

# C–H Bond Activation by Radical Ion Pairs Derived from $R_3P/Al(C_6F_5)_3$ Frustrated Lewis Pairs and $N_2O$

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## Supporting Information

**ABSTRACT:**  $Al(C_6F_5)_3/R_3P$  [ $R = tert$ -butyl ( $tBu$ ), mesityl ( $Mes$ ), naphthyl ( $Nap$ )] frustrated Lewis pairs react with  $N_2O$  to form species having the formula  $R_3P(N_2O)Al(C_6F_5)_3$ , which react with additional alane to generate proposed frustrated radical ion pairs formulated as  $[R_3P^+][(\mu-O\cdot)(Al(C_6F_5)_3)_2]$  that can activate C–H bonds. For  $R = tBu$ , C–H activation of a  $tBu$  group affords  $[tBu_2PMe(C(CH_2)Me)][(\mu-OH)(Al(C_6F_5)_3)_2]$ . In the case of  $R = Mes$ , the radical cation salt  $[Mes_3P^+][(\mu-HO)(Al(C_6F_5)_3)_2]$  is isolated, while for  $R = Nap$ , the activation of toluene and bromobenzene gives  $[(Nap)_3PCH_2Ph][(\mu-OH)(Al(C_6F_5)_3)_2]$  and  $[(Nap)_3PC_6H_4Br][(\mu-HO)(Al(C_6F_5)_3)_2]$ , respectively.

The activation of C–H bonds has evolved dramatically in the last 30 years.<sup>1–8</sup> A variety of systems offering considerable synthetic utility have been developed. Several mechanistic pathways are known, including direct oxidative addition of C–H bonds at a transition-metal center as well as radical-based processes employing odd-electron transition-metal species. Of the latter type, oxygen-based radical clusters<sup>4</sup> and transition-metal–oxo radicals<sup>9,10</sup> can also participate in hydrogen atom transfer processes, thus effecting C–H bond activation of alkanes. While Tolman has reviewed the metal– $N_2O$  complexes,<sup>11</sup> Chang and co-workers<sup>12,13</sup> have exploited the oxidant  $N_2O$  to generate a reactive Fe(IV) pyrrole–oxo radical to effect C–H bond activations. While the reactivity of main-group radicals has garnered less attention, the team of Warren, Studer, Erker, and Grimme<sup>14,15</sup> has uncovered a fascinating radical derived from the capture of NO by an intramolecular phosphorus–boron-based frustrated Lewis pair (FLP). The resulting stable aminoxyl radicals, such as  $Mes_2PCH_2CH_2B(C_6F_5)_2(NO)$ , were shown to activate C–H bonds as well as initiate radical polymerization reactions.<sup>15</sup>

As part of our own efforts in FLP chemistry,<sup>16</sup> we have previously reported the capture of  $N_2O$  by the FLP combination of  $tBu_3P$  and  $B(C_6F_5)_3$ .<sup>17</sup> The product  $tBu_3P(N_2O)B(C_6F_5)_3$  proved remarkably robust, and indeed, only thermolysis or photolysis of this diamagnetic product resulted in the ejection of  $N_2$  and the formation of the classical Lewis acid–base adduct  $tBu_3POB(C_6F_5)_3$ . Alternatively, the  $PN_2O$  fragment can be transferred to other metal centers.<sup>18,19</sup> In the present study, we show that altering the Lewis acid has a dramatic impact on the chemistry. The analogous species

$R_3P(N_2O)Al(C_6F_5)_3$  are shown to react with additional  $Al(C_6F_5)_3$  to liberate  $N_2$  and generate proposed transient “frustrated radical pairs” comprising phosphoniumyl ( $[R_3P^+]$ ) and  $Al_2$ -oxyl radical anions  $[(\mu-O\cdot)(Al(C_6F_5)_3)_2]^-$ . Such pairs are shown to effect alkyl and aryl C–H bond activations.

Slow addition of  $N_2O$  to a cooled ( $-78$  °C) solution containing an excess of  $tBu_3P$  (2 equiv) to  $Al(C_6F_5)_3$ ·tol in toluene (tol) followed by subsequent workup afforded the product, **1**, in 91% yield. The  $^{31}P\{^1H\}$  NMR spectrum of **1** contained a single peak at 66 ppm, while the  $^{19}F\{^1H\}$  NMR spectrum contained a set of three peaks at  $-121.4$ ,  $-154.0$ , and  $-161.7$  ppm, consistent with the formulation  $tBu_3P(N_2O)Al(C_6F_5)_3$ . This was confirmed by a crystallographic study [see the Supporting Information (SI)] to be the Al analogue of the previously reported P/B derivative  $tBu_3P(N_2O)B(C_6F_5)_3$ . In **1**, the O–Al bond length of 1.820(2) Å is significantly longer than the O–B bond length of 1.543(2) Å<sup>17</sup> in the B analogue. All of the other metric parameters are similar.

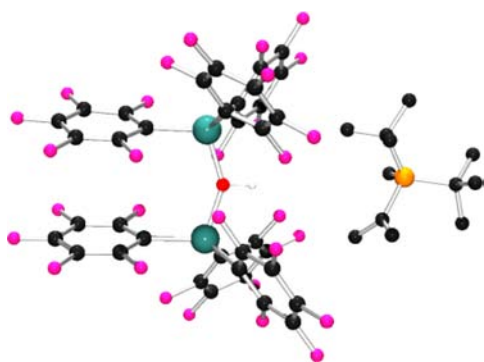
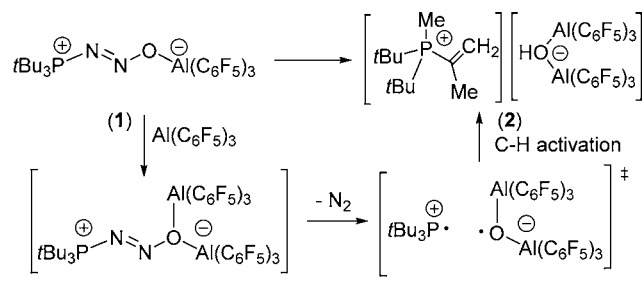
Altering the ratio of  $tBu_3P$  to  $Al(C_6F_5)_3$ ·tol to 1:2 in fluorobenzene and adding  $N_2O$  at  $-40$  °C resulted in the formation and subsequent isolation of a new product, **2**, in 62% yield. This species exhibited a  $^{31}P\{^1H\}$  NMR resonance at 43 ppm and three peaks at  $-122.5$ ,  $-153.5$ , and  $-161.3$  ppm in the  $^{19}F\{^1H\}$  NMR spectrum. The  $^1H$  NMR spectrum consisted of three doublets exhibiting  $^1H$ – $^{31}P$  coupling in a ratio of 18:3:3. In addition, two  $^1H$ – $^{31}P$  doublets at 5.67 and 5.23 ppm and a broad singlet centered at 5.64 ppm were observed.  $^1H$ – $^1H$  and  $^1H$ – $^{13}C$  2D NMR correlation experiments (see the SI) inferred the presence of a P-bound 2-propenyl group at the central carbon. An X-ray crystallographic study confirmed **2** as  $[tBu_2PMe(C(CH_2)Me)][(\mu-OH)(Al(C_6F_5)_3)_2]$  (Scheme 1 and Figure 1). Alternatively, **2** could also be synthesized by addition of  $Al(C_6F_5)_3$ ·tol (1 equiv) to **1**.

In a similar fashion, exposure of a 1:2 solution of  $PMes_3$  ( $Mes = mesityl$ ) and  $Al(C_6F_5)_3$ ·tol in  $C_6D_5Br$  to  $N_2O$  resulted in an intensely deep purple solution. While  $^{19}F\{^1H\}$  and  $^1H$  NMR spectroscopy revealed the resonances attributable to the  $[(\mu-HO)(Al(C_6F_5)_3)_2]^-$  anion, the resonances attributable to the phosphine moiety were largely absent in the  $^1H$  and  $^{31}P$  NMR spectra. This observation, together with the fact that the X-band EPR spectrum of dissolved crystals of the product, **3**, in bromobenzene (Figure 2) revealed a doublet ( $g = 2.0056$ ,  $a_p =$

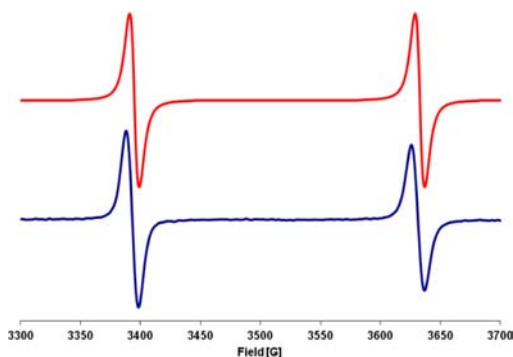
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Scheme 1. Synthesis of 2 from 1

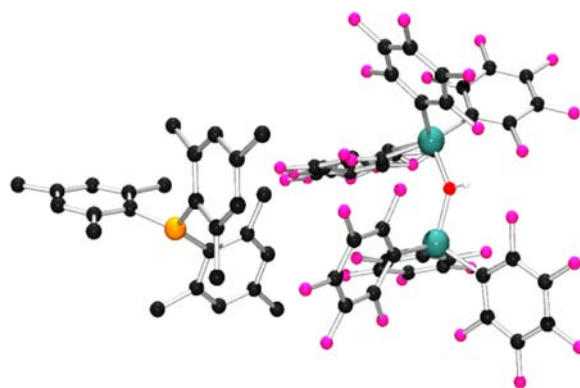


**Figure 1.** POV-Ray depiction of 2. C, black; P, orange; F, pink; Al, teal; O, red; H, white. H atoms, except for the OH hydrogen, have been omitted for clarity.



