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# Aryldiazonium Salts as Nitrogen-Based Lewis acids: Facile Synthesis of Tuneable Azophosphonium Salts

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**Abstract:** Inspired by the commercially available azoimidazolium dyes (e.g., Basic Red 51) that can be obtained from aryldiazonium salts and N-heterocyclic carbenes, we developed the synthesis of a unique set of arylazophosphonium salts. A range of colours was obtained by applying readily tuneable phosphine donor ligands and *para*-substituted aryldiazonium salts as nitrogen-based Lewis acids. With cyclic voltammetry, a general procedure was designed to establish whether the reaction between a Lewis acid and Lewis base occurs via single-electron transfer or electron-pair transfer.

The metal-free activation and functionalization of dinitrogen is one of the key challenges of modern main-group chemistry.<sup>1,2</sup> The low-lying N<sub>2</sub>  $\sigma$  orbital (HOMO) and high-lying  $\pi^*$  orbital (LUMO) makes dinitrogen a weak Lewis base and a weak Lewis acid and, therefore, a relatively inert substrate (Figure 1).<sup>2c</sup> Inspired by the recently reported interaction of boranes with metal-N2 complexes enabling facile N-protonation,<sup>3</sup> borylation and silylation,<sup>4</sup> Stephan and co-workers demonstrated that diphenyldiazomethane, a formal diphenylcarbene-N2 adduct, can function as a Lewis base (HOMO: -7.31 eV; Figure 1) forming a labile adduct with  $B(C_6F_5)_3$ .<sup>5</sup> While the direct interaction of dinitrogen with boranes has only been observed spectroscopically under forcing conditions,<sup>6</sup> the use of transient borylenes afforded a stable bis(borylene)-N<sub>2</sub> complex as recently reported by Braunschweig et al.7 We were intrigued by the reaction of the strongly Lewis acidic phenyl cation with N2 that affords the phenyldiazonium ion in cryogenic argon matrices,8 and found that the planar C<sub>6</sub>H<sub>5</sub>+ activates N<sub>2</sub> by greatly lowering its  $\pi^*$  acceptor orbital (LUMO: from 1.30 (N<sub>2</sub>) to -6.24 eV; see Figure 1). This makes aryldiazonium salts suitable nitrogen-based Lewis acids,9 which we were keen on investigating.

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**Figure 1.** Lewis acid ( $C_6H_5^+$ ) and base ( $Ph_2C$ ) augmented activation of  $N_2$ , including HOMO (bottom) and LUMO (top) energies (in eV) calculated at the  $\omega$ B97X-D/6-311+G(d,p) level of theory.<sup>[10]</sup>



Figure 2. Reported aryldiazonium-phosphine adducts.

N-coordination of diazonium salts to Lewis basic Nheterocyclic carbenes is well established affording the strongly coloured. industrially produced azoimidazolium salts [RN<sub>2</sub>(NHC)][X] (X = e.g., CI, BF<sub>4</sub>, PF<sub>6</sub>).<sup>11</sup> Surprisingly, to date the corresponding azoammonium salts [RN<sub>2</sub>(NR<sub>3</sub>)][X] are unknown,<sup>12</sup> while the phosphine-diazonium Lewis adducts are barely studied. So far, Horner and Stöhr postulated the red azophosphonium chlorides A (R = H, Me, Cl, NO<sub>2</sub>, CO<sub>2</sub>H, OMe, OC(O)Me; Figure 2) as unstable species<sup>13</sup> that are susceptible to N<sub>2</sub> elimination affording the corresponding arylphosphonium salts [ArPPh<sub>3</sub>][Cl].<sup>14</sup> Later, Yasui et al. found that aryldiazonium tetrafluoroborates are readily dediazoniated by triphenylphosphine via single-electron transfer, when mixed in alcoholic solvents at room temperature.<sup>15,16</sup> Flower et al. synthesized **B**, but only reported its <sup>31</sup>P NMR resonance ( $\delta^{31}$ P{<sup>1</sup>H} = 40; R = 6-naphthalen-2-ol),<sup>17</sup> and Wokaun and co-workers characterized C only spectroscopically (R = CI, CN, SO<sub>2</sub>NH<sub>2</sub>, C(O)OEt; Figure 2).<sup>18</sup> Herein, we report on the facile synthesis of readily tuneable azophosphonium salts, simply from phosphines and aryldiazonium tetrafluoroborates in

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acetonitrile, and provide detailed mechanistic insight by experimental and computational means. The related reactions of phenyldiazonium tetrafluoroborate with tertiary amines are also investigated.



Scheme 1. Synthesis of arylazophosphonium tetrafluoroborates 1 and 2a–e and molecular structure of  $[(C_6H_5)N_2(PfBu_3)][BPh_4]$  (2a-BPh\_4; displacement ellipsoids are set at 30% probability, hydrogen atoms and the noncoordinating BPh\_4 anion are omitted for clarity, one disorder component is shown). Selected bond lengths [Å] and torsion angles [°] (values for the second disorder component in square brackets): P1–N1A 1.742(5) [1.766(7)], N1A–N2A 1.245(6) [1.245(6)], N2A–C1A 1.437(7) [1.439(8)]; P1–N1A–N2A–C1A 173.4(7) [-167.3(11)].

We found that treatment of the phenyldiazonium salt [PhN2][BF4]<sup>19</sup> with triphenylphosphine (1.0 equiv) in acetonitrile at 0 °C afforded after work-up the red azophosphonium salt  $[PhN_2(PPh_3)][BF_4]$  1 ( $\delta^{31}P\{^{1}H\}$  = 39.4; Scheme 1;  $\Delta E = -43.5$ kcal·mol<sup>-1</sup> at the ωB97X-D/6-311+G(d,p) level of theory)<sup>10</sup> in near quantitative yield; only a minor byproduct could be detected by <sup>31</sup>P NMR spectroscopy (~2%;  $\delta^{31}P{^1H} = 43.9$  and 52.5,  ${^3J_{P,P}} =$ 18.8 Hz)<sup>10</sup> that we tentatively ascribed to bis-phosphine adduct [PhN(PPh<sub>3</sub>)N(PPh<sub>3</sub>)][BF<sub>4</sub>].<sup>20</sup> As Horner and Stöhr indicated<sup>13</sup> 1 is unstable, both in solution and in the solid state,<sup>10</sup> therefore we resorted to the stronger and sterically more encumbered donor tritert-butylphosphine that according to DFT calculations at @B97X-D/6-311+G(d,p) should provide a more stable product ( $\Delta E = -53.2$ kcal·mol<sup>-1</sup>).<sup>10</sup> The reaction of phenyldiazonium tetrafluoroborate with tBu<sub>3</sub>P (1.1 equiv) in acetonitrile resulted in an immediate colour change from colourless to pink and afforded azophosphonium salt  $[PhN_2(PtBu_3)][BF_4]$  **2a**  $(\delta^{31}P\{^{1}H\} = 69.4;$ Scheme 1) as the sole product in 95% isolated yield. Gratifyingly, this cationic Lewis adduct is stable towards air, moisture and even an aqueous 2M HCl solution (only the tetrafluoroborate anion hydrolysed over time).<sup>21</sup> The molecular structure of 2a (Scheme 1),<sup>22,23</sup> determined by X-ray crystal structure analysis of suitable crystals of its tetraphenylborate analogue (obtained after anion exchange with NaBPh<sub>4</sub> in DCM),<sup>10</sup> displays an almost planar (P1-N1-N2-C1 173.4(7)) trans arylazophosphonium moiety with a

disordered azo group. The C–N and N–N bond lengths (1.437(7) and 1.245(6) Å, respectively) are comparable to the ones of the related arylazoimidazolium borates [ArN<sub>2</sub>(IMes)][BPh<sub>4</sub>] (Ar = Mes, *o*/*p*-ClC<sub>6</sub>H<sub>4</sub>) reported by Severin et al. (C–N: 1.411(2)/1.395(4)/1.455(13) and N–N: 1.265(2)/1.266(9)/1.24(2) Å, respectively),<sup>11e</sup> illustrating that in these cationic azo dyes phosphines behave similar to carbenes.

As the colour of the arylazophosphonium salts can be readily tuned by changing the donor ligand (1 (L = PPh<sub>3</sub>): red, 2a  $(L = tBu_3P)$ : pink), we next investigated the influence of the parasubstituent on the arene ring on the photophysical properties of 2. Treatment of the 4-substituted phenyldiazonium salts [(p-R- $C_6H_4N_2$ [BF<sub>4</sub>] (R = NO<sub>2</sub> (b), Br (c), OMe (d), NMe<sub>2</sub> (e))<sup>19</sup> with tritert-butylphosphine (1.1 equiv) in acetonitrile afforded the intensely coloured (from purple to red/brown) arylazophosphonium salts [(p-R-C<sub>6</sub>H<sub>4</sub>)N<sub>2</sub>(PtBu<sub>3</sub>)][BF<sub>4</sub>] 2b-e in 87-96% isolated yield (Scheme 1; Figure 3).<sup>10</sup> Evidently, the parasubstituent has a direct influence on the <sup>31</sup>P NMR chemical shift as well as the colour (see Table 1, Figure 3), which we further substantiated with UV-vis spectroscopy. Compounds 2a-e show an intense absorption maximum ranging from  $\lambda_{max} = 303$  to 464 nm along with a weak absorption in the visual spectrum at  $\lambda_{max}$  = 453-523 nm that displays a gradual bathochromic shift from electron-donating to electron-withdrawing para-substituent (Table 1). Changing the solvent from acetonitrile to DCM led to a small bathochromic shift ( $\Delta \lambda_{max} = 4-11$  nm), indicating a minor influence of the solvent.<sup>10</sup> Time-dependent DFT calculations at the CAM-B3LYP/TZ2P level of theory<sup>10,24</sup> reveal two low-lying excitations for **2a-e** that present  $n \rightarrow \pi^*$  (E-S<sub>1</sub>) and  $\pi \rightarrow \pi^*$  (E-S<sub>2</sub>) character. The first excitation corresponds to the HOMO→LUMO transition (with 89-95% weight contribution) from the n orbital, which is an out-of-phase combination of lone pairs on the two azo nitrogen atoms (Figure S10). As the azophosphonium dyes are not perfectly planar, this excitation has non-zero oscillator strength due to the admixture of  $\pi$ -orbitals from the aromatic ring (TD-DFT: 508 nm, f = 0.0005 for 2a). The change in colour is determined by the para-substituents that have a stabilizing effect on the HOMO and HOMO-1 and to a lesser extent on the LUMO (Table 1). The second excitation ( $\pi \rightarrow \pi^*$  transition) is allowed (295 nm, f = 0.5749 for 2a), but outside the visible range (except for 2e, R = NMe<sub>2</sub>). The  $\pi$  and  $\pi^*$  orbitals involved in these two excitations are bonding/antibonding orbitals centered mostly on the N=N moiety (Figure S10).



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Table 1.  $^{31}\text{P}\{^{1}\text{H}\}$  NMR chemical shifts, optical properties and energies of frontier orbitals for azophosphonium salts  $2a\text{-}e.^{[a]}$ 

	<sup>31</sup> P{ <sup>1</sup> H} [ppm]	$\lambda_{abs} [nm]^{[b]}$ (log $\epsilon_{max}$ )	$\lambda_{ m abs}  [nm]^{[c]}$ (log $\epsilon_{ m max}$ )	HOMO [eV]	HOMO-1 [eV]	LUMO [eV]
2a	69.4	316 (4.21)	515 (2.16)	-12.1	-12.2	-4.3
2b	73.8	303 (4.29)	453 (2.68) 523 (2.26) <sup>[d]</sup>	-12.6	-12.8	-4.9
2c	70.3	336 (4.33)	517 (2.18)	-11.6	-12.2	-4.4
2d	65.8	373 (4.44)	500 (2.49)	-11.2	-11.9	-4.0
2e	59.6	464 (4.62)	_ [e]	-10.3	-11.5	-3.8

[a] Absorption wavelength corresponding to the lowest energy transition ( $\lambda_{abs}$ ); molar extinction coefficients ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>, solvent: CH<sub>3</sub>CN); HOMO, HOMO-1 and LUMO energies at  $\omega$ B97X-D/6-311+G(d,p), [b]  $\pi \rightarrow \pi^*$  transition, [c]  $n \rightarrow \pi^*$  transition, [d] initial yellow colour turns in a few hours into pink and purple in a few days indicating secondary interactions, [e]  $n \rightarrow \pi^*$  transition not visible.

Intuitively, the phosphine–diazonium Lewis adducts **1** and **2** are the result of classical donor–acceptor reactivity. Yet, aryldiazonium salts are also known to undergo one-electron reduction in the presence of organic electron-donors generating aryldiazo radicals (ArN<sub>2</sub>').<sup>25</sup> Subsequent radical coupling with the concomitantly formed phosphine radical cation (R<sub>3</sub>P<sup>++</sup>) presents an alternative pathway to afford these readily tuneable azophosphonium salts. Since N-based Lewis bases, such as arylamines, are known to undergo one-electron oxidation by Lewis acids generating the corresponding radical cations,<sup>26</sup> we also included triphenylamine and tri-*iso*-propylamine (*t*Bu<sub>3</sub>N is still elusive)<sup>27</sup> in our mechanistic study.



Scheme 2. Reaction of [PhN2][BF4] with tertiary amines.

In contrast to the reaction with triphenylphosphine, phenyldiazonium tetrafluoroborate treatment of with triphenylamine yields azobenzene 3 (Scheme 2) 28 via an electrophilic aromatic substitution of the arylamine.<sup>29</sup> Blocking the para-position resulted in a different outcome. We discovered that treatment of [PhN<sub>2</sub>][BF<sub>4</sub>] with tri-p-tolylamine in CH<sub>3</sub>CN afforded an immediate colour change to deep blue, characteristic of the formation of the radical cation [p-tol<sub>3</sub>N\*+], which we confirmed by EPR spectroscopy (Figure S6). 30 Compared to the cyclic voltammogram of triphenylamine ( $E_p^{ox} = 0.97 \text{ V vs. Fc/Fc}^+$ ), the oxidation potential of the more electron-rich p-tolylamine is shifted to more negative potentials ( $E_p^{ox} = 0.78 \text{ V vs. Fc/Fc}^+$ ; Table 2), -which supports the notion that tri-p-tolylamine is more prone to one-electron oxidation than triphenylamine ( $\Delta G^0 = 20.3$  vs. 24.7 kcal·mol<sup>-1</sup>, respectively; Table 2).

Interestingly, the bulky tri-iso-propylamine 31 provided a different reaction course. Treatment of phenyldiazonium tetrafluoroborate with IPr<sub>3</sub>N (2 equiv) in CH<sub>3</sub>CN resulted in the formation of triazene PhN=NN*i*Pr<sub>2</sub> 5 (72%),<sup>12b</sup> diisopropylammonium borate [H<sub>2</sub>N/Pr<sub>2</sub>][BF<sub>4</sub>] (2 equiv; 92%) and propene (2 equiv; detected by MS), instead of the anticipated amine-diazonium Lewis adduct [PhN<sub>2</sub>(N*i*Pr<sub>3</sub>)][BF<sub>4</sub>] **4** ( $\Delta E = -24.9$ kcal-mol<sup>-1</sup>: Scheme 2).<sup>10</sup> Cvclic voltammetry shows that the reaction of tri-iso-propylamine with [PhN2][BF4] is for thermodynamic reasons unlikely to be initiated by single-electron transfer  $(E_{\rm p}^{\rm ox} (i Pr_3 N/i Pr_3 N^{+}) = 1.20 \text{ V vs. } Fc/Fc^{+}; \Delta G^0 = 30.0$ kcal·mol<sup>-1</sup>; Table 2). Therefore, we postulate the transient azoammonium salt 4 to undergo Hofmann elimination, which is commonly observed for sterically hindered tri-tert-alkylamines.<sup>27</sup>

 Table 2. Frontier molecular orbitals and oxidation potentials of selected

 Lewis bases (LB), incl. free energy change for radical cation formation.

	HOMO [eV] <sup>[a]</sup>	LUMO [eV] <sup>[a]</sup>	<i>E</i> <sub>p</sub> <sup>ox</sup> (LB/LB <sup>•+</sup> ) vs. Fc/Fc <sup>+ [b]</sup>	$\Delta G^{0} = (E_{p}^{ox} \cdot F) - (E_{p}^{red} \cdot F)^{[c]}$
Ph₃N	-7.10	0.95	0.97 V	24.7
<i>p</i> -tol₃N	-6.80	1.04	0.78 V	20.3
<i>i</i> Pr₃N	-7.33	1.69	1.20 V	30.0
Ph₃P	-7.97	0.92	1.23 V	30.7
<i>t</i> Bu₃P	-7.69	1.53	0.90 V	23.1

[a] calculated at  $\omega$ B97X-D/6-311+G(d,p), [b] CH<sub>3</sub>CN, 0.1 M [*n*Bu<sub>4</sub>N][PF<sub>6</sub>], glassy carbon working electrode,  $v = 100 \text{ mV s}^{-1}$ , [c]  $\Delta G^0 = -nF \cdot E^0_{cell} = -RTInK_{eq}$ ; F = Faraday constant;  $E_p^{red}$  (PhN<sub>2</sub><sup>+</sup>/PhN<sub>2</sub><sup>+</sup>) = -0.10 V vs. Fc/Fc<sup>+</sup>.

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Next, we measured the cyclic voltammograms of triphenylphosphine ( $E_p^{ox} = 1.13$  V vs. Fc/Fc<sup>+</sup>) and tri-*tert*butylphosphine ( $E_p^{ox} = 0.80$  V vs. Fc/Fc<sup>+</sup>) in acetonitrile (0.1 M [ $nBu_4N$ ][PF<sub>6</sub>]) and compared them to the reduction potential of the phenyldiazonium cation ( $E_p^{red}$  (PhN<sub>2</sub><sup>+</sup>/PhN<sub>2</sub><sup>+</sup>) = -0.10 V vs. Fc/Fc<sup>+</sup>).<sup>32</sup> Based on the sizable free energy change for radical cation formation by one-electron oxidation of the phosphines ( $\Delta G^0 = > 23$  kcal·mol<sup>-1</sup>; Table 2) and the facile formation of **1** and **2** at low temperatures (even at -20 °C),<sup>10</sup> we conclude that these azophosphonium salts are most likely formed via a two-electron Lewis acid-base coupling rather than single-electron transfer followed by radical coupling.



**Scheme 3.** Reaction of *t*Bu<sub>3</sub>P with [NO][BF<sub>4</sub>] together with experimental (black) and simulated (red) EPR spectrum of *t*Bu<sub>3</sub>P-NO<sup>•</sup>. Simulated *g* value and hyperfine coupling constants (*A*):  $g_{Iso} = 2.0071$ ,  $A^{N}_{Iso} = +29.55$  MHz,  $A^{P}_{Iso} = -34.10$  MHz.

Oxidation of tri-*tert*-butylphosphine by single-electron transfer (SET) is feasible when using stronger oxidants.

Treatment of  $tBu_3P$  with the nitrosonium salt [NO][BF4] ( $E_p^{red}$  (NO<sup>+</sup>/NO<sup>•</sup>) = 0.87 V vs. Fc/Fc<sup>+</sup>)<sup>32</sup> in acetonitrile resulted in the formation of [ $tBu_3PH$ ][BF4] as the major product ( $\delta^{31}P = 56.1$ ,  $^1J_{P,H} = 445.6$  Hz; Scheme 3),<sup>10,33</sup> which could be attributed to H atom abstraction from the solvent by the reactive [ $tBu_3P^{++}$ ] radical cation intermediate ( $\Delta G^0 = 0.7$  kcal·mol<sup>-1</sup>).<sup>34</sup> In addition, we detected small amounts of a radical species by EPR spectroscopy (Scheme 3) that features a six-line pattern at  $g_{lso} = 2.0071$ , which is consistent with an organic doublet with hyperfine coupling interactions (A) with nitrogen ( $A^{N}_{iso} = +29.55$  MHz) and an I =  $\frac{1}{2}$  nucleus, likely phosphorus ( $A^{P}_{iso} = -34.10$  MHz; Scheme 3).<sup>10</sup> We postulate this to be the nitrosyl–phosphine adduct  $tBu_3P$ -NO<sup>•</sup> ( $\Delta E = -0.5$  kcal·mol<sup>-1</sup>).<sup>10</sup> which can be formed by the capture of the in situ generated NO<sup>•</sup> by residual  $tBu_3P$ .

In summary, aryldiazonium salts react in acetonitrile as nitrogen-based Lewis acids with phosphines resulting in the facile synthesis of tuneable azophosphonium salts. The corresponding azoammonium salts [RN<sub>2</sub>(NR<sub>3</sub>)][X] are still elusive, but should be accessible when using strongly donating tertiary amines that lack  $\beta$ -hydrogen atoms. We have shown that Lewis acids and bases can undergo, next to the established donor-acceptor reactivity, one-electron processes which will have profound impact on (frustrated) Lewis acid/base chemistry and catalysis.<sup>35</sup> Currently, we are exploring the synthesis of azophosphonium salts by the direct functionalization of dinitrogen with aryl cations <sup>36</sup> and phosphines.

