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A strained intramolecular P/Al-FLP and its reactivity toward allene†

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FLPs featuring aluminum–phosphane interactions, spring-loaded by a rigid biphenylene linker, have been accessed through a route where trimethyltin units at phosphane-functionalized organic backbones are exchanged by an AlCl$_2$ moiety. Upon contact with substrates like CO$_2$ these are readily bound by the Al/P site with release of strain. The system could also be utilized for a unique reactivity, namely the activation of allene.

Since the discovery of frustrated Lewis pairs (FLP) in 2006 a large number of small molecules have been activated and even catalytic applications have been reported by both inter- and intramolecular systems.[1] Their reactivity is primarily influenced by the HOMO–LUMO gap between the Lewis acid and base (often a combination of group 13 and 15 elements).[2] For intramolecular FLPs in which the two reactive centers are separated by a linker the spatial distance is also of decisive importance. It is generally assumed that the latter should be in a range of 3–5 Å, as with larger distances cooperative interaction of the Lewis acid and base with a substrate is impeded; shorter distances lead to an interaction between the HOMO$_{LB}$ and LUMO$_{LA}$ such that the potential is (partly) quenched.[3] This can be exemplified considering four intramolecular FLPs from the literature with Lewis acidic B(C$_6$F$_5$)$_2$ and Lewis basic phosphine moieties bound to different rigid linker scaffolds (Fig. 1): at 5.67 Å, the reactive centers fixed to a dibenzofuran scaffold (A)[4] are too far apart, while the short distance of 2.06 Å mediated by an acenaphthyl scaffold (D)[5] originates from a pronounced interaction. For both molecules no reactivity toward substrates was observed. In contrast, the xanthene- and biphenylene-based systems (B and C) readily react with dihydrogen, nitrous oxide, terminal alkynes, and dioxygen.[4,6] Solid state structures of the active FLPs to determine the P···B

distances could not be determined, yet spectroscopic data indicate no interaction between the reactive sites, which is in line with the widely accepted assumption that these backbones prevent an interaction.[7]

An analogous chemistry utilizing aluminum as acceptor has not been explored for such a variety of linker scaffolds because of the synthetic difficulties associated with its higher intrinsic Lewis acidity compared to boron.[8]

Reported examples feature close arrangements of Lewis acid and base and often an interaction is observed that stabilizes the Lewis acidic alane, thereby rendering the FLP more exothermic and synthetically easier to access.[8,9]

In previous work we reported the synthesis of xanthene-based P/Al-FLPs *via* an aluminum-tin exchange between a stannylated backbone and a methylaluminum precursor.[10] However, two equivalents of the respective alane reagent were required, as the envisaged FLP upon formation immediately spans a further alane precursor molecule, which short-circuits the FLP. This was shown to not be detrimental for reactivity, as the bridging alane molecules are readily displaced by external substrates with O-donors such as THF or CO$_2$, which get activated between the phosphine and the two alane functions, rendering the system an inter-/intramolecular hybrid.

Herein, we present the exploitation of the aluminum-tin exchange route for the synthesis of a P/Al-based FLP with a highly Lewis acidic acceptor site on the biphenylene backbone. This was envisaged to permit a small degree of interaction between the Lewis acidic and basic moieties thus leading to a reactive intramolecular 1:1 P/Al-FLP with a large spatial separation.

Following the same synthetic strategy as for the xanthene-based P/Al-FLPs the precursor for an Al–Sn exchange [8-trimethylstannyl-1-biphenylenyl]diphenylphosphine **1-Ph**, was synthesized from the parent 1,8-dibromobiphenylene[11] in an overall yield of 79% over two steps (Scheme 1). Single crystal XRD analysis confirms the successful attachment of the diphenylphosphine and trimethylstannyl units in a distance ($d_{P–Sn} \sim 4.02$ Å) typical for the biphenylene backbone.

