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

Evi R. M. Habraken, Nicolaas P. van Leest, Pim Hooijschuur, Bas de Bruin, Andreas W. Ehlers, Martin Lutz, and J. Chris Slootweg*

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 aryldiazophosphonium salts. A range of colours were 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 a Lewis base occurs by 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. The low-lying nitrogen orbitals (HOMO) and high-lying nitrogen orbital (LUMO) make dinitrogen a weak Lewis base and a weak Lewis acid and, therefore, a relatively inert substrate (Figure 1). Inspired by the recently reported interaction of boranes with metal–nitrogen complexes enabling facile nitrogen protonation, borylation, and silylation, Stephan and co-workers demonstrated that diphenyldiazomethane, a formal diphenylcarbene–nitrogen adduct, can function as a Lewis base (HOMO: −7.31 eV; Figure 1), forming a labile adduct with B(C6F5)3.[9]

While the direct interaction of dinitrogen with boranes has only been observed spectroscopically under forcing conditions,[5] the use of transient borylenes afforded a stable bis(borylene)–nitrogen complex as recently reported by Braunschweig and co-workers.[17] We were intrigued by the reaction of the strongly Lewis acidic phenyl cation with nitrogen that affords the phenyl diazonium ion in cryogenic argon matrices,[8] and found that the planar C6H5N+ activates N2 by greatly lowering its acceptor orbital (LUMO: from 1.30 (N2) to −6.24 eV; see Figure 1). This makes aryldiazonium salts suitable nitrogen-based Lewis acids,[9] which we were keen on investigating.

N Coordination of diazonium salts to Lewis basic N-heterocyclic carbenes is well established and affords the strongly coloured, industrially produced azoimidazolium salts [RN=NHC][X] (X = Cl, BF3, PF5, etc.).[11] Surprisingly, to date the corresponding azoammonium salts [RN3(NR)][X] are unknown,[12] while the phosphine-diazonium Lewis adducts have been barely studied. Thus far, Horner and Stöhr postulated the red azophosphonium chlorides A (R = H, Me, Cl, NO2, CO2H, OMe, OC(O)Me; Figure 2) as unstable species[13] that are susceptible to N2 elimination, affording the corresponding azophosphonium salts [ArPPh3]-[Cl][14]. Later, Yasui and co-workers found that aryldiazonium tetrafluoroborates are readily diazoniating by triphenylphosphine by single-electron transfer when mixed in alcoholic solvents at room temperature.[15,16] Flower and co-workers synthesized B, but only reported its 31P NMR resonance (δ[31P]H = 40 ppm; R = 6-naphthalen-2-ol).[17] and Wokaun

Figure 1. Lewis acid (C6H5+) and base (PH3) augmented activation of N2, including the HOMO (bottom) and LUMO (top) energies (in eV) calculated at theωB97X-D/6-311 + G(d,p) level of theory.[9]

Figure 2. Reported aryldiazonium–phosphine adducts.
and co-workers characterized C only spectroscopically (R = Cl, CN, SO₂NH₂, C(O)OEt: Figure 2). Herein, we report on the facile synthesis of readily tuneable azophosphonium salts simply from phosphines and aryldiazonium tetrafluoroborates in acetonitrile, and provide detailed mechanistic insight by experimental and computational means. Related reactions of phenyldiazonium tetrafluoroborate with tertiary amines have also been investigated.

We found that treatment of the phenyldiazonium salt [PhN⁺(PPh₃)]BF₄⁻ with triphenylphosphine (1.0 equiv) in acetonitrile at 0°C afforded the red azophosphonium salt [PhN⁺(PPh₃)][BF₄⁻] (1) (δ¹³P[¹H] = 39.4 ppm; Scheme 1; ΔE = −43.5 kcal mol⁻¹ at the oB97X-D/6-311 + G(d,p) level of theory) in near-quantitative yield after work-up; only a minor side product could be detected by ³¹P NMR spectroscopy (ca. 2%; δ¹³P[¹H] = 43.9 and 52.5 ppm, ³Jₚp = 18.8 Hz), which we tentatively ascribed to the bis-phosphine adduct [PhN(PPh₃)N(PPh₃)][BF₄⁻]. As Horner and Stöhr had indicated⁹ that compound 1 is unstable both in solution and in the solid state,¹⁰ we resorted to the stronger and sterically more encumbered donor tri-tert-butylphosphine, which, according to DFT calculations at the oB97X-D/6-311 + G(d,p) level of theory, should provide a more stable product (ΔE = −53.2 kcal mol⁻¹).¹⁰ The reaction of phenyldiazonium tetrafluoroborate with tBuPH (1.1 equiv) in acetonitrile resulted in an immediate colour change from colourless to pink and afforded azophosphonium salt [(PhN(PBu₃)]BF₄⁻ (2a). A δ¹³P[¹H] = 69.4 ppm; Scheme 1) as the sole product in 95% yield upon isolation. Gratifyingly, this cationic Lewis adduct is stable towards air, moisture, and even an aqueous 2 m HCl solution (only the tetrafluoroborate anion hydrolysed over time).¹¹ The molecular structure of 2a (Scheme 1),²²,²³ determined by X-ray crystal-structure analysis of suitable crystals of its tetraphenylborate analogue (obtained after anion exchange with NaBPh₄ in DCM),²⁰ displays an almost planar (P1-N1-N2-C1 173.4(7)°) trans azaphosphonium 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 those of the related arylazoimidazolium borates [ArN⁺(IMes)][BPh₄⁻] (Ar = Mes, o/p-CIC₆H₄) reported by Severin and co-workers (C–N: 1.411(2)/1.395(4)/1.455(13); N–N: 1.265(2)/1.266(9)/1.24(2) Å, respectively), illustrating that in these cationic azo dyes, phosphines behave similar to carbenes.