**Figure 2.** X-band EPR spectrum of 3 in bromobenzene (observed spectrum in blue, simulated spectrum in red;  $g = 2.0056$ ,  $a_p = 239$  G).

239 G), suggested the generation of the phosphoniumyl radical cation<sup>20</sup>  $[\text{Mes}_3\text{P}^{\bullet+}]$  and the formulation of 3 as  $[\text{Mes}_3\text{P}^{\bullet+}][(\mu\text{-HO})(\text{Al}(\text{C}_6\text{F}_5)_3)_2]^-$ . Moreover, the UV-vis spectrum of a dilute sample of 3 in bromobenzene (see the SI) featured strong absorption bands at 286, 382 (max), and 573 nm, similar to literature reports of bulky  $\text{R}_3\text{P}^{\bullet+}$  radicals.<sup>21,22</sup> Careful crystallization at  $-40$  °C yielded deep-purple single crystals of 3. X-ray diffraction studies of 3 (Figure 3) were consistent with the above formulation. The sum of the angles about phosphorus in 3 is  $349.5^\circ$ , which is slightly greater than that observed for previously reported  $[\text{Mes}_3\text{PH}]^+$  salts ( $345.2$  and  $344.7^\circ$ ),<sup>23,24</sup> consistent with the presence of a radical cation.<sup>25</sup> A very recent report described the first examples of structurally characterized phosphoniumyl radical cations, for which the sum of the angles about P range from  $349.2$  to  $359.9^\circ$ .<sup>21</sup> The move toward  $sp^2$  hybridization affords some stabilization of the radical through potential  $\pi$  conjugation to the aryl rings in an analogous fashion to Gomberg's isoelectronic radical,  $\text{Ph}_3\text{C}^{\bullet}$ .<sup>26</sup> An analysis of the solution and anisotropic solid-state EPR



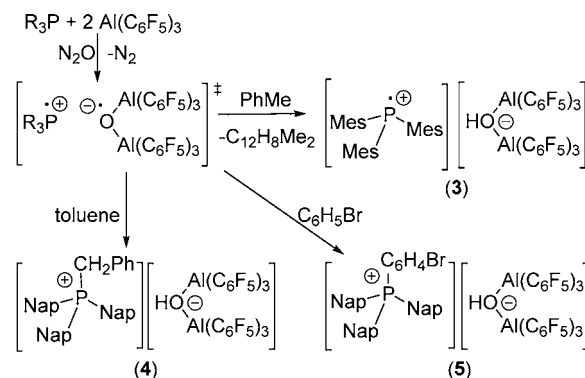
**Figure 3.** POV-Ray depiction of 3. C, black; P, orange; F, pink; Al, teal; O, red; H, white. H atoms, except for the OH hydrogen, have been omitted for clarity.

spectra (see the SI) permitted the total spin density at P to be estimated as 69.6% (5.2% s character, 64.4% p character).

The origin of the H atom in the anion  $[(\mu\text{-HO})(\text{Al}(\text{C}_6\text{F}_5)_3)_2]^-$  in 3 was shown to be the toluene solvent, as monitoring the solution by GC-MS revealed the presence of dimethylbiphenyl and/or phenyltolylmethane isomers, consistent with hydrogen atom abstraction from the solvent by the transient radical anion  $[(\mu\text{-O}^{\bullet})(\text{Al}(\text{C}_6\text{F}_5)_3)_2]^-$ . The use of  $\text{PMes}_3\text{-}d_{27}$  (95% deuteration) in the preparation and subsequent isolation of  $3\text{-}d_{27}$  generated the anion  $[(\mu\text{-DO})(\text{Al}(\text{C}_6\text{F}_5)_3)_2]^-$  in  $\sim 10\%$  yield, as evidenced by  $^2\text{H}$  NMR spectroscopy. The  $^31\text{P}\{^1\text{H}\}$  and  $^1\text{H}\text{-}^2\text{H}$  NMR spectra revealed the presence of a corresponding amount of the  $[\text{Mes}_2\text{P}(\text{CD}_2\text{C}_6\text{H}_2(\text{CD}_3)_2)]^+$  cation. These data demonstrate that hydrogen (deuterium) abstraction from the phosphoniumyl radical cation by the  $[(\mu\text{-O}^{\bullet})(\text{Al}(\text{C}_6\text{F}_5)_3)_2]^-$  radical anion is also possible but occurs to a limited extent under the reaction conditions. It should be noted that Meyer and Berben<sup>27</sup> recently reported hydrogen atom abstraction by  $\text{Al}(\text{III})\text{-oxo}$  species.