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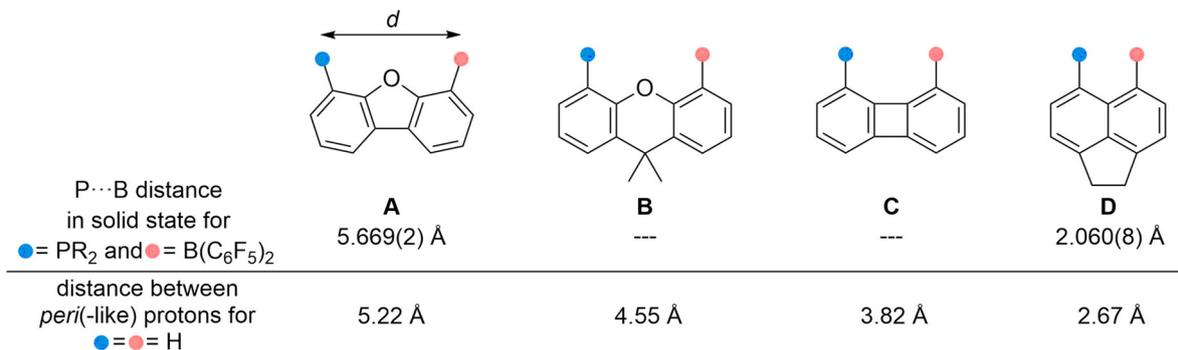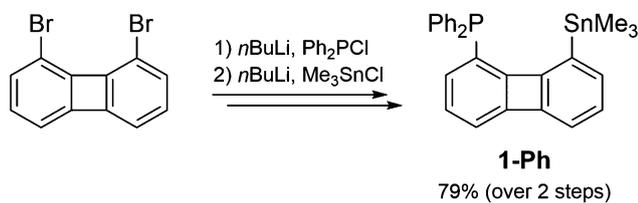
Fig. 1   Intramolecular P/B-based FLPs on rigid carbon scaffolds to adjust the P···B distance.

Scheme 1   Synthesis of the precursor for an Al–Sn exchange **1-Ph**.

The reactivity of the precursor **1-Ph** toward one equivalent of MeAlCl$_2$ in C$_6$D$_6$ was monitored by NMR spectroscopy. In the ^{1}H NMR spectrum recorded after 15 minutes at room temperature an intense signal with tin satellites at δ = 0.00 ppm was noted which could be assigned to Me$_4$Sn. The absence of resonances of the starting material **1-Ph** indicated a complete reaction. In the ^{31}P{^{1}H} NMR spectrum the formation of a new species resonating as a broadened singlet at δ = −19.1 ppm ($\nu_{\frac{1}{2}} \approx$ 60 Hz) was observed. Due to the high selectivity of the reaction the new compound Biph(PPh$_2$)(AlCl$_2$), **2-Ph**, could be isolated as a highly air and water sensitive solid with satisfying purity simply through removal of the solvent and Me$_4$Sn *in vacuo* (Scheme 2). Our attempts to detect the ^{27}Al{^{1}H} NMR resonance of **2-Ph**, which would provide information about the coordination number of the alane in solution remained unsuccessful.[12]

The solid-state structure determined *via* single crystal XRD analysis confirms the successful introduction of the AlCl$_2$ moiety beside the Ph$_2$P unit on the biphenylene scaffold in 1,8 positions (Fig. 2). Most conspicuous is the bending of both substituents towards each other, so that compared with **1-Ph** a much shorter *peri*-like distance of $d_{P–Al}$ = 2.5456(6) Å results. The ratio between this distance and the sum of the covalent
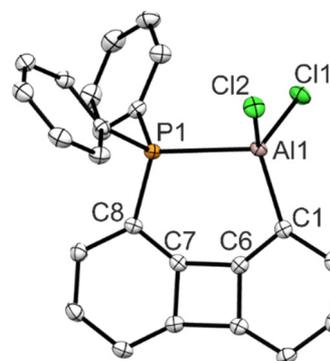

Fig. 2   Molecular structure of **2-Ph**. H atoms omitted for clarity; thermal ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: P1–C8 1.807(1), Al1–C1 1.960(1), Al1–P1 2.5456(6), Cl1–Al1–Cl2 111.39(2), Cl1–Al1–C1 115.46(4), C1–Al1–Cl2 116.36(4).

radii (228 pm) is r = 1.12 indicating a strong interaction.[13] r values in this magnitude are usually observed for element 13 and 15 combinations on the (ace)naphthalene scaffold,[7] *e.g.* the corresponding acenaphthalene compound Ace(PPh$_2$)(AlCl$_2$) exhibits a P–Al distance of 2.4305(6) Å (r = 1.07).[14] The bay angles P1–C8–C7 113.6(1)° and Al1–C1–C6 111.6(1)° deviate significantly from 120° indicating a high strain within the molecule. The donation of the phosphine's lone pair into the empty p$_z$ orbital triggers a rehybridization at the aluminum center, and hence the sum of the angles around the aluminum center $\left(\sum_{\alpha} Al = 343°\right)$ substantially differs from 360°. The tetrahedral character was determined to be 92%.[15]

By calculation (B3PW91/6-311+G(2df,p)) of an isodesmic reaction (see ESI†) a *peri*-interaction energy[16] of α-PIE(P → Al) = −84.9 kJ mol^{-1} was revealed (compare α-PIE = −106.5 kJ mol^{-1} for Ace(PPh$_2$)(AlCl$_2$)).

To investigate in how far this prominent P → Al interaction in **2-Ph** diminishes the Lewis acidity of the alane function, which an external substrate experiences, the Fluoride Ion Affinity (FIA) was calculated and the Gutmann–Beckett acceptor number (AN) was ascertained experimentally (see ESI†). Notably, in spite of the repulsion between the phosphine and the negatively charged fluoridoaluminiate unit in the calculated

Scheme 2   Al–Sn exchange starting from **1-Ph** and MeAlCl$_2$ to give **2-Ph**.
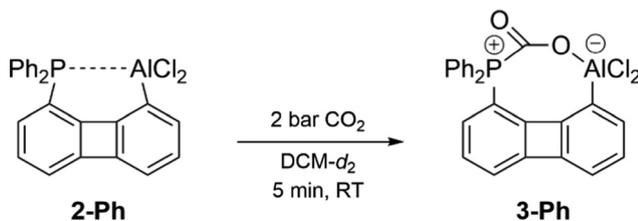
Scheme 3 Activation of CO_2 by **2-Ph**.

product the FIA is 412 kJ mol^{-1}. By reaction with the neutral compound Et_3PO an AN of 82 was determined which is as high as reported for $B(C_6F_5)_3$ and close to $AlCl_3$ (AN = 87)[17] despite the +I effect of the biphenylene substituent and the proximity to the Ph_2P unit. These results exemplify the capability of the P–Al bond to open up when an external donor is presented. Consequently, **2-Ph** reacts with O-donors like Et_2O or THF to the corresponding adducts, and evaporation/heating did not lead back to **2-Ph**. Interestingly, unlike in case of the xanthene-based analogue,[10,18] no ring-opening reaction of THF was observed, which confirms the importance of the appropriate distance for a certain activation process.

Next, we investigated the capability of **2-Ph** to activate CO_2 – a benchmark substrate in FLP chemistry.[1,8,9a,9b,19] Therefore, a solution of **2-Ph** in DCM-d_2 was treated with 2 bar CO_2. ^1H and $^{31}P\{^1H\}$ NMR spectra recorded subsequently confirmed the full conversion of **2-Ph** and the selective formation of a new product (Scheme 3). In the ATR-IR spectrum recorded for the solid isolated after evaporation of all volatiles two bands in the characteristic carbonyl region were found at $\nu = 1720$ cm^{-1} and 1643 cm^{-1} ($\nu = 1680$ cm^{-1} and 1598 cm^{-1} when $^{13}CO_2$ was used) underpinning the formation of the CO_2 adduct **3-Ph**.

The solid-state structure of **3-Ph** determined by single crystal XRD analysis revealed the successful fixation of CO_2 within the reaction pocket generated in the course of breaking the P–Al bond (Fig. 3). As expected, a P–C and an Al–O bond have been

formed but in contrast to the CO_2 adduct of the previously reported xanthene-based P/Al-FLP[10] the second oxygen atom doesn't interact with another Al center. Hence, the CO_2 molecule has been activated asymmetrically through breaking of one of the π-bonds, so that one C–O bond (1.28 Å) is longer than the other (1.20 Å). Even under high vacuum CO_2 is not released again. Having proven the general capability of FLP **2-Ph** to react with small molecules despite the strong P → Al interaction a more challenging substrate, lacking an O-donor was targeted. We considered allene to be an interesting candidate, since – in spite of a rich chemistry of allenes reacting with Lewis acidic boranes, particularly in hydroboration reactions with $HB(C_6F_5)_2$[20] – the activation of simple allenes by an FLP remains unknown, which is particularly surprising as reports on the conversion of isolated C=C and C≡C bonds are extensive.[1c] In a study of Melen and coworkers $B(C_6F_5)_3$ and a bulky phosphine were added to different 2,3-butadienones, leading to transformations, in which the ketone group plays an active role.[21] The reactivity of non-activated (and activated) allenes towards a P/B-FLP has only been investigated in a predictive computational study but has not been achieved experimentally.[22]

When a sample of **2-Ph** in C_6D_6 was exposed to a pressure of 1.6 bar propadiene a very slow reaction at room temperature could be observed as indicated by a rising resonance at $\delta = 23.0$ ppm in the $^{31}P\{^1H\}$ NMR spectrum. Heating to 70 °C accelerates the reaction, leading to full consumption of **2-Ph** within 3 days. In the ^1H NMR spectrum, three doublets were found at chemical shifts of $\delta = 6.59$, 5.00, and 1.65 ppm with ^1H–^{31}P coupling constants of $J = 53.3$, 24.4, and 19.8 Hz, respectively, and an integral ratio of 1 : 1 : 2. These spectroscopic data are in line with the regioselective formation of an allene-FLP-complex, **4-Ph** (Scheme 4). Attempts to isolate the product failed, however, from the crude oil obtained after evaporation of the reaction mixture crystals suitable for XRD analysis formed after standing for several weeks.

