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


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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 carbens, we developed the synthesis of a unique set of azaphosphonium salts. A range of colours were obtained by applying readily tuneable phosphate 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 Nπ orbital (HOMO) and high-lying π* orbital (LUMO) make dinitrogen a weak Lewis base and a weak Lewis acid and, therefore, a relatively inert substrate (Figure 1)1 Inspired by the recently reported interaction of boranes with metal–Nπ complexes enabling facile N protonation,2 borylation, and silylation,2 we were intrigued by the reaction of boranes with aryldiazonium salts and explored the synthesis of a unique set of aryldiazonium–phosphine adducts.3

While the direct interaction of dinitrogen with boranes has only been observed spectroscopically under forcing conditions,4 the use of transient borylenes afforded as stable borylene–Nπ complex as recently reported by Braunschweig and co-workers.5 We were intrigued by the reaction of the strongly Lewis acidic phenyl cation with Nπ that affords the phenyldiazonium ion in cryogenic argon matrices,6 and found that the planar C6H5Nπ activates Nπ by greatly lowering its π* acceptor orbital (LUMO: from 1.30 (Nπ) to −6.24 eV; see Figure 1). This makes aryldiazonium salts suitable nitrogen-based Lewis acids,7 which we were keen on investigating.

N Coordination of diazonium salts to Lewis basic N-heterocyclic carbens is well established and affords the strongly coloured, industrially produced azoimidazolium salts [RN+(NHC)][X] (X = Cl, BF4, PF6, etc.).8 Surprisingly, to date the corresponding azoammonium salts [RN+(NR2)][X] are unknown,9 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 that are susceptible to Nπ elimination, affording the corresponding arylphosphonium salts [ArPPh]+[Cl].10 Later, Yasui and co-workers found that aryldiazonium tetrafluoroborates are readily deazoniated by triphenylphosphine by single-electron transfer when mixed in alcoholic solvents at room temperature.11 Flower and co-workers synthesized B, but only reported its 31P NMR resonance (δP[H] = 40 ppm; R = 6-naphthalen-2-ol)12 and Wokaun and Stöhr postulated the red azophosphonium chlorides A (R = H, Me, Cl, NO2, CO2H, OMe, OC(O)Me; Figure 2) as unstable species that are susceptible to Nπ elimination, affording the corresponding arylphosphonium salts [ArPPh]+[Cl].10 Later, Yasui and co-workers found that aryldiazonium tetrafluoroborates are readily deazoniated by triphenylphosphine by single-electron transfer when mixed in alcoholic solvents at room temperature.11 Flower and co-workers synthesized B, but only reported its 31P NMR resonance (δP[H] = 40 ppm; R = 6-naphthalen-2-ol)12 and Wokaun
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 aryl diazonium 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 [PhN₂][BF₄] with triphenylphosphine (1.0 equiv) in acetonitrile at 0°C afforded the red azophosphonium salt [PhN₃-(PPh₃)][BF₄] (ΔE = 39.4 ppm; Scheme 1), and we tentatively ascribed to the bis-phosphine adduct [PhN(PPh₃)N(PPh₃)][BF₄], which we further substantiated by UV/Vis spectroscopy. Compounds 1 and 2a (L = Ph; red; L = Bu₃P; pink) were investigated by experimental and computational means. Related reactions of phenyldiazonium tetrafluoroborate with tertiary amines have also been investigated.

![Image](image18x803.png)

**Scheme 1.** Synthesis of azophosphonium tetrafluoroborates 1 and 2a-e and molecular structure of [(C₆H₅)₄N][BF₄]. 2a-BP₃, displacement ellipsoids are set at 30% probability, hydrogen atoms and the noncoordinating BP₃ 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)].

![Image](image319x143.png)

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

<table>
<thead>
<tr>
<th></th>
<th>$\delta_{\text{ppm}}$</th>
<th>$\lambda_{\text{max}}$ [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>
</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>517 (2.18)</td>
<td>$-11.6$</td>
<td>$-12.2$</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>
</tr>
<tr>
<td>2e</td>
<td>59.6</td>
<td>464 (4.62)</td>
<td>$-26$</td>
<td>$-10.3$</td>
<td>$-13.5$</td>
</tr>
</tbody>
</table>

[a] Absorption wavelength corresponding to the lowest energy transition ($\lambda_{\text{abs}}$); molar extinction coefficients ($\epsilon$, M$^{-1}$ cm$^{-1}$), solvent: CH$_3$CN; HOMO, HOMO-1, and LUMO energies at oB97X-D/6-311+G(d,p).
[b] $\pi$–$\pi^*$ transition. [c] $n$–$n^*$ transition. [d] The initially yellow solution becomes pink after a few hours and purple after a few days, indicating secondary interactions, [e] $n$–$n^*$ transition not visible.

e 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[20,24] reveal two low-lying excitations for 2a–e with $n$–$\pi^*$ ($E_{1s}$) and $\pi$–$\pi^*$ ($E_{2s}$) 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 pairs on the two azo nitrogen atoms (Figure S10). The change in colour is determined by the frontier orbitals for azophosphonium salts.[24,25]

Next, we recorded the cyclic voltammograms of triphe-nylammonium borate [H$_3$NiPr$_2$][BF$_4$] (Scheme 2). Therefore, we postulate the transient azoammonium salt 4 to undergo Hofmann elimination, which is commonly observed for sterically hindered tri-tert-alkylamines.[27]

Interestingly, the bulky triisopropylamine[31] provided a different reaction course. Treatment of phenylazidobenzotrifluoroborate with iPr$_2$N (2 equiv) in CH$_3$CN resulted in the formation of triazene PhN–NiPr$_2$ (72%),[32] dissoxi-pyliumammonium borate [H$_3$NiPr$_2$][BF$_4$] (2 equiv; 92%), and propene (2 equiv; detected by MS), instead of the anticipated amine–diazenium Lewis adduct [PhN$_2$(NiPr)$_2$][BF$_4$] 4 ($\Delta E$ = $-24.9$ kcal mol$^{-1}$; Scheme 2).[33] 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 ($E_{\text{ox}}$ [PhN$_2$/NiPr$_2$] = $-1.20$ V vs. Fe/Fe$^{+}$); therefore, we postulate the transient azoammonium salt 4 to undergo Hofmann elimination, which is commonly observed for sterically hindered tri-tert-alkylamines.[27]

Next, we recorded the cyclic voltammograms of triphe-nylphosphine ($E_{\text{ox}}$ = 1.13 V vs. Fe/Fe$^{+}$) and tri-tert-butylphosphine ($E_{\text{ox}}$ = 0.80 V vs. Fe/Fe$^{+}$) in acetonitrile (0.1 M [Bu$_3$P][PF$_6$]) and compared them to the reduction potential of the position resulted in a different outcome. We discovered that treatment of [PhN$_2$][BF$_4$] with tri-p-tolylamine in CH$_3$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).[34] Compared to the cyclic voltammogram of triphenylamine ($E_{\text{ox}}$ = 0.97 V vs. Fe/Fe$^{+}$), the oxidation potential of the more electron-rich $p$-tolylamine is shifted to more negative potentials ($E_{\text{ox}}$ = 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 ($\Delta G^0$ = 20.3 vs. 24.7 kcal mol$^{-1}$, respectively; Table 2).

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>LB</th>
<th>HOMO [eV][a]</th>
<th>LUMO [eV][b]</th>
<th>$E_{\text{ox}}$(LB/LB$^{\text{ox}}$) vs. Fe/Fe$^{\text{ox}}$[c]</th>
<th>$\Delta G^0$ = $E_{\text{ox}}$(LB$^{\text{ox}}$) – ($E_{\text{ox}}$(LB$^{\text{ox}}$) – $E_{\text{ox}}$(Fe/Fe$^{\text{ox}}$))[c]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ph$_3$N</td>
<td>$-7.10$</td>
<td>$0.95$</td>
<td>$0.97$ V</td>
<td>$24.3$</td>
</tr>
<tr>
<td>p-tol$_3$N</td>
<td>$-6.80$</td>
<td>$1.04$</td>
<td>$0.78$ V</td>
<td>$23.0$</td>
</tr>
<tr>
<td>iPr$_2$N</td>
<td>$-7.33$</td>
<td>$1.69$</td>
<td>$1.20$ V</td>
<td>$30.0$</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>
</tr>
<tr>
<td>tBu$_3$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 [Bu$_3$P][PF$_6$], glassy carbon working electrode, $\nu$ = 100 mV s$^{-1}$. [c] $\Delta G^0$ = $-nFE_{\text{red}}$ – $-nFE_{\text{ox}}$; $F$ = Faraday constant; $E_{\text{red}}$(Ph$_3$N) = $-0.10$ V vs. Fe/Fe$^{\text{c}}$.

Scheme 2. Reaction of [PhN$_2$][BF$_4$] with tertiary amines.
phenyldiazonium cation \(E_p^{18}(\text{PhN}_2^+;\text{PhN}_2^-) = -0.10 \text{ V vs. Fe/Fe}^+\).\[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 \(-20^\circ\text{C}\)),\[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 \(f\text{Bu}_2\text{P}\) with the nitratosonium salt \([\text{NO}][\text{BF}_4]^{-}\) \((E_p^{18}(\text{NO}^+;\text{NO}) = 0.87 \text{ V vs. Fe/Fe}^+)\[32]\) in acetonitrile resulted in the formation of \([f\text{Bu}_2\text{PH}][\text{BF}_4]\) as the major product \((\delta^{13}\text{P} = 56.1 \text{ ppm}, J_{\text{PH}} = 445.6 \text{ Hz}; \text{Scheme 3})\[10,33]\)

![Scheme 3](image)

which could be attributed to \(H\) atom abstraction from the solvent by the reactive \([f\text{Bu}_2\text{PP}^+]\) radical cation intermediate \(\Delta G_0 = 0.7 \text{ kcal mol}^{-1}\).[34] In addition, we detected small amounts of a radical species by EPR spectroscopy (Scheme 3) that features a six-line pattern at \(g_{\text{iso}} = 2.0071\), which is consistent with an organic doublet with hyperfine coupling interactions \((A)\) with nitrogen \((A^{14}_{\text{N iso}} = +29.55 \text{ MHz})\) and an \(I = \frac{1}{2}\) nucleus, likely phosphorus \((A^{31}_{\text{P iso}} = -34.10 \text{ MHz}; \text{Scheme 3})\[10]\). We postulate this to be the nitrosyl–phosphine adduct \(f\text{Bu}_2\text{P}^+-\text{NO}\) \((\Delta E = -0.5 \text{ kcal mol}^{-1})[30]\) which can be formed by the capture of the in situ generated NO by residual \(f\text{Bu}_2\text{P}\).

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 \(\text{[RN}_2(\text{NR}_2)][X]\) 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.[35] 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 the Supporting Information.


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