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 carbones, we developed the synthesis of a unique set of arylazophosphonium salts. A range of colors 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 N\textsubscript{1} 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). Inspired by the recently reported interaction of boranes with metal–N\textsubscript{2} complexes enabling facile N protonation, borylation, and silylation, we were intrigued by the reaction of low-lying N\textsubscript{1} which we were keen on investigating. Reported aryldiazonium–phosphine adducts afford postulated the red azophosphonium chlorides unstable species that are susceptible to N\textsubscript{2} elimination, affording the corresponding aryldiazonium salts [ArPPh\textsubscript{3}]\textsuperscript{+} (Ar = Ph, 4-MeC\textsubscript{6}H\textsubscript{4}, 4-ClC\textsubscript{6}H\textsubscript{4}, etc.).

Later, Yasui and co-workers found that aryldiazonium elimination, its π* acceptor orbital (LUMO: from 1.30 (N\textsubscript{2}) to −6.24 eV; see Figure 1) makes aryldiazonium salts suitable nitrogen-based Lewis acids, 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 azoimidazolium salts [RN\textsubscript{2}(NHC)][X] (X = Cl, BF\textsubscript{4}, PF\textsubscript{6}, etc.). Surprisingly, to date the corresponding azaazommonium salts [RN\textsubscript{2}(NR\textsubscript{2})][X] are unknown, 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, NO\textsubscript{2}, CO\textsubscript{2}H, OMe, OC(O)Me; Figure 2) as unstable species that are susceptible to N\textsubscript{2} elimination, affording the corresponding aryldiazonium salts [ArPPh\textsubscript{3}]\textsuperscript{+} (Ar = Ph, 4-MeC\textsubscript{6}H\textsubscript{4}, 4-ClC\textsubscript{6}H\textsubscript{4}, etc.).

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. Flower and co-workers synthesized B, but only reported its \textsuperscript{31}P NMR resonance (δ\textsuperscript{31}P\textsubscript{[H]} = 40 ppm; R = 6- naphthalen-2-01), 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 tunable azophosphonium salts simply from phosphines and aryl diazonium tetrafluoroborates in anecitoline, and provide detailed mechanistic insight by experimental and computational means. Related reactions of phenyl diazonium tetrafluoroborates with tertiary amines have also been investigated.

We found that treatment of the phenyldiazonium salt [PhN₃][BF₄] with triphenylphosphine (1.0 equiv) in acetonitrile at 0°C afforded the red azophosphonium salt [PhN₃(PPh₃)][BF₄] 1 (δP[H] = 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%; δ³¹P[H] = 43.9 and 52.5 ppm, ⁴²P[H] = 18.8 Hz).[(10)] We tentatively ascribed to the bis-phosphine adduct [PhN(PPh₃)₃][BF₄].[(10)] As Horner and Stöhr had indicated[(10)] 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(PBu₄)][BF₄] 2a (δP[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 NaBPh₄ 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 arylazimidazolium borates [ArN₃(IMes)][BPh₄] (Ar = Mes, o/p-C₆H₄Cl) 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)/1.242(2) Å, respectively),[(119)] 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 aren ring on the photophysical properties of 2. Treatment of the 4-substituted phenyldiazonium salts [p-R-C₆H₄]₃[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) arylazophosphonium salts [p-R-C₆H₄]₃[N–P(Bu₄)]I[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–
Table 1: $^1{^3}P$-[H] NMR chemical shifts, optical properties, and energies of the frontier orbitals for azophosphonium salts 2a–e.a)

<table>
<thead>
<tr>
<th></th>
<th>$^1{^3}P$-[H]</th>
<th>$\lambda_{\text{max}}$ [nm]</th>
<th>$\lambda_{\text{max}}$ [nm]</th>
<th>HOMO</th>
<th>HOMO-1</th>
<th>LUMO</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>69.4</td>
<td>316 (4.27)</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>2e</td>
<td>70.3</td>
<td>336 (4.33)</td>
<td>517 (2.26)</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>-11.2</td>
<td>-11.9</td>
<td>-4.0</td>
</tr>
<tr>
<td>2e</td>
<td>69.6</td>
<td>464 (4.62)</td>
<td>-30</td>
<td>-10.3</td>
<td>-13.5</td>
<td>-3.8</td>
</tr>
</tbody>
</table>

[a] Absorption wavelength corresponding to the lowest-energy transition ($\lambda_{\text{max}}$); molar extinction coefficients ($\varepsilon$, $\text{M}^{-1} \text{cm}^{-1}$); solvent: CH$_2$CN; HOMO, HOMO-1, and LUMO energies at 0.097 V vs. Fe/Fe$^+$.

Next, we recorded the cyclic voltammograms of triphenylamine in CH$_2$CN and found that triphenylamine is more prone to one-electron oxidation than triphenylamine ($\Delta G^0 = 20.3 \text{ vs. } 24.7 \text{ kcal mol}^{-1}$, respectively; Table 2).

Interestingly, the bulky triisopropylamine$^{[31]}$ provided a different reaction course. Treatment of phenylazidoxylon tetrafluoroborate with Pr$_3$N (2 equiv) in CH$_2$CN resulted in the formation of triazene PhN=N=Pr$_3$ (72%,$^{[26]}$)dissipoprolammonium borate [H$_2$NiPr$_3$]BF$_4$ (2 equiv; 92%), and propene (2 equiv; detected by MS), instead of the anticipated amine–azidoxylon Lewis adduct [PhN$_3$(NiPr$_3$)]BF$_4$.

In contrast to the reaction with triphenylphosphine, treatment of phenylazidoxylon tetrafluoroborate with triphenylamine yields azobenzene 3 (Scheme 2)$^{[2a]}$ by electrophilic aromatic substitution of the arylamine.$^{[2a]}$ Blocking the para position resulted in a different outcome. We discovered that treatment of [PhN$_3$][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).$^{[30]}$ Compared to the cyclic voltammogram of triphenylamine ($E_{\text{pa}}^{\infty}$ = 0.78 V vs. Fe/Fe$^+$), the oxidation potential of the more electron-rich p-tolylamine is shifted to more negative potentials ($E_{\text{pa}}^{\infty}$ = 0.78 V vs. Fe/Fe$^+$; Table 2), which supports the notion that p-tolylamine is more prone to one-electron oxidation than triphenylamine ($\Delta G^0 = 20.3 \text{ vs. } 24.7 \text{ kcal mol}^{-1}$, 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></th>
<th>HOMO</th>
<th>LUMO</th>
<th>$E_{\text{pa}}^{\infty}(\text{LB}/\text{LB}^-)$</th>
<th>$\Delta G^0$</th>
<th>$\Delta G^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhN</td>
<td>-7.10</td>
<td>0.95</td>
<td>0.97 V</td>
<td>24.3</td>
<td>20.4</td>
</tr>
<tr>
<td>p-tol N</td>
<td>-6.80</td>
<td>1.04</td>
<td>0.78 V</td>
<td>20.3</td>
<td>17.9</td>
</tr>
<tr>
<td>Ph$_3$N</td>
<td>-7.33</td>
<td>1.69</td>
<td>1.20 V</td>
<td>30.0</td>
<td>27.4</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>28.1</td>
</tr>
<tr>
<td>fBu$_3$P</td>
<td>-7.69</td>
<td>1.53</td>
<td>1.90 V</td>
<td>23.3</td>
<td>20.5</td>
</tr>
</tbody>
</table>

[a] Calculated at 0.097 V vs. Fe/Fe$^+$; [b] CH$_2$CN, 0.1 M [nBu$_3$N][PF$_6$], glassy carbon working electrode, $\nu = 100 \text{ mV s}^{-1}$.

The change in colour is determined by the frontier orbitals for azophosphonium salts (Table 2).

References:

phenylidiazonium cation \((E_p^{m+}(\text{PhN}_2^2/\text{PhN}_2^-)) = -0.10 \text{ V vs. Fe/Fe}^+\)\(^{[32]}\). Based on the sizable free energy change for radical cation formation by one-electron oxidation of the phosphines \((\Delta G^0 > 23 \text{ kcal mol}^{-1}; \text{ Table 2})\) 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 \(t\text{Bu}_3\text{P}\) with the nitrosium salt [NO][BF]\(_4\) \((E_p^{m+}(\text{NO}^+/\text{NO}^-) = 0.87 \text{ V vs. Fe/Fe}^+)\)^{[32]} in acetonitrile resulted in the formation of \([t\text{Bu}_3\text{P}][\text{BF}_4]\) as the major product \((\delta^{13}\text{P} = 56.1 \text{ ppm}, \text{ } \Gamma_{\text{iso}} = 445.6 \text{ Hz}; \text{ Scheme 3})^{[10,33]}

\[
\begin{align*}
\text{[NO][BF}_4\] + t\text{Bu}_3\text{P} & \rightarrow \text{NