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## SET processes in Lewis acid–base reactions: the tritylation of N-heterocyclic carbenes†

Zhaowen Dong,<sup>a</sup> Cristian Pezzato,<sup>a</sup> Andrzej Sienkiewicz,<sup>b</sup> Rosario Scopelliti,<sup>a</sup> Farzaneh Fadaei-Tirani<sup>a</sup> and Kay Severin<sup>a\*</sup>

Reactions between N-heterocyclic carbenes (NHCs) and the trityl cation,  $[\text{Ph}_3\text{C}]^+$ , give covalent adducts of type  $[\text{NHC}-\text{CPh}_3]^+$  and/or  $[\text{NHC}-\text{C}_6\text{H}_5-\text{CPh}_2]^+$ . EPR spectroscopy, UV-Vis analyses, and trapping experiments imply that adduct formation involves carbene radical cations and the trityl radical. The results demonstrate that single electron transfer (SET) processes should be considered for reaction of NHCs with oxidizing Lewis acids.

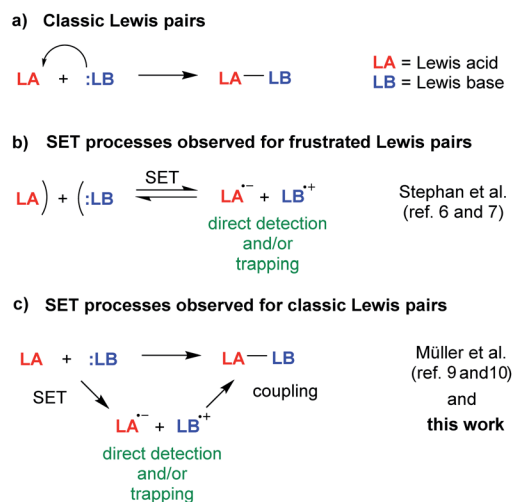
## Introduction

The classification of electron-pair donors as bases and electron-pair acceptors as acids was proposed by G. N. Lewis in 1923.<sup>1</sup> The concept gained influence in the 1940s, and today it is widely used as a systemizing tool in chemical teaching and research.<sup>2</sup> Reactions between Lewis acids (LAs) and bases (LBs) are typically described as two-electron processes (Scheme 1a). However, the possible involvement of single electron transfer (SET) processes in reactions of this kind has been discussed early on.<sup>3</sup> Experimental evidence for the participation of radicals was obtained for frustrated Lewis pairs (Scheme 1b).<sup>4–8</sup> Stephan and co-workers have reported that mixtures of  $\text{PMes}_3$  and  $\text{E}(\text{C}_6\text{F}_5)_3$  ( $\text{E} = \text{B}, \text{Al}$ ) are in equilibrium with the frustrated radical pair  $[\text{Mes}_3\text{P}]^{\cdot+}$  and  $[\text{E}(\text{C}_6\text{F}_5)_3]^{\cdot-}$ .<sup>6</sup> The former was detected by EPR spectroscopy, whereas the latter was evidenced by trapping experiments. In a follow-up study, they were able to show that the  $\text{PMes}_3/\text{B}(\text{C}_6\text{F}_5)_3$  pair is able to cleave the O–O bond of benzoyl peroxide in a homolytic fashion.<sup>7</sup> These results corroborate the radical reactivity of this FLP. Recently, the group of Müller described classic Lewis pair systems, for which SET pathways are also of relevance (Scheme 1c). A mixture of a phosphine and a solvent-stabilized trialkylsilylium ion was found to give radicals, even though silylphosphonium adducts can form.<sup>9</sup> Furthermore, they were able to show that the reaction between a germylene Lewis base and  $\text{B}(\text{C}_6\text{F}_5)_3$  is initiated by a SET process.<sup>10</sup> The intermediates germylene radical cation and  $[\text{B}(\text{C}_6\text{F}_5)_3]^{\cdot-}$  could be detected by EPR spectroscopy.

Below, we provide experimental evidence for the relevance of SET processes in reactions of NHCs with the Lewis acid  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ . In particular, we show that adduct formation involves the formation of a carbene radical cation and the trityl radical.

## Results and discussion

N-heterocyclic carbenes are not only important ligands in transition metal chemistry,<sup>11</sup> but they are also used extensively as Lewis bases in main group chemistry.<sup>12</sup> For the present study, we have investigated the reaction of NHCs with the Lewis acid  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ . When 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene (IDipp, **1a**) was allowed to react with the trityl salt in toluene at  $-40^\circ\text{C}$ , we observed the clean formation of adduct **2a**



**Scheme 1** The formation of classic Lewis pairs via a 2-electron process (a), and SET processes observed for frustrated (b) and classic (c) Lewis pairs.

<sup>a</sup>Institut des Sciences et Ingénierie Chimiques, École Polytechnique Fédérale de Lausanne (EPFL), 1015 Lausanne, Switzerland. E-mail: kay.severin@epfl.ch

<sup>b</sup>Institute of Physics, EPFL, Switzerland

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(Scheme 2). The structure of **2a** was established by NMR spectroscopy and by single crystal X-ray diffraction (XRD) analysis (see the ESI†). The formation of **2a** was expected, since a structurally related compound was reported by the group of Stephan for the reaction of 1,3-di-*tert*-butylimidazol-2-ylidene (ItBu, **1b**) and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ .<sup>13</sup>

When the reaction between **1a** and the trityl salt was performed in toluene at room temperature, side products were formed, as revealed by NMR spectroscopic analysis of the reaction mixture. Adduct **2a** was still the main product (76%), but the imidazolium salt  $[\text{IDipp-H}][\text{B}(\text{C}_6\text{F}_5)_4]$  (**3a**) was formed in 24% yield, along with a small amount of triphenylmethane,  $\text{Ph}_3\text{CH}$  (~5%).

During our investigations, we were intrigued by the following observation: when **1a** was added to a solution of the trityl salt (either RT or  $-40^\circ\text{C}$ ), the color of the solution turned from yellow to purple. The purple color quickly faded away, and at the end of the reaction, a nearly colorless solution was observed (Fig. 1a).

When the beginning of the reaction was followed by UV-vis spectroscopy at room temperature, one could observe a gradual decrease of the band at 438 nm, which can be attributed to the trityl cation. Simultaneously, a band 343 nm and a weaker band at 591 nm started to grow (Fig. 1c). The latter disappeared with time, and after 1 min, no significant absorption at wavelengths higher than 500 nm could be observed. This finding is in line with the fact that solutions of the products are either colorless or weakly yellow. When the pink solution was exposed to air, the bands at 343 and 591 nm disappeared nearly instantaneously (ESI, Fig. S8†).

The results imply that adduct formation proceeds *via* one (or more) short-lived intermediate(s). In order to examine if radicals are involved, we investigated mixtures of **1a** and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  by EPR spectroscopy. We were able to detect a signal with a complex hyperfine coupling, which can be attributed to the trityl radical (Fig. 1b).<sup>16</sup> The formation of  $[\text{Ph}_3\text{C}]^\bullet$  provides an explanation for the absorption at 343 nm, because the trityl radical is known to have a band in that region.<sup>17</sup> We propose that the purple color (broad band at 591 nm), which we

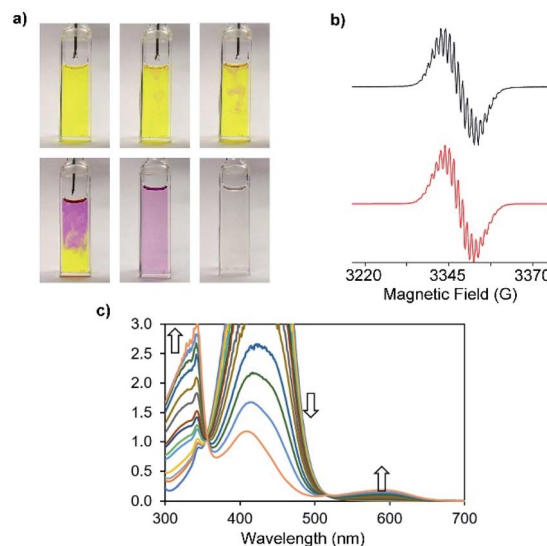
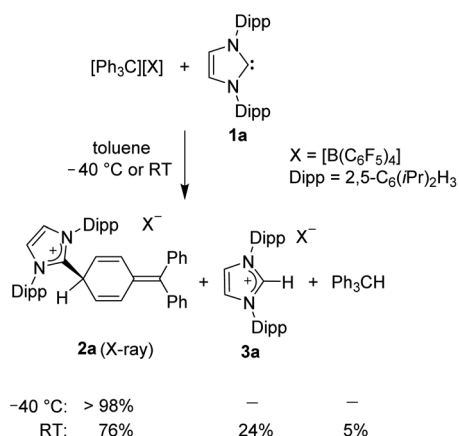


