400 or 300 MHz in dry degassed deuterated solvents. For the kinetic studies, we used a Migratek Spinsolve 80 Benchtop NMR spectrometer. ^{1}H, and ^{13}C{^{1}H} chemical shifts were reported against $SiMe_4$ (TMS), ^{31}P{^{1}H} against H_3PO_4 and ^{19}F against BF_3OEt_2. Coupling constants (*J*) were given in Hertz as positive values, regardless of their real individual signs. Infrared (IR) spectra were measured on a Bruker Alpha spectrometer using the attenuated reflection technique (ATR) and the data are quoted in wavenumbers (cm^{-1}). Melting points were measured with a Thermo Fischer melting point apparatus and were not corrected. Elemental analyses were carried out in the institutional technical laboratories of the Karlsruhe Institute of Technology (KIT).

General Procedures

For the reactivity study, $\mathbf{1^R}$ or $\mathbf{2^R}$ (10 mg) was placed in a young NMR tube in benzene-d_6 and the corresponding substrate was added. In the case of gaseous substrates, the solution was degassed and then gassed with the substrate (1.1 bar). Liquid substrates were added in equimolar amounts or in slight excess using an Eppendorf pipette inside the glove box. Solid substrates were weighed and added in equimolar amounts inside a glove box. The NMR tubes were first stored at RT and then ^{1}H and ^{31}P NMR spectra were recorded. If no reaction was observed, the NMR tubes were heated to 90 °C overnight in an oil bath and measured again.

Decomposition of $\mathbf{1^{Et}}$ in the Presence of NH_3

$\mathbf{1^{Et}}$ was dissolved in benzene-d_6, degassed, and then gassed with NH_3. The reaction solution immediately turned red/orange and after a few minutes ^{1}H and ^{31}P NMR spectra were measured. Excess ammonia and solvent were removed in the vacuum, the solid was redissolved in benzene-d_6 and measured again. After 24 h, NMR spectra were recorded again. Results are shown in Figure 2 and S5, Supporting Information. This reaction was repeated with 50 mg of $\mathbf{1^{Et}}$ but no specific pure products were isolated in several attempts.

Catalytic Trimerization Reactions

For the catalytic reactions, $\mathbf{1^R}$ or $\mathbf{2^R}$ (5 mol%, 13 μmol) were added to 0.6 mL of a premixed solution of *p*-CF_3-C_6H_4—NCO (406 mg, 2.17 mmol)

and $C_6H_5CF_3$ (348 mg, 2.38 mmol as internal standard) in THF-d_8 (total volume of the premix: 5 mL) in a Young capped NMR tube. The mixtures were heated to 75 °C for 14.5 h in an oil bath and then ^{19}F NMR spectra were recorded. Conversions are listed in Table 1.

Reaction of 1^{tBu} with MeOH in the Presence of NH_3

$\mathbf{1^{tBu}}$ (10 mg, 22.5 μmol) was placed in a Young capped NMR tube and dissolved in CD_2Cl_2 (0.4 mL). An excess of dried MeOH was added (4.00 μL, 98.6 μmol). The solution was degassed and subsequently gassed with ≈2 bars of NH_3. As broad signals were observed in the ^1H NMR spectrum, all volatile components were evaporated in vacuo. The remaining solid was dissolved in benzene-d_6. ^1H NMR (300 MHz, 298 K, C_6D_6, ppm): $\delta = 8.58–8.50$ (*m*, H_{PhAl_ortho}, 1H), 7.35–7.21 (*m*, H_{Ar}, 6H), 7.12–7.00 (*m*, H_{Ar}, 3H), 6.98–6.89 (*m*, H_{Ar}, 5H), 6.13 (*s*, H_{CHMe2}, 1H), 3.96 (*s*, H_{OMe}, 3H), 1.37 (*s*, H_{CMe3}, 18H), 0.90 (*dd*, $^3J_{PH} = 18.6$ Hz, $^3J_{HH} = 7.0$ Hz, H_{CMe2}, 6H). ^{13}C NMR (75 MHz, 298 K, C_6D_6, ppm): $\delta = 142.51$ (*d*, $^2J_{PC} = 24.2$ Hz, C_{PhAl_ortho}), 134.60 (*d*, $^4J_{PC} = 8.2$ Hz, C_{PPh2_para}), 133.29 (*d*, $^2J_{PC} = 17.1$ Hz, C_{PPh2_ortho}), 132.80 (*d*, $^4J_{PC} = 2.9$ Hz, C_{PhAl_para}), 129.63 (*d*, $^4J_{PC} = 4.0$ Hz, C_{PhAl_meta}), 128.86 (*d*, $^3J_{PC} = 11.3$ Hz, C_{PPh2_meta}), 126.40 (*d*, $^1J_{PC} = 88.4$ Hz, C_{PPh2_ipso}), 125.21 (*d*, $^2J_{PC} = 13.0$ Hz, C_{PhP_ortho}), 121.80 (*d*, $^1J_{PC} = 78.9$ Hz, C_{CMe2}), 52.01 (*s*, C_{OCH3}), 33.37 (*s*, C_{Me3}), 22.09 (*d*, $^1J_{PC} = 45.4$ Hz, C_{CMe2}), 17.73 (*d*, $^2J_{PC} = 2.7$ Hz, C_{Me2} and C_{CMe3}). ^{31}P NMR (121 MHz, 298 K, C_6D_6, ppm): $\delta = 33.57$ (s). IR (ATR, cm^{-1}): $\tilde{U} = 2921$ (vw), 2860 (vw), 2795 (m), 2681 (vw), 1487 (vw), 1462 (vw), 1436 (w), 1393 (vw), 1374 (vw), 1350 (vw), 1257 (vw), 1229 (vw), 1180 (vw), 1111 (m), 1086 (w), 1052 (vw), 1023 (vw), 999 (vw), 938 (vw), 879 (vw), 809 (m), 760 (w), 747 (w), 730 (w), 717 (m), 691 (m), 649 (m), 620 (s), 556 (w), 535 (vs), 489 (w), 481 (w), 445 (w), 426 (s). Elemental analysis (%): (calcd., found for $C_{30}H_{42}OAlP…0.3\ C_6D_6$); C (76.11, 76.37), H (8.44, 8.79).

Reaction of 1^{tBu} with H_2O in Presence of NH_3

$\mathbf{1^{tBu}}$ (10 mg, 22.5 μmol) was placed in a Young capped NMR tube and dissolved in CD_2Cl_2 (0.4 mL). An excess of degassed H_2O was added (5 μL, 278 μmol). The solution was degassed and subsequently gassed with ≈2 bars of NH_3. All volatile components were evaporated in vacuo and the remaining solid was dissolved in benzene-d_6. ^1H NMR (300 MHz, 298 K, C_6D_6, ppm): $\delta = 8.58–8.51$ (*m*, H_{PhAl_ortho}, 1H), 7.46–7.23 (*m*, H_{Ar}, 6H), 7.08–6.95 (*m*, H_{Ar}, 3H), 6.94–6.84 (*m*, H_{Ar}, 5H), 6.70–6.54 (*s*, H_{CHMe2}, 1H), 1.33 (*s*, H_{CMe3}, 18H), 0.87 (*dd*, $^3J_{PH} = 18.8$ Hz, $^3J_{HH} = 6.9$ Hz, H_{CMe2}, 6H). ^{31}P NMR (121 MHz, 298 K, C_6D_6, ppm): $\delta = 33.52$ (s).

Decomposition of 1^{tBu} with MeOH

$\mathbf{1^{tBu}}$ (50 mg, 115 μmol) was placed in dried MeOH (2 mL) and heated to 70 °C. The solvent was removed, and no reaction was detected in the NMR spectra. This was due to the low solubility of $\mathbf{1^{tBu}}$ in methanol. The solid was dissolved in dried benzene (2 mL) and MeOH (1 mL) was added. The mixture was heated to 70 °C overnight. The solvent was removed under reduced pressure and the remaining colorless sticky residue was collected in CH_2Cl_2 (2 mL) and was layered with pentane (5 mL). Only powder and no single crystals were observed. The mother liquor was removed and the solid dried under high vacuum. The ^1H and ^{31}P NMR spectra showed only decomposition products.

Decomposition of 1^{tBu} *with* H_2O

$\mathbf{1^{tBu}}$ (50 mg, 115 μmol) was placed in non-dried benzene (3 mL) and heated to 70 °C overnight. The mixture became hazy and then the solvent was removed under reduced pressure and the remaining colorless powder was collected in CH_2Cl_2 (2 mL) and was layered with pentane (5 mL). Only powder and no single crystals were observed. The mother liquor was removed and the solid dried under high vacuum. The ^1H and ^{31}P NMR spectra showed only decomposition products.

Reaction with SiH_4

Reactions were carried out in an apparatus setup as follows. A suitable apparatus for this reaction consisted of a spider with an outlet to the Schlenk line and an outlet to the outside atmosphere (sealed with a stopper). Two Young flasks and a Young-NMR tube were connected to the spider. One flask contained $SiCl_4$ (110 mg, 0.61 mmol) dissolved in Et_2O. The other flask contained $LiAlH_4$ (100 mg, 2.61 mmol) dissolved in Et_2O. The NMR tube contained a solution of $\mathbf{1^{tBu}}$ (10 mg, 23 μmol) in benzene-d_6. The solutions were degassed one after the other via three freeze–pump–thaw cycles and the outlet to the Schlenk line was sealed so that a vacuum was present in the apparatus and work could be carried out under the inlet vapor pressures of the substances and solvents. The $SiCl_4$ was condensed onto the $LiAlH_4$ by cooling with liquid nitrogen, the flask was sealed, and the mixture was allowed to warm to 0 °C. During this process, a strong gas evolution was observed. Stirring was then continued for half an hour to ensure complete reduction of the $SiCl_4$ to SiH_4. A small amount of SiH_4 was then condensed to $\mathbf{1^{tBu}}$ and the reaction mixture was allowed to reach RT. After no reaction was detected at RT after 16 h, the mixture was heated to 90 °C for 16 h and again no reaction was detected in the NMR spectra. Excess SiH_4 was quenched directly into a hot flame by flooding the apparatus with argon and then opening the apparatus under argon flow.

Reaction with $PhSiH_3$ *and Acetophenone*

To a solution of $\mathbf{1^{tBu}}$ (10 mg, 23 μmol) in benzene-d_6, $PhSiH_3$ (excess) was added via syringe. After no reaction was detected at RT after 16 h, the mixture was heated to 90 °C for 16 h and again no reaction was detected in the NMR spectra. The same procedure was repeated after the addition of one drop of acetophenone. No reaction was observed.

Crystallographic Details

Deposition number 2386440 (**7**) contained the supplementary crystallographic data for this article. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

Computational Details

Geometry optimizations of the molecules were performed without symmetry constraints using the Gaussian16 (RevB.01) suite of programs[26] at the dispersion-corrected M06-2X[27]/def2-SVP[28] level including solvent effects (solvent = benzene) with the polarization continuum model (PCM) method.[29] Reactants and adducts were characterized by frequency calculations and have positive definite Hessian matrices. Transition states showed only one negative eigenvalue in their diagonalized force constant matrices, and their associated eigenvectors were confirmed to correspond to the motion along the reaction coordinate under consideration using the intrinsic reaction coordinate method.[30] Energy refinements were carried out by means of single-point calculations at the same DFT level using the much larger triple-ζ basis set def2-TZVPP.[28] This level is denoted PCM(benzene)-M06-2X/def2-TZVPP//PCM(benzene)-M06-2X/def2-SVP. The computed thermochemistry data were corrected following Grimme's quasi-harmonic (QHA) model for entropy[31] using the GoodVibes[32] program at 298.15 K.[33,34]

Acknowledgements

The authors acknowledge support from the German Research Foundation (DFG) through grant no BR 2169/5-1 (535548579). The authors are also grateful for financial support from grants PID2022-139318NB-I00 and RED2022-134331-T, funded by MICIU/AEI/10.13039/501100011033. Financial support by the Fonds der Chemischen Industrie through a Kekulé Fellowship for P.W. is acknowledged.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: aluminum · bond activations · density-functional theory calculations · frustrated Lewis Pairs · phosphorus ylides

[1] Selected Reviews: a) D. W. Stephan, G. Erker, *Angew. Chem., Int. Ed.* **2010**, *49*, 46; b) D. W. Stephan, G. Erker, *Chem. Sci.* **2014**, *5*, 2625; c) D. W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306; d) D. W. Stephan, *J. Am. Chem. Soc.* **2015**, *137*, 10018; e) D. W. Stephan, G. Erker, *Angew. Chem., Int. Ed.* **2015**, *54*, 6400; f) S. A. Weicker, D. W. Stephan, *Bull. Chem. Soc. Jpn.* **2015**, *88*, 1003; g) D. W. Stephan, *Science* **2016**, *354*, aaf7229; h) F.-G. Fontaine, D. W. Stephan, *Phil. Trans. R. Soc. A* **2017**, *375*, 20170004; i) A. R. Jupp, D. W. Stephan, *Trends Chem.* **2019**, *1*, 35; j) J. Lam, K. M. Szkop, E. Mosaferi, D. W. Stephan, *Chem. Soc. Rev.* **2019**, *48*, 3592; k) J. Paradies, *Eur. J. Inorg. Chem.* **2019**, *2019*, 283; l) J. Paradies, *Coord. Chem. Rev.* **2019**, *380*, 170; m) N. Li, W.-X. Zhang, *Chin. J. Chem.* **2020**, *38*, 1360; n) D. W. Stephan, *J. Am. Chem. Soc.* **2021**, *143*, 20002; o) B. L. Frenette, E. Rivard, *Chem. Eur. J.* **2023**, *29*, e202302332; p) M. Ghara, H. Mondal, R. Pal, P. K. Chattaraj, *J. Phys. Chem. A* **2023**, *127*, 4561; q) M. N. Khan, Y. van Ingen, T. Boruah, A. McLauchlan, T. Wirth, R. L. Melen, *Chem. Sci.* **2023**, *14*, 13661; r) D. W. Stephan, *Chem. Soc. Rev.* **2023**, *52*, 4632; s) K. Lye, R. D. Young, *Chem. Sci.* **2024**, *15*, 2712.

[2] F. Krämer, *Angew. Chem., Int. Ed.* **2024**, *63*, e202405207.

[3] D. Mandal, R. Gupta, R. D. Young, *J. Am. Chem. Soc.* **2018**, *140*, 10682.

[4] A. Brar, S. Mummadi, D. K. Unruh, C. Krempner, *Organometallics* **2020**, *39*, 4307.

[5] N. S. Lambic, R. D. Sommer, E. A. Ison, *ACS Catal.* **2017**, *7*, 1170.

[6] a) J. A. Hatnean, J. W. Thomson, P. A. Chase, D. W. Stephan, *Chem. Commun.* **2014**, *50*, 301; b) A. Friedrich, J. Eyselein, H. Elsen, J. Langer, J. Pahl, M. Wiesinger, S. Harder, *Chem. Eur. J.* **2021**, *27*, 7756.

[7] C. Appelt, J. C. Slootweg, K. Lammertsma, W. Uhl, *Angew. Chem., Int. Ed.* **2013**, *52*, 4256.

[8] F. Krämer, J. Paradies, I. Fernández, F. Breher, *Nat. Chem.* **2024**, *16*, 63.

[9] a) F. Krämer, J. Paradies, I. Fernández, F. Breher, *Chem. Eur. J.* **2024**, *30*, e202303380; b) G. Ménard, D. W. Stephan, *J. Am. Chem. Soc.* **2010**, *132*, 1796; c) M.-A. Courtemanche, J. Larouche, M.-A. Légaré, W. Bi, L. Maron, F.-G. Fontaine, *Organometallics* **2013**, *32*, 6804.

[10] a) Y. Zhang, G. M. Miyake, E. Y.-X. Chen, *Angew. Chem., Int. Ed.* **2010**, *49*, 10158; b) Y. Zhang, G. M. Miyake, M. G. John, L. Falivene, L. Caporaso, L. Cavallo, E. Y. X. Chen, *Dalton Trans.* **2012**, *41*, 9119; c) J. He, Y. Zhang, E. Y. X. Chen, *Synlett* **2014**, *25*, 1534; d) J. He, Y. Zhang, L. Falivene, L. Caporaso, L. Cavallo, E. Y. X. Chen, *Macromolecules* **2014**, *47*, 7765; e) Q. Wang, W. Zhao, J. He, Y. Zhang, E. Y. X. Chen, *Macromolecules* **2017**, *50*, 123; f) M. Hong, J. Chen, E. Y. X. Chen, *Chem. Rev.* **2018**, *118*, 10551; g) W. Zhao, Q. Wang, J. He, Y. Zhang, *Polym. Chem.* **2019**, *10*, 4328.