In a similar manner, exposure of a 1:2 mixture of  $(\text{Nap})_3\text{P}$  (Nap = naphthyl) and  $\text{Al}(\text{C}_6\text{F}_5)_3\cdot\text{tol}$  in  $\text{C}_6\text{H}_5\text{Br}$  to 1 atm  $\text{N}_2\text{O}$  gave a mixture of products attributable to hydrogen atom abstraction. In this case, the products of C-H activation could not be individually isolated. Nonetheless, the NMR data support the formulation of one of the products as  $[(\text{Nap})_3\text{PCH}_2\text{Ph}][(\mu\text{-OH})(\text{Al}(\text{C}_6\text{F}_5)_3)_2]$  (4) (Scheme 2). In this case, the nature of the cation was confirmed via independent synthesis of the bromide salt,  $[(\text{Nap})_3\text{PCH}_2\text{Ph}]$

Scheme 2. Syntheses of 3–5



[Br] (see the SI). This postulate was further supported by the exposure of a 1:2 mixture of  $(\text{Nap})_3\text{P}$  and  $\text{Al}(\text{C}_6\text{F}_5)_3\cdot\text{PhH}$  in  $\text{C}_6\text{D}_5\text{Br}$  to 1 atm  $\text{N}_2\text{O}$ , which afforded **5** in 50% isolated yield. This species gives rise to a peak at 23 ppm in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum and  $^{19}\text{F}$  NMR signals consistent with the presence of the  $[(\mu\text{-HO})\text{Al}(\text{C}_6\text{F}_5)_3)_2]^-$  anion. The cation was unambiguously identified by X-ray diffraction, which affirmed the formulation of **5** as  $[(\text{Nap})_3\text{PC}_6\text{H}_4\text{Br}][(\mu\text{-HO})\text{Al}(\text{C}_6\text{F}_5)_3)_2]$  (Figure 4).



**Figure 4.** POV-Ray depiction of **5**. C, black; P, orange; F, pink; Al, teal; O, red; Br, scarlet; H, white. H atoms, except for the OH hydrogen, have been omitted for clarity.

The above observations infer that these reactions proceed via the generation of a transient radical pair<sup>28</sup> of the form  $[\text{R}_3\text{P}\cdot][(\mu\text{-O}\cdot)\text{Al}(\text{C}_6\text{F}_5)_3)_2]$ . In the synthesis of **2**, the monitored reaction mixtures were EPR-silent, suggesting that such a radical pair is rapidly quenched by hydrogen atom abstraction from a *t*Bu group of the transient phosphoniumyl radical cation, prompting rearrangement to give the  $[\text{tBu}_2\text{PMe}(\text{C}(\text{CH}_2)\text{Me})]$  cation of **2**. In addition, this chemistry suggests that the coordination of a second alane to the O of **1** prompts  $\text{N}_2$  release and the formation of the radical ion pair, which then effects the observed C–H activation. It is noteworthy the analogous boron derivative of **1**<sup>17</sup> does not react with excess borane, presumably because steric conflict disfavors coordination of a second borane to oxygen. It is also noteworthy that the radical pair  $[\text{R}_3\text{P}\cdot][(\mu\text{-O}\cdot)\text{Al}(\text{C}_6\text{F}_5)_3)_2]$  is not accessible from phosphine oxide and alane, which instead afford the simple adducts  $(\text{R}_3\text{PO})\text{Al}(\text{C}_6\text{F}_5)_3$ . The above mechanistic proposition for the present chemistry is further supported by the isolation of radical cation salt **3** in addition to the C–H activation products **4** and **5**. It should be noted that the involvement of phosphorus radical cations in C–H activation of benzene has been reported previously, as the radical cation  $[\text{Ph}_3\text{P}\cdot]^+$  generated by anodic oxidation in the presence of benzene affords the phosphonium cation  $[\text{Ph}_4\text{P}]^+$ .<sup>29</sup>

In conclusion, the combination of phosphines and  $\text{Al}(\text{C}_6\text{F}_5)_3$  under  $\text{N}_2\text{O}$  generates highly reactive radical salts that can effect C–H bond-cleavage reactions. The generated  $\text{Al}_2$ -oxyl radical anion abstracts hydrogen atoms from C–H bonds, while the phosphoniumyl radical cation may trap the resulting C-based radical to generate a phosphonium cation. We are continuing to probe radical processes in FLP chemistry, in particular those that can effect the homolytic activation of strong bonds, targeting applications in stoichiometric and catalytic processes.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental procedures, spectral data, and crystallographic data (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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