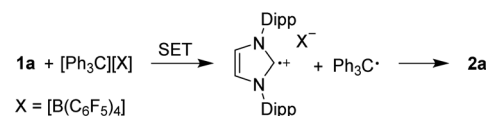
Fig. 1 (a) Color of a solution of  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in chlorobenzene<sup>14</sup> upon dropwise addition of a solution of IDipp; (b) experimental (black lines) and simulated (red lines) EPR spectra of the trityl radical in chlorobenzene ( $g = 2.0025$ ,  $A(\text{o-H}) = 2.6$  G,  $A(\text{m-H}) = 1.1$  G,  $A(\text{p-H}) = 2.8$  G),<sup>15</sup> and (c) evolution of the UV-vis spectra of a chlorobenzene solution containing **1a** and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ .

observed at the beginning of the reaction, is due to  $[\mathbf{1a}]^{+\bullet}$ . This assumption is substantiated by the following control experiment: when IDipp was deliberately oxidized with  $[\text{NO}][\text{SbF}_6]$  in toluene at room temperature, a short-lived purple color was also observed (for details, see ESI†). The main product of this reaction was the imidazolium salt  $[\text{IDipp-H}][\text{SbF}_6]$ , which is presumably formed by reaction of the intermediate  $[\mathbf{1a}]^{+\bullet}$  with the solvent (see Fig. S14†). Taken together, the experimental data suggest that the reaction between **1a** and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  proceeds *via* single electron transfer to give  $[\text{Ph}_3\text{C}]^\bullet$  and  $[\mathbf{1a}]^{+\bullet}$  (Scheme 3).<sup>18</sup> At  $-40^\circ\text{C}$ , selective cross-coupling results in formation of adduct **2a**, whereas hydrogen atoms abstraction becomes a competing pathway for reactions performed at room temperature. The carbene radical cation  $[\mathbf{1a}]^{+\bullet}$  is more reactive than the persistent  $[\text{Ph}_3\text{C}]^\bullet$ ,<sup>19</sup> which provides an explanation that we were not able to detect the former by EPR spectroscopy.

It is worth noting that NHC-based radical cations have been suggested as intermediates of reactions between NHCs and oxidants such as tetracyanoethylene,<sup>20</sup> ferrocenium salts,<sup>20</sup> and  $\text{PhI}(\text{OTf})_2$ .<sup>21</sup> The products of these reactions are either imidazolium salts (formed *via* H atom abstraction from the solvent) or dicationic dimers (formed by homo-coupling of the NHC radical cations). In our case, cross-coupling of  $[\text{Ph}_3\text{C}]^\bullet$  and  $[\mathbf{1a}]^{+\bullet}$  is



Scheme 2 Reaction of IDipp (**1a**) with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in toluene.



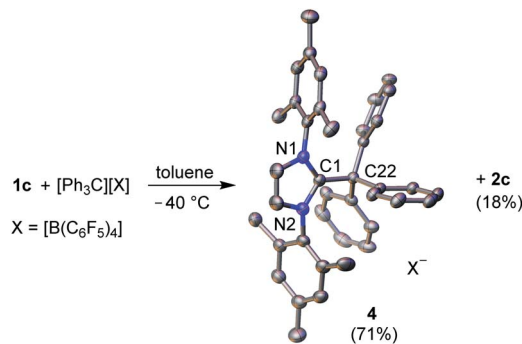
Scheme 3 Formation of the Lewis acid–base adduct **2a** proceeds *via* the radicals  $[\text{Ph}_3\text{C}]^\bullet$  and  $[\mathbf{1a}]^{+\bullet}$ .

strongly favored over homo-coupling reactions. We have analyzed reaction mixtures by mass spectroscopy, and we were able to detect peaks for the coupling adduct **2a** and the imidazolium salt **3a**, but not for a dicationic dimer  $[(\mathbf{1a})_2]^{2+}$ .