[11] a) W. Beker, E. P. Gajewska, T. Badowski, B. A. Grzybowski, *Angew. Chem., Int. Ed.* **2019**, *58*, 4515; b) I. W. Davies, *Nature* **2019**, *570*, 175; c) C. W. Coley, N. S. Eyke, K. F. Jensen, *Angew. Chem., Int. Ed.* **2020**, *59*, 22858; d) C. W. Coley, N. S. Eyke, K. F. Jensen, *Angew. Chem., Int. Ed.* **2020**, *59*, 23414; e) M. I. Jordan, T. M. Mitchell, *Science* **2015**, *349*, 255; f) A. F. de Almeida, R. Moreira, T. Rodrigues, *Nat. Rev. Chem.* **2019**, *3*, 589; g) F. Strieth-Kalthoff, F. Sandfort, M. H. S. Segler, F. Glorius, *Chem. Soc. Rev.* **2020**, *49*, 6154.

[12] F. Strieth-Kalthoff, F. Sandfort, M. Kühnemund, F. R. Schäfer, H. Kuchen, F. Glorius, *Angew. Chem., Int. Ed.* **2022**, *61*, e202204647.

[13] N. Graulich, H. Hopf, P. R. Schreiner, *Chem. Soc. Rev.* **2010**, *39*, 1503.

[14] Y. Guo, M. Muuronen, F. Lucas, R. P. Sijbesma, Ž. Tomović, *ChemCatChem* **2023**, *15*, e202201362.

[15] T. Yoichi, S. Isao, Y. Masahiko, T. Tohru, Y. Katsumi, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3486.

[16] a) Z. Pusztai, G. Vlád, A. Bodor, I. T. Horváth, H. J. Laas, R. Halpaap, F. U. Richter, *Angew. Chem., Int. Ed.* **2006**, *45*, 107; b) S. M. Raders, J. G. Verkade, *J. Org. Chem.* **2010**, *75*, 5308; c) J. Tang, T. Mohan, J. G. Verkade, *J. Org. Chem.* **1994**, *59*, 4931; d) X. Liu, Y. Bai, J. G. Verkade, *J. Organomet. Chem.* **1999**, *582*, 16.

[17] H. A. Duong, M. J. Cross, J. Louie, *Org. Lett.* **2004**, *6*, 4679.

[18] Y. Nambu, T. Endo, *J. Org. Chem.* **1993**, *58*, 1932.

[19] a) D. Heift, Z. Benkő, H. Grützmacher, A. R. Jupp, J. M. Goicoechea, *Chem. Sci.* **2015**, *6*, 4017; b) W. Yi, J. Zhang, L. Hong, Z. Chen, X. Zhou, *Organometallics* **2011**, *30*, 5809.

[20] a) A. Hernán-Gómez, T. D. Bradley, A. R. Kennedy, Z. Livingstone, S. D. Robertson, E. Hevia, *Chem. Commun.* **2013**, *49*, 8659; b) H. R. Sharpe, A. M. Geer, H. E. L. Williams, T. J. Blundell, W. Lewis, A. J. Blake, D. L. Kays, *Chem. Commun.* **2017**, *53*, 937; c) S. G. Lee, K.-Y. Choi, Y.-J. Kim, S. Park, S. W. Lee, *Dalton Trans.* **2015**, *44*, 6537; d) Y. Wu, S. Wang, X. Zhu, G. Yang, Y. Wei, L. Zhang, H.-B. Song, *Inorg. Chem.* **2008**, *47*, 5503; e) A. J. Bloodworth, A. G. Davies, *J. Chem. Soc.* **1965**, 6858; f) X.-G. Zhou, L.-B. Zhang, M. Zhu, R.-F. Cai, L.-H. Weng, Z.-X. Huang, Q.-J. Wu, *Organometallics* **2001**, *20*, 5700; g) X. Zhu, J. Fan, Y. Wu, S. Wang, L. Zhang, G. Yang, Y. Wei, C. Yin, H. Zhu, S. Wu, H. Zhang, *Organometallics* **2009**, *28*, 3882; h) A. Flamini, A. M. Giuliani, N. Poli, *Tetrahedron Lett.* **1987**, *28*, 2169.