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**Keywords:** diazonium salts • N-based Lewis acids • phosphines • donor–acceptor adducts • single-electron transfer

- [5] C. Tang, Q. Liang, A. R. Jupp, T. C. Johnstone, R. C. Neu, D. Song, S. Grimme, D. W. Stephan, *Angew. Chem. Int. Ed.* **2018**, *57*, 16588–16592.
- [6] For N<sub>2</sub>–BF<sub>3</sub>, see: a) K. C. Janda, L. S. Bernstein, J. M. Steed, S. E. Novick, W. Klemperer, J. Am. Chem. Soc. **1978**, 100, 8074–8079; For the parent borabenzene–N<sub>2</sub> adduct, see: b) G. Maier, H. P. Reisenauer, J. Henkelmann, C. Kliche, Angew. Chem. Int. Ed. Engl. **1988**, 27, 295–296; 1,2-Azaborine also reacts with dinitrogen, see: c) K. Edel, S. A. Brough, A. N. Lamm, S.-Y. Liu, H. F. Bettinger, Angew. Chem. Int. Ed. **2015**, *54*, 7819–7822.
- [7] a) M.-A. Légaré, G. Bélanger-Chabot, R. D. Dewhurst, E. Welz, I. Krummenacher, B. Engels, H. Braunschweig, *Science* 2018, *359*, 896– 900; For an unstabilized borylene that binds N<sub>2</sub>, see: b) K. Edel, M. Krieg, D. Grote, H. F. Bettinger, *J. Am. Chem. Soc.* 2017, *139*, 15151– 15159.
- [8] M. Winkler, W. Sander, J. Org. Chem. 2006, 71, 6357–6367.
- a) A. Pogoreltsev, Y. Tulchinsky, N. Fridman, M. Gandelman, J. Am. Chem. Soc. 2017, 139, 4062–4067; b) J. Zhou, L. L. Liu, L. L. Cao, D. W. Stephan, Chem. Commun. 2018, 54, 4390–4393; c) J. Zhou, L. L.

a) R. L. Melen, Angew. Chem. Int. Ed. 2018, 57, 880–882; b) A. J. Ruddy, D. M. C. Ould, P. D. Newman, R. L. Melen, Dalton Trans. 2018, doi: 10.1039/C8DT01168K; c) C. Hering-Junghaus, Angew. Chem. Int. Ed. 2018, 57, doi: 10.1002/anie.201802675.

<sup>[2]</sup> For reviews on the homogeneous transition-metal mediated activation and functionalization of N<sub>2</sub>, see: a) Y. Tanabe, Y. Nishibayashi, *Chem. Rec.* 2016, 16, 1549–1577; b) M. J. Bezdek, P. J. Chirik, *Angew. Chem. Int. Ed.* 2016, 55, 7892–7896; c) H.-P.Jia, E. A. Quadrelli, *Chem. Soc. Rev.* 2014, 43, 547–564; d) K. C. MacLeod, P. L. Holland, *Nat. Chem.* 2013, 5, 559–565; for a recent overview of sustainable routes to nitrogen commodity chemicals, see: e) J. G. Chen, R. M. Crooks, L. C. Seefeldt, K. L. Bren, R. M. Bullock, M. Y. Darensbourg, P. L. Holland, B. Hoffman, M. J. Janik, A. K. Jones, M. G. Kanatzidis, P. King, K. M. Lancaster, S. V. Lymar, P. Pfromm, W. F. Schneider, R. R. Schrock, *Science* 2018, *360*, eaar6611; doi: 10.1126/science.aar6611.

<sup>[3]</sup> J. B. Geri, J. P. Shanahan, N. K. Szymczak, J. Am. Chem. Soc. 2017, 139, 5952–5956.

 <sup>[4]</sup> a) A. Simonneau, R. Turrel, L. Vendier, M. Etienne, *Angew. Chem. Int. Ed.* 2017, *56*, 12268–12272; b) A. Simonneau, M. Etienne, *Chem. Eur. J.* 2018; doi: 10.1002/chem.201800405.

# COMMUNICATION

Liu, L. L. Cao, D. W. Stephan, Angew. Chem. Int. Ed. 2018, 57, 3322-3326.

- [10] See the Supporting Information for further details.
- A. S. Yamada, (Fuji Photo Film Co., LTD), US20070015912 A1, 2007; b) S. Yamada, (Fuji Photo Film Co., LTD), JP2006176745, 2006; c) S. Yamada, (Fuji Photo Film Co., LTD), JP2006176745, 2006; d) S. Yamada, (Fuji Photo Film Co., LTD), JP2006176745, 2006; d) S. Yamada, (Fuji Photo Film Co., LTD), JP2006328257, 2006; For alternative syntheses of azoimidazolium salts, see: e) A. G. Tskhovrebov, L. C. E. Naested, E. Solari, R. Scopelliti, K. Severin, *Angew. Chem. Int. Ed.* 2015, *54*, 1289–1292; f) L. Y. M. Eymann, A. G. Tskhovrebov, A. Sienkiewicz, J. L. Bila, I. Živković, H. M. Rønnow, M. D. Wodrich, L. Vannay, C. Corminboeuf, P. Pattison, E. Solari, R. [11] Scopelliti, K. Severin, J. Am. Chem. Soc. 2016, 138, 15126-15129.
- [12]
- [13]
- Scopelliti, K. Severin, J. Am. Chem. Soc. 2016, 138, 15126–15129.
  For the reaction of diazonium salts with tertiary amines, see: a) L. Horner, H. Stöhr, Chem. Ber. 1953, 86, 1066–1071; Note the reaction with secondary amines leads to triazenes, see: b) G. Kiefer, T. Riedel, P. J. Dyson, R. Scopelliti, K. Severin, Angew. Chem. Int. Ed. 2015, 54, 302–305.
  a) L. Horner, H. Stöhr, Chem. Ber. 1953, 86, 1073–1076; see also: b) P. C. Ray, S. Medikonduri, G. S. Ramanjaneyulu, WO2007083320 A2, 2007; c) P. C. Ray, S. Medikonduri, G. S. Ramanjaneyulu, US20110313171 A1, 2011.
  a) L. Horner, H. Hoffmann, Chem. Ber. 1958, 91, 45–49; For the corresponding fluoroborate analogues, see: b) J. A. Carroll, D. R. Fisher, G. W. Rayner Canham, D. Sutton, Can. J. Chem. 1974, 52, 1914–1922; c) G. C.-Y. Kim, R. J. Batchelor, X. Yan, F. W. B. Einstein, D. Sutton, Inorg. Chem. 1995, 34, 2020. [14] 6163-6172; d) F. W. B. Einstein, D. Sutton, P. L. Vogel, Can. J. Chem. 1978, 56, 891-895.
- S. Yasui, M. Fujii, C. Kawano, Y. Nishimura, K. Shioji, A. Ohno, J. Chem. Soc. Perkin Trans. 2 1994, 177-183. [15]
- For related examples of SET from phosphines, see: a) S. Yasui, K. Itoh, A. Ohno, N. Tokitoh, Org. Biomol. Chem. 2005, 3, 4188–4192; b) S. Yasui, K. Itoh, A. Ohno, N. Tokitoh, Org. Biomol. Chem. 2006, 4, 2928–2931; c) S. Yasui, K. Shioji, M. Tsujimotoa, A. Ohnob, J. Chem. Soc., Perkin Trans. 2, 1999, 855– [16] 862
- M. J. Alder, W. I. Cross, K. R. Flower, R. G. Pritchard, J. Chem. Soc., Dalton Trans. 1999, 2563–2573. [17] D. Franzke, C. Scherer, O. Nuyken, A. Wokaun, J. Photoch. Photobio. A 1997, 111, 47-50. [18]
- [19] a) M. P. Doyle, W. J. Bryker, J. Org. Chem. 1979, 44, 1572–1574; b) M. J. Hansen, M. M. Lerch, W. Szymanski, B. L. Feringa, Angew. Chem. Int. Ed. 2016, 55,13514-13518.
- A. E. Waked, R. Ostadsharif Memar, D. W. Stephan, Angew. Chem. Int. Ed. 2018, doi.org/10.1002/anie.201804183 [20]
- M. G. Freire, C. M. S. S. Neves, I. M. Marrucho, J. A. P. Coutinho, A. M. Fernandes, J. Phys. Chem. A 2010, 114, 3744–3749.
- [22] CCDC 1846991 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. For the experimental details of the X-ray crystal structure determination, see the Supporting Information
- For the P2 analogue, see: V. D. Romanenko, V. L. Rudzevich, E. B. Rusanov, A. N. Chernega, A. Senio, J.-M. Sotiropoulos, G. Pfister-Guillouzo, M. [23] Sanchez, J. Chem. Soc., Chem. Commun. 1995, 1383–1385.
- [24] J. A. Rombouts, A. W. Ehlers, K. Lammertsma, J. Comp. Chem. 2017, 38, 1811–1818.
- For reviews on organic electron donors as powerful single-electron reducing agents, see: a) J. Broggi, T. Terme, P. Vanelle, Angew. Chem. Int. Ed. 2014, [25] 53, 384–413; b) J. A. Murphy, J. Org. Chem. 2014, 79, 3731–3746; c) A. Houmam, Chem. Rev. 2008, 108, 2180–2237.
- Sold-413, 03. A. Mulphy, J. Og. Chem. 2014, 79, 0731-5740, 05. A. Mulphy, A. Og. Chem. 2014, 79, 0731-5740, 05. A. Mulphy, J. Og. Chem. 2014, 79, 0731-5740, 05. A. Mulphy, J. Og. Chem. 2015, 135, 14912-14915, b) C. J. Harlan, T. Hascall, E. Fujita, J. R. Norton, J. Am. Chem. Soc. 1999, 121, 7274-7275.
  For other bulky tri-*tert*-alkylamines, see: K. Banert, M. Heck, A. Ihle, J. Kronawitt, T. Pester, T. Shoker, J. Org. Chem. 2018, 83, 5138-5148.
  a) E. Ishow, C. Bellaïche, L. Bouteiller, K. Nakatani, J. A. Delaire, J. Am. Chem. Soc. 2003, 125, 15744–15745; b) J. Epperleilt, B. Blau, Z. Chem. 1987, 27, [26]
- [27] [28] 175–176; c) M. Matsui, M. Suzuki, M. Hayashi, K. Funabiki, Y. Ishigure, Y. Doke, H. Shiozaki, Bull. Chem. Soc. Jpn. 2003, 76, 607–612.
- The one-electron oxidation of Ph<sub>3</sub>N affords tetraphenylbenzidines via homocoupling of [Ph<sub>3</sub>N\*] and subsequent deprotonation, see: K. Sreenath, C. V. [29] Suneesh, V. K. R. Kumar, K. R. Gopidas, J. Org. Chem. 2008, 73, 3245-3251; and references therein.
- [30]
- a) S. Granick, L. Michaelis, J. Am. Chem. Soc. 1940, 62, 2241–2242; b) E. T. Seo, R. F. Nelson, J. M. Fritsch, L. S. Marcoux, D. W. Leedy, R. N. Adams, J. Am. Chem. Soc. 1966, 88, 3498–3503; c) O. Yurchenko, D. Freytag, L. zur Borg, R. Zentel, J. Heinze, S. Ludwigs, J. Phys. Chem. B 2012, 116, 30–39.
  a) H. Bock, I. Goebei, Z. Havlas, S. Liedle, H. Oberhammer, Angew. Chem. Int. Ed. 1991, 30, 187–190; b) R. Boese, D. Bläser, M. Y. Antipin, V. Chaplinskic, A. de Meijere, Chem. Commun. 1998, 781–782; c) A. de Meijere, V. Chaplinski, F. Gerson, P. Merstetter, E. Haselbach, J. Org. Chem. 1999, 64, 667. [31] 64, 6951-6959.
- N. G. Connelly, W. E. Geiger, Chem. Rev. 1996, 96, 877-910. [32]
- [33] For NMR data of the tBu3PH cation, see: M. H. Holthausen, J. M. Bayne, I. Mallov, R. Dobrovetsky, D. W. Stephan, J. Am. Chem. Soc. 2015, 137, 7298-7301
- [34]
- M. Iwaizumi, T. Kishi, T. Isobe, F. Watari, J. Chem. Soc., Faraday Trans. 2, **1976**, 72, 113–117. For single-electron transfer processes in FLP chemistry, see: a) L. L. Liu, L. L. Cao, Y. Shao, G. Ménard, D. W. Stephan, Chem **2017**, 3, 259–267; b) L. Liu, L. L. Cao, Y. Shao, D. W. Stephan, J. Am. Chem. Soc. **2017**, 139, 10062–10071; c) L. L. Liu, L. L. Cao, D. Zhu, J. Zhou, D. W. Stephan, Chem. [35] Commun. 2018, doi: 10.1039/C8CC03522A.
- B. Shao, A. L. Bagdasarian, S. Popov, H. M. Nelson, Science 2017, 355, 1403–1407. [36]

# COMMUNICATION

#### **Entry for the Table of Contents**

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Para-substituted aryldiazonium salts were reacted as nitrogen-based Lewis acids with phosphine donor ligands affording the readily tuneable azophosphonium salts. By cyclic voltammetry and DFT calculations, it was established that this reaction between a Lewis acid and Lewis base occurs via electron-pair transfer. Evi R. M. Habraken, Nicolaas P. van Leest, Pim Hooijschuur, Bas de Bruin, Andreas W. Ehlers, Martin Lutz, and J. Chris Slootweg\*

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Aryldiazonium Salts as Nitrogen-Based Lewis acids: Facile Synthesis of Tuneable Azophosphonium Salts