Further evidence for the formation of radicals was obtained by trapping experiments with the hydrogen atom donors THF or  $\text{Ph}_3\text{SnH}$  (Table 1). When the reaction between **1a** and the trityl salt was performed in the presence of 25 vol% THF, adduct formation was impeded, and the imidazolium salt **3a** was formed in 73% yield, along with equimolar amounts of  $\text{Ph}_3\text{CH}$ . Similar results were observed for reactions with  $\text{Ph}_3\text{SnH}$ . When a solution of  $\text{Ph}_3\text{SnH}$  in toluene was added to an equimolar mixture of **1a** and  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ , the dominant imidazolium-based product was **3a** (42%). Furthermore, we were able to detect  $\text{Ph}_3\text{SnSnPh}_3$  by  $^{119}\text{Sn}$  NMR spectroscopy ( $\delta^{119}\text{Sn} = 131.1$ , ESI, Fig. S16b†). The formation of the distannane is further evidence for the involvement of radicals.<sup>6,22</sup> We noted that the starting materials (**1a** and the trityl salt) do also react with  $\text{Ph}_3\text{SnH}$ . However, these reactions gave alternative products, and  $\text{Ph}_3\text{SnSnPh}_3$  was not observed.

Next, we re-examined the addition of *ItBu* (**1b**) to  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ . When the reaction was performed in toluene at  $-40^\circ\text{C}$ , the known coupling product **2b**<sup>13</sup> was obtained in nearly quantitative yield. In contrast, only a small amount of **2b** was formed when the reaction was carried out at room temperature in the presence of 25 vol% THF (Table 1 and ESI†). Under these conditions, the main products were the imidazolium salt  $[\text{ItBu-H}][\text{B}(\text{C}_6\text{F}_5)_4]$  (**3b**, characterized also by X-ray crystallography) and  $\text{Ph}_3\text{CH}$  (both 79%). Using  $\text{Ph}_3\text{SnH}$  as radical scavenger, the yield of the imidazolium salt was even higher (87%). As in the case of reactions with IDipp, the dimer  $\text{Ph}_3\text{SnSnPh}_3$  was detected by  $^{119}\text{Sn}$  NMR spectroscopy.

Similar results were obtained for reactions of IMes (**1c**) with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in the presence of the radical scavenger THF: the main products were the imidazolium salt **3c** and  $\text{Ph}_3\text{CH}$  (Table 1), indicating an initial SET process between the carbene and the trityl salt.<sup>23</sup> However, reactions performed in toluene at  $-40^\circ\text{C}$  gave a surprising result. The expected adduct **2c** was only formed in 18% yield. The main product (71%) was the



**Scheme 4** Reaction of IMes (**1c**) with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in toluene. The graphic representation of the cation of **4** is based on a crystallographic analysis. The yields were determined by  $^1\text{H}$  NMR spectroscopy.

isomeric coupling product **4**, with a C–C bond to the central carbon atom of the trityl group (Scheme 4). The formation of **4** can be explained by the reduced steric demand of the mesityl wingtip groups.<sup>24</sup>

## Conclusions

To conclude, we have investigated the formation of adducts between N-heterocyclic carbenes and the trityl cation, a mildly oxidizing Lewis acid.<sup>23</sup> EPR spectroscopy, UV-vis analyses, and trapping experiments indicate that the reactions proceed *via* an initial SET step, giving highly reactive carbene radical cations and the trityl radical. The adducts are then formed by selective cross-coupling. So far, there is scarce experimental evidence for the involvement of radical processes in Lewis acid–base reactions, in particular for systems which form stable acid–base adducts.<sup>4,6–10</sup> The results demonstrate that SET chemistry is a viable option for reactions of NHC Lewis bases with oxidizing Lewis acids. For the present study, we have focused on the trityl cation, but our findings should be considered for reactions of NHCs with oxidizing metal ions/complexes.<sup>25</sup>

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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**Table 1** Reactions of NHCs **1** with  $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$  in the presence of the radical scavengers THF and  $\text{Ph}_3\text{SnH}$

	Radical scavenger	Yield of <b>3</b> <sup>a</sup>
<b>1a</b> (R = Dipp)	THF (25 vol%)	73%
<b>1a</b> (R = Dipp)	$\text{Ph}_3\text{SnH}$ (2 equiv.)	42%
<b>1b</b> (R = <i>t</i> Bu)	THF (25 vol%)	79%
<b>1b</b> (R = <i>t</i> Bu)	$\text{Ph}_3\text{SnH}$ (2 equiv.)	87%
<b>1c</b> (R = Mes)	THF (25 vol%)	63%

<sup>a</sup> Yields were determined by  $^1\text{H}$  NMR spectroscopy.



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