[21] M. A. Bahili, E. C. Stokes, R. C. Amesbury, D. M. C. Ould, B. Christo, R. J. Horne, B. M. Kariuki, J. A. Stewart, R. L. Taylor, P. A. Williams, M. D. Jones, K. D. M. Harris, B. D. Ward, *Chem. Commun.* **2019**, *55*, 7679.

[22] a) K. Mitsuo, H. Takakazu, S. Hideki, *Chem. Lett.* **1992**, *21*, 555; b) N. Asao, T. Sudo, Y. Yamamoto, *J. Org. Chem.* **1996**, *61*, 7654; c) Y.-S. Song, B. R. Yoo, G.-H. Lee, I. N. Jung, *Organometallics* **1999**, *18*, 3109; d) T. Sudo, N. Asao, V. Gevorgyan, Y. Yamamoto, *J. Org. Chem.* **1999**, *64*, 2494; e) F. Buch, J. Brettar, S. Harder, *Angew. Chem., Int. Ed.* **2006**, *45*, 2741; f) A. Berkefeld, W. E. Piers, M. Parvez, *J. Am. Chem. Soc.* **2010**, *132*, 10660; g) D. Chen, V. Leich, F. Pan, J. Klankermayer, *Chem. Eur. J.* **2012**, *18*, 5184; h) X. Feng, H. Du, *Tetrahedron Lett.* **2014**, *55*, 6959; i) S. Tamke, C.-G. Daniliuc, J. Paradies, *Org. Biomol. Chem.* **2014**, *12*, 9139; j) Y. Nakajima, S. Shimada, *RSC Adv.* **2015**, *5*, 20603; k) J. M. Bayne, D. W. Stephan, *Chem. Soc. Rev.* **2016**, *45*, 765; l) M. Hirai, J. Cho, F. P. Gabbaï, *Chem. Eur. J.* **2016**, *22*, 6537; m) W. Meng, X. Feng, H. Du, *Acc. Chem. Res.* **2018**, *51*, 191; n) R. J. Andrews, S. S. Chitnis, D. W. Stephan, *Chem. Commun.* **2019**, *55*, 5599; o) S. Balasubramaniam, S. Kumar, A. P. Andrews, B. Varghese, E. D. Jemmis, A. Venugopal, *Eur. J. Org. Chem.* **2019**, *2019*, 3265; p) H.-C. Tseng, C.-T. Shen, K. Matsumoto, D.-N. Shih, Y.-H. Liu, S.-M. Peng, S. Yamaguchi, Y.-F. Lin, C.-W. Chiu, *Organometallics* **2019**, *38*, 4516.

[23] L. Greb, P. Oña-Burgos, B. Schirmer, S. Grimme, D. W. Stephan, J. Paradies, *Angew. Chem., Int. Ed.* **2012**, *51*, 10164.

[24] D. González-Pinardo, F. Krämer, F. Breher, I. Fernández, *ChemistryEurope* **2024**, *2*, e202400020.

[25] a) R. Roesler, W. E. Piers, M. Parvez, *J. Organomet. Chem.* **2003**, *680*, 218; b) M. Klahn, A. Spannenberg, U. Rosenthal, *Acta Crystallogr. Sect. E: Struct. Rep. Online* **2012**, *68*, o1549-o1549; c) Z. Mo, T. Szilvási, Y.-P. Zhou, S. Yao, M. Driess, *Angew. Chem., Int. Ed.* **2017**, *56*, 3699.

[26] A. M. Borys, *Organometallics* **2023**, *42*, 182.

[27] G. Becker, G. Gresser, W. Uhl, *Z. Naturforsch. B* **1981**, *36*, 16.

[28] Gaussian16, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi,

J. Goings, B. Peng, A. Petrone, et al., *Revision B.01*, Gaussian, Inc., Wallingford CT **2016**.
[29] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215.
[30] F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297.
[31] a) S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys.* **1981**, *55*, 117; b) J. L. Pascual-Ahuir, E. Silla, I. Tuñón, *J. Comput. Chem.* **1994**, *15*, 1127; c) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995.
[32] C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523.
[33] S. Grimme, *Chem. Eur. J.* **2012**, *18*, 9955.
[34] G. Luchini, J. V. Alegre-Requena, I. Funes-Ardoiz, R. S. Paton, *F1000Research* **2020**, *9*, 291.

Manuscript received: April 4, 2025
Version of record online: May 21, 2025