The solid-state structure (Fig. 4) reveals that the allene has indeed been captured in such a way that the phosphine binds to the central carbon atom of the allene and the aluminum center to a terminal one. As can be seen from the C–C bond length (1.500(2) Å) between these carbon atoms, the activation of the allene by the FLP cleaves the π-bond. Compared to free allene (d(C=C) = 1.308 Å) also the C19–C27 bond (1.338(2) Å) is elongated. This can be rationalized by the increasing p-character of the central carbon atom which rehybridizes from sp to sp^2, adapting a trigonal planar coordination sphere.
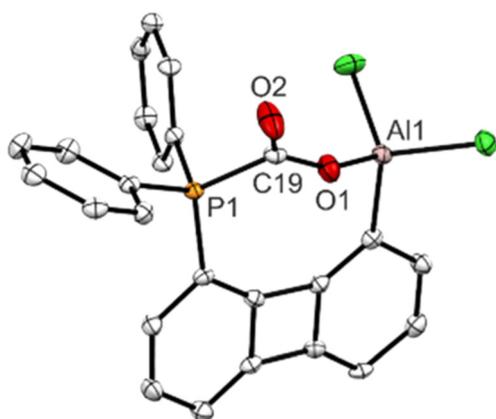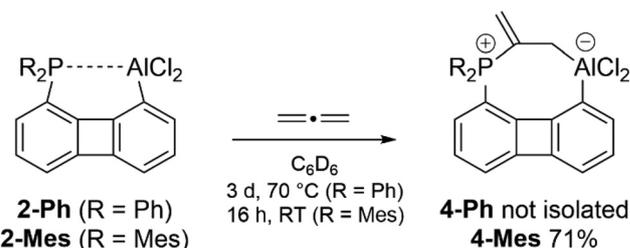

Fig. 3 Molecular structure determined for one of the two independent molecules within the asymmetric unit of **3-Ph**. H atoms omitted for clarity; thermal ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: P1–C19 1.883(3), C19–O1 1.281(3), C19–O2 1.202(3), O1–Al1 1.784(2), O1–C19–O2 128.2(3), Al1–O1–C19 150.5(2).

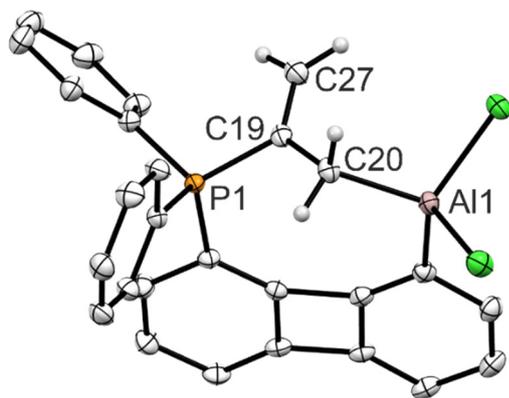**Scheme 4** Activation of propadiene by **2-R**.

Fig. 4 Molecular structure of **4-Ph**. H atoms omitted for clarity except for the allene unit; thermal ellipsoids drawn at the 50% probability level. Selected bond lengths [Å] and angles [°]: P1–C19 1.811(2), C20–Al1 1.976(2), C20–C19–C27 125.8(2).

The carbon atom bound to aluminum changes from a sp^2 to a sp^3 hybridization.

We were able to isolate and fully characterize the product of allene activation when the substituents of the phosphine in **1-Ph** were altered from phenyl to mesityl. Following the route described above, **1-Mes** could be converted into **2-Mes** by MeAlCl$_2$ and the resulting solution was exposed to a slight excess of C$_3$H$_4$. Within 16 hours at room temperature the allene adduct **4-Mes** precipitated from the reaction mixture and could be isolated in 71% yield. The far more rapid reaction found for **2-Mes** toward allene in contrast to **2-Ph** can be explained by the fact that the mesityl substituents, cause both a weaker interaction between the P and Al centers due to their increased steric demand and an improved nucleophilicity of the phosphorus atom due to the electron donating properties.

In conclusion, we report here the convenient synthesis of an intramolecular P/Al-based FLP on the biphenylene backbone *via* aluminum–tin exchange. It was shown that by steric strains the reactive centers can overcome the large distance spanned by the scaffold to coordinatively saturate the highly Lewis acidic AlCl$_2$ moiety. Despite this interaction the FLP exhibits pronounced reactivity toward a common substrate like carbon dioxide and also binds allene which has not been activated by an FLP before. Future research will aim at exploiting the latter for organic transformations.

Conflicts of interest

There are no conflicts to declare.

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