As the colour of the azaphosphonium salts can be readily tuned by changing the donor ligand (1 (L = PPh₃): red; 2a (L = tBuP): pink), we next investigated the influence of the para substituent on the aren ring on the photophysical properties of 2. Treatment of the 4-substituted phenyldiazonium salts [(p-R-C₆H₄)N⁺(BF₄⁻)] (R = NO₂ (b), Br (e), OMe (d), NMe₂ (e)) with tri-tert-butylphosphine (1.1 equiv) in acetonitrile afforded the intensely coloured (from purple to red/brown) azaphosphonium salts [(p-R-C₆H₄)N⁺(PhBu₃)]BF₄⁻ 2b–e in 87–96% yield upon isolation (Scheme 1 and Figure 3).¹⁰ Evidently, the para substituent has a direct influence on the ³¹P NMR chemical shift as well as the colour (see Table 1 and Figure 3), which we further substantiated by UV/Vis spectroscopy. Compounds 2a–

![Scheme 1. Synthesis of arylazophosphonium tetrafluoroborates 1 and 2a–e and molecular structure of [(C₆H₄)N⁺(PhBu₃)]BF₄⁻ (2a-BPh₃; displacement ellipsoids are set at 30% probability, hydrogen atoms and the noncoordinating BPh₃ 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(8)], N2A–C1A 1.437(7) [1.439(8)]; P1–N1A–N2A–C1A 173.4(7)° [167.3(11)].

![Figure 3. UV/Vis spectra and colours of azaphosphonium salts 2a–e in solution (0.006 m in CH₃CN) and in the solid state (from left to right: 2a, 2b, 2c, 2d, and 2e).](image-url)
Table 1: $^{31}$P[1H] NMR chemical shifts, optical properties, and energies of the frontier orbitals for azophosphonium salts 2a–e.[b]

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{max}$ [ppm][a]</th>
<th>$\lambda_{max}$ [nm][b]</th>
<th>$\lambda_{min}$ [nm][b]</th>
<th>HOMO</th>
<th>HOMO-1</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>69.4</td>
<td>316 (4.21)</td>
<td>515 (2.16)</td>
<td>−12.1</td>
<td>−12.2</td>
<td>−4.3</td>
</tr>
<tr>
<td>2b</td>
<td>73.8</td>
<td>303 (4.29)</td>
<td>453 (2.68)</td>
<td>−12.6</td>
<td>−12.8</td>
<td>−4.9</td>
</tr>
<tr>
<td>2c</td>
<td>70.3</td>
<td>336 (4.33)</td>
<td>517 (2.18)</td>
<td>−11.6</td>
<td>−12.2</td>
<td>−4.4</td>
</tr>
<tr>
<td>2d</td>
<td>65.8</td>
<td>373 (4.44)</td>
<td>500 (2.49)</td>
<td>−11.9</td>
<td>−11.9</td>
<td>−4.0</td>
</tr>
<tr>
<td>2e</td>
<td>59.6</td>
<td>464 (4.62)</td>
<td>−[3]</td>
<td>−10.3</td>
<td>−11.5</td>
<td>−3.8</td>
</tr>
</tbody>
</table>

[a] Absorption wavelength corresponding to the lowest-energy transition ($\lambda_{max}$); molar extinction coefficients ($\epsilon$, M$^{-1}$ cm$^{-1}$), solvent: CH$_2$CN; HOMO, HOMO-1, and LUMO energies at o897X-D/6-311 + G(d,p).

[b] π→π$^*$ transition.

Intuitively, the phosphine–diazonium Lewis adducts provide another out-of-plane combination of lone pairs on the two azo nitrogen atoms (Table S10). The change in colour is determined by the π→π$^*$ transition.

Table 2: Frontier molecular orbitals and oxidation potentials of selected Lewis bases (LB), including the free energy changes for radical cation formation.

<table>
<thead>
<tr>
<th></th>
<th>HOMO</th>
<th>LUMO</th>
<th>$E_{ox}$(LB/LB$^+$) vs. Fe/Fe$^+$</th>
<th>$\Delta G^\circ$</th>
<th>$E_{ox}$(PhN$_3$/BF$<em>4$) − $E</em>{red}$(PhN$_3$/) $\Delta G^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_3$N</td>
<td>−7.10</td>
<td>0.95</td>
<td>0.97 V</td>
<td>24.7</td>
<td></td>
</tr>
<tr>
<td>p-tol$_2$N</td>
<td>−6.80</td>
<td>1.04</td>
<td>0.78 V</td>
<td>20.3</td>
<td></td>
</tr>
<tr>
<td>Ph$_3$P</td>
<td>−7.33</td>
<td>1.69</td>
<td>1.20 V</td>
<td>30.0</td>
<td></td>
</tr>
<tr>
<td>Ph$_3$P</td>
<td>−7.97</td>
<td>0.92</td>
<td>1.23 V</td>
<td>30.7</td>
<td></td>
</tr>
<tr>
<td>tBu$_3$N</td>
<td>−7.69</td>
<td>1.53</td>
<td>0.90 V</td>
<td>23.1</td>
<td></td>
</tr>
</tbody>
</table>

[a] Calculated at o897X-D/6-311 + G(d,p). [b] CH$_2$CN, 0.1 M [nBu$_3$N]-[PF$_6$], glassy carbon working electrode, $\nu = 100$ mV s$^{-1}$.

Interestingly, the bulky triisopropylammonium tetrafluoroborate with tBu$_3$N (2 equiv) in CH$_2$CN resulted in the formation of triazene Ph$_3$N=NNtBu$_3$P$_2$ (72%), dichloropalladionium boreate [H$_2$NiPr$_3$][BF$_4$] (2 equiv; 92%), and propane (2 equiv; detected by MS), instead of the anticipated amine–diazenium Lewis adduct [Ph$_3$N(NiPr$_3$)][BF$_4$] (ΔE = −24.9 kcal mol$^{-1}$; Scheme 2). Cyclic voltammetry shows that the reaction of triisopropylamine with [Ph$_3$N][BF$_4$] is, for thermodynamic reasons, unlikely to be initiated by single-electron transfer ($E_{ox}$(Ph$_3$N)/NiPr$_3$/Pr$_3$N$^+$) = 1.20 V vs. Fe/Fe$^+$; $\Delta G^\circ$ = 30.0 kcal mol$^{-1}$; Table 2). Therefore, we postulate the transient azoominozinc salt 4 to undergo Hofmann elimination, which is commonly observed for sterically hindered tri-tert-alkylamines.

Next, we recorded the cyclic voltammograms of triphenylphosphine ($E_{ox}^\circ$ = 1.13 V vs. Fe/Fe$^+$) and tri-tert-butylphosphine ($E_{ox}^\circ$ = 0.80 V vs. Fe/Fe$^+$) in acetonitrile (0.1 M [nBu$_3$N]-[PF$_6$]) and compared them to the reduction potential of the position resulted in a different outcome. We discovered that treatment of [Ph$_3$N$_2$][BF$_4$] with tri-p-tolylamine in CH$_2$CN afforded an immediate colour change to deep blue, characteristic of the formation of the radical cation [p-tol,N$^+$], which was confirmed by EPR spectroscopy (Figure S6). Compared to the cyclic voltammogram of triphenylamine ($E_{ox}^\circ$ = 0.97 V vs. Fe/Fe$^+$), the oxidation potential of the more electron-rich p-tolylamine is shifted to more negative potentials ($E_{ox}^\circ$ = 0.78 V vs. Fe/Fe$^+$; Table 2), which supports the notion that tri-p-tolylamine is more prone to one-electron oxidation than triphenylamine ($\Delta G^\circ$ = 20.3 vs. 24.7 kcal mol$^{-1}$, respectively; Table 2).
which could be attributed to H atom abstraction from the solvent by the reactive \([\text{Bu}_3\text{P}]^+\) radical cation intermediate (\(\Delta G^0 = 0.7\ \text{kcalmol}^{-1}\)).[34] In addition, we detected small amounts of a radical species by EPR spectroscopy (Scheme 3) that features a six-line pattern at 8 = 20071, \(A^0 = +29.55\ \text{MHz}\), \(A^0_{\text{iso}} = -34.10\ \text{MHz}\).

In summary, in acetonitrile, aryldiazonium salts react as nitrogen-based Lewis acids with phosphines, enabling the facile synthesis of tuneable azophosphonium salts. The corresponding azoammonium salts \([\text{RN}=(\text{NR})_2][X]\) are still elusive, but should be accessible with strongly donating tertiary amines that lack \(\beta\)-hydrogen atoms. We have shown that in addition to the established donor–acceptor reactivity, Lewis acids and bases can undergo one-electron processes, which will have profound impact on (frustrated) Lewis acid/ base chemistry and catalysis.[30] Currently, we are exploring the synthesis of azophosphonium salts by the direct functionalization of dinitrogen with aryl cations[36] and phosphines.

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**Conflict of interest**

The authors declare no conflict of interest.

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

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[22] CCDC 1846991 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre. For experimental details of the X-ray crystal structure determination, see: Supporting Information.