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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 azoimidazolidinyl dyes (e.g., Basic Red 51) that can be obtained from aryldiazonium salts and \( N \)-heterocyclic carbones, 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.\(^{[1,2]}\) The low-lying \( N_2 \) \( \sigma \) orbital (HOMO) and high-lying \( \pi^* \) orbital (LUMO) make dinitrogen a weak Lewis base and a weak Lewis acid and, therefore, a relatively inert substrate (Figure 1).\(^{[3]}\) Inspired by the recently reported interaction of boranes with metal–\( N_2 \) complexes enabling facile \( N \) protonation,\(^{[3]}\) borylation, and silylation,\(^{[4]}\) Stephan and co-workers demonstrated that diphenyldiazomethane, a formal diphenylcarbene–\( N_2 \) adduct, can function as a Lewis base (HOMO: \(-7.31 \text{ eV}\); Figure 1), forming a labile adduct with \( \text{B}(\text{C}_6\text{F}_5)_3 \).\(^{[5]}\) 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)–\( N_2 \) complex as recently reported by Braunschweig and co-workers.\(^{[7]}\) We were intrigued by the reaction of the strongly Lewis acidic phenyl cation with \( \text{N}_2 \) that affords the phenyl diazonioum ion in cryogenic argon matrices,\(^{[8]}\) and found that the planar \( \text{C}_6\text{H}_5^+ \) activates \( \text{N}_2 \) by greatly lowering its \( \pi^* \) acceptor orbital (LUMO: from \( 1.30 \text{ (N}_2 \) to \(-6.24 \text{ eV}; \) see Figure 1). This makes aryldiazonium salts suitable nitrogen-based Lewis acids,\(^{[9]}\) which we were keen on investigating.

Coordination of diazonium salts to Lewis basic \( N \)-heterocyclic carbones is well established and affords the strongly coloured, industrially produced azoimidazolidinyl salts \( \left[ \text{RN}(\text{NHC})\right]\left[\text{X}\right] \) (\( \text{X} = \text{Cl}, \text{BF}_4, \text{PF}_6, \text{etc.} \)).\(^{[10]}\) Surprisingly, to date the corresponding azoammonium salts \( \left[ \text{RN}_2(\text{NR})\right]\left[\text{X}\right] \) are unknown,\(^{[12]}\) while the phosphate–diazonium Lewis adducts have been barely studied. Thus far, Horner and Stöhr postulated the red azophosphonium chlorides \( \text{A} (\text{R} = \text{H}, \text{Me}, \text{Cl}, \text{NO}_2, \text{CO}_2\text{H}, \text{OMe}, \text{OC(O)Me}; \) Figure 2) as unstable species\(^{[11]}\) that are susceptible to \( \text{N}_2 \) elimination, affording the corresponding aryolphosphonium salts \( \left[ \text{ArPPh}_2\right]-[\text{Cl}] \).\(^{[14]}\) Later, Yasui and co-workers found that aryldiazonium tetrafluoroborates are readily dediazoniated by triphenylphosphine by single-electron transfer when mixed in alcoholic solvents at room temperature.\(^{[15,16]}\) Flower and co-workers synthesized \( \text{B} \), but only reported its \( ^{31}\text{P} \) NMR resonance (\( \delta^{31}\text{P}\{\text{H}\} = 40 \text{ ppm}; \) \( \text{R} = 6\text{-naphthalen}-2\text{-ol} \)) and Wokaun

\[ \begin{align*}
\text{A} \quad \text{N}\text{PPh}_3 \quad \text{Me} \quad \text{N} \quad \text{PPh}_3 \quad \text{R} \\
\text{B} \quad \text{N} \quad \text{Cl} \quad \text{N} \quad \text{BF}_4 \\
\text{C} \quad \text{N} \quad \text{P(NMe)}_3 \quad \text{Cl} \quad \text{N} \quad \text{BF}_4
\end{align*} \]

\[ \text{Figure 2.} \] Reported aryldiazonium–phosphine adducts.
and co-workers characterized C only spectroscopically (R = Cl, CN, SO₂NH₂, C(O)OEt; Figure 2).[19] Herein, we report on the facile synthesis of readily tuneable azophosphonium salts simply from phosphines and aryl diazonium tetrafluoroborates in acetonitrile, and provide detailed mechanistic insight by experimental and computational means. Related reactions of phenyl diazonium tetrafluoroborate with tertiary amines have also been investigated.

We found that treatment of the phenyldiazonium salt [PhN⁺][BF₄⁻] with triphenylphosphine (1.0 equiv) in acetonitrile at 0 °C afforded the red azophosphonium salt [PhN⁺(PPh₃)₂][BF₄⁻] (1) (δ³¹P[H] = 39.4 ppm; Scheme 1; ΔE = −43.5 kcal mol⁻¹ at the oB97X-D/6-311 + G(d,p) level of theory)¹⁰ in near-quantitative yield after work-up; only a minor side product could be detected by ³¹P NMR spectroscopy (ca. 2%; δ³¹P[H] = 43.9 and 52.5 ppm, Jpp = 18.8 Hz).¹⁰ We tentatively assigned the bis-phosphine adduct [PhN(PPh₃)₂N(PPh₃)] [BF₄⁻].¹⁰ As Horner and Stöhr had indicated¹⁰ 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 Bu₄P (1.1 equiv) in acetonitrile resulted in an immediate colour change from colourless to pink and afforded azophosphonium salt [PhN⁺]{Bu₄P} [BF₄⁻] (2a) (δ³¹P[H] = 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).²¹ 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 NaB₄H₄ in DCM).²⁰ displays an almost planar (P1-N1-N2-C1 173.4(7)°) trans azophosphonium 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 aryloimidazolium 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),²⁴ illustrating that in these cationic azo dyes, phosphines behave similar to carbenes.

As the colour of the azophosphonium salts can be readily tuned by changing the donor ligand (1 (L = PPh₃): red; 2a (L = tBu₄P): pink), we next investigated the influence of the para substituent on the amine 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), NMes (e)) with tri-tert-butylphosphine (1.1 equiv) in acetonitrile afforded the intensely coloured (from purple to red/brown) aryloimidazolium borates [(p-R-C₆H₄)N⁺(pBu₄)][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–

![Figure 3](image-url)

**Figure 3.** UV/Vis spectra and colours of azophosphonium 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).
show an intense absorption maximum ranging from $\lambda_{\text{max}} = 303$ to 464 nm along with a weak absorption in the visible region at $\lambda_{\text{max}} = 453–523$ nm that displays a gradual bathochromic shift from electron-withdrawing to electron-donating para substituents (Table 1). Changing the solvent from acetonitrile to DCM led to a small bathochromic shift ($\Delta\lambda_{\text{max}} = 4–11$ nm), indicating a minor influence of the solvent.[10] Time-dependent DFT calculations at the CAM-B3LYP/TZ2P level of theory[26,27] reveal two low-lying transitions not visible.

In contrast to the reaction with triphenylphosphine, treatment of phenyldiazonium tetrafluoroborate with triisopropylamine ($\pi\rightarrow\pi^*$ transition not visible.) has as tabilizing effect on HOMO and HOMO-1 and LUMO (Scheme 2). $\Delta G^0 = 20.3$ vs $24.7 \text{ kcal mol}^{-1}$ respectively; Table 2).

Interestingly, the bulky triisopropylammonium salt treatment of phenyldiazonium tetrafluoroborate with tripropene (2 equiv; detected by MS), instead of the anticipated triazene PhN=C=C=N-C=Pr$_3$, glassy carbon working electrode, $\nu = 100 \text{ mVs}^{-1}$. $\Delta G^0 = -24.9 \text{ kcal mol}^{-1}$; Scheme 2). Cyclic voltammetry shows that the reaction of triisopropylamine with [PhN$_2$][BF$_4$] is for thermodynamic reasons, unlikely to be initiated by single-electron transfer ($E_{\text{ox}}^\circ(\text{PhN$_2$}) = 1.20 \text{ V vs. Fc/Fc}^+$). We postulate the transient azoammonium salt 4 to undergo Hofmann elimination, which is commonly observed for sterically hindered tri-tert-alkylamines[25].

Next, we recorded the cyclic voltammograms of triphenylphosphine ($E_{\text{ox}}^\circ = 1.13 \text{ V vs. Fc/Fc}^+$) and tri-tert-butylphosphine ($E_{\text{ox}}^\circ = 0.80 \text{ V vs. Fc/Fc}^+$) in acetonitrile (0.1 M [nBu$_4$N][PF$_6$]) and compared them to the reduction potential of the

### Table 1: $^{31}$P{H} NMR chemical shifts, optical properties, and energies of the frontier orbitals for azophosphonium salts 2a-e[11]

<table>
<thead>
<tr>
<th>$^{31}$P{H} [ppm]</th>
<th>$\lambda_{\text{max}}$ [nm]$^a$</th>
<th>$\lambda_{\text{max}}$ [nm]$^b$</th>
<th>HOMO [eV]</th>
<th>HOMO-1 [eV]</th>
<th>LUMO [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>69.4</td>
<td>316 (4.21)</td>
<td>315 (2.16)</td>
<td>12.1</td>
<td>12.2</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>
</tr>
<tr>
<td>2c</td>
<td>70.3</td>
<td>336 (4.33)</td>
<td>523 (2.26)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2d</td>
<td>65.8</td>
<td>373 (4.44)</td>
<td>500 (2.49)</td>
<td>11.6</td>
<td>12.2</td>
</tr>
<tr>
<td>2e</td>
<td>70.3</td>
<td>464 (4.62)</td>
<td></td>
<td>10.3</td>
<td>11.5</td>
</tr>
</tbody>
</table>

**Notes:**

[a] Absorption wavelength corresponding to the lowest energy transition ($\lambda_{\text{max}}$).

[b] Molar extinction coefficients (m$^{-1}$ cm$^{-1}$), solvent: CH$_3$CN.

[c] $\pi\rightarrow\pi^*$ transition.

[d] $\pi\rightarrow\pi^*$ transition.

[e] n--n* transition not visible.

### 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>Lewis base (LB)</th>
<th>HOMO [eV]$^b$</th>
<th>LUMO [eV]$^b$</th>
<th>$E_{\text{ox}}^\circ$(LB/LB$^+$) vs. Fc/Fc$^+$ [V]$^c$</th>
<th>$\Delta G^0$ [eV]</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>
</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>
</tr>
<tr>
<td>Ph$_3$P</td>
<td>-7.33</td>
<td>1.69</td>
<td>1.20 V</td>
<td>30.0</td>
</tr>
<tr>
<td>Pr$_3$P$_2$</td>
<td>-7.97</td>
<td>0.92</td>
<td>1.23 V</td>
<td>30.7</td>
</tr>
<tr>
<td>Bu$_4$P</td>
<td>-7.69</td>
<td>1.53</td>
<td>0.90 V</td>
<td>23.1</td>
</tr>
</tbody>
</table>

[a] Calculated at oB97X-D/6-311+G(d,p).

[b] CH$_3$CN, 0.1 M [nBu$_4$N][PF$_6$], glassy carbon working electrode, $\nu = 100 \text{ mVs}^{-1}$.

[c] $\Delta G^0 = -\nu F E_{\text{ox}} - RT \ln K_{\text{eq}} F = \text{Faraday constant}$; $E_{\text{ox}}^{\circ}(\text{PhN$_2$}/\text{PhN$_2$}) = -0.10 \text{ V vs. Fc/Fc}^+$.

**Scheme 2.** Reaction of [PhN$_2$][BF$_4$] with tertiary amines.
phenyldiazonium cation \((E_p^{+}=\text{PhN}_2^+/>\text{PhN}_2^-) = -0.10 \text{ V vs. Fe/Fc}^-\)\textsuperscript{[32]}. Based on the sizable free energy change for radical cation formation by one-electron oxidation of the phosphines \(\Delta G^0 > 23 \text{ kcal mol}^{-1}\); Table 2) and the facile formation of 1 and 2 at low temperatures (even at \(-20^\circ\text{C}\))\textsuperscript{[30]} we conclude that these azophosphonium salts are most likely formed by a two-electron Lewis acid–base coupling rather than single-electron transfer followed by radical coupling.

Oxidation of tri-tert-butylphosphine by single-electron transfer (SET) is feasible when using stronger oxidants. Treatment of \(\text{tBu}_3\text{P}\) with the nitrosonium salt \([\text{NO}]\left[\text{BF}_4\right]\) \((E_p^{+}=\text{NO}^+/\text{NO}) = 0.87 \text{ V vs. Fe/Fc}^-\)\textsuperscript{[32]} in acetonitrile resulted in the formation of \([\text{tBu}_3\text{P}]\left[\text{BF}_4\right]\) as the major product \((\delta^{13}\text{P} = 56.1 \text{ ppm}, \quad \nu_{\text{p}1} = 445.6 \text{ Hz}; \quad \text{Scheme 3})\textsuperscript{[10,33]}

\[\text{[NO][BF}_4\right] + \text{tBu}_3\text{P} \rightarrow \text{NO}^- + \text{tBu}_3\text{P}^+ \left[\text{BF}_4\right] \rightarrow \text{CH}_3\text{CN} \rightarrow \text{tBu}_3\text{P}^-\text{NO}^- \left[\text{BF}_4\right] \rightarrow \text{tBu}_3\text{P}^+\text{NO}^- \left[\text{BF}_4\right] \]

\textit{Scheme 3. Reaction of tBu}_3\text{P with [NO][BF}_4\right] together with the experimental (black) and simulated (red) EPR spectra of tBu}_3\text{P-NO}^-\left[\text{BF}_4\right].

Simulated g value and hyperfine coupling constants (A): \(g_{\text{ex}}=2.0071, \quad A_{\text{iso}}^N = +29.55 \text{ MHz}, \quad A_{\text{iso}}^P = -34.10 \text{ MHz.}\)

which could be attributed to H atom abstraction from the solvent by the reactive \([\text{tBu}_3\text{P}^+]\) radical cation intermediate \(\Delta G^0 = 0.7 \text{ kcal mol}^{-1}\)\textsuperscript{[14]}. In addition, we detected small amounts of a radical species by EPR spectroscopy (Scheme 3) that features a six-line pattern at \(g_{\text{ex}}=2.0071,\) which is consistent with an organic doublet with hyperfine coupling interactions \((A)\) with nitrogen \((A_{\text{iso}}^N = +29.55 \text{ MHz})\) and an \(I = \frac{1}{2}\) nucleus, likely phosphorus \((A_{\text{iso}}^P = -34.10 \text{ MHz}; \quad \text{Scheme 3})\textsuperscript{[10]}.\)

We postulate this to be the nitrosyl–phosphine adduct \(\text{tBu}_3\text{P}^-\text{NO}^- \left(\Delta E = -0.5 \text{ kcal mol}^{-1}\right)\textsuperscript{[10]}\) which can be formed by the capture of the in situ generated \text{NO} by residual \(\text{tBu}_3\text{P}\).

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 \([\text{RN}_2\text{(NR)}_2][\text{X}]\) 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.\textsuperscript{[9]} Currently, we are exploring the synthesis of azophosphonium salts by the direct functionalization of dinitrogen with aryl cations\textsuperscript{[36]} and phosphines.

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**Conflict of interest**

The authors declare no conflict of interest.

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[9] 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 The Supporting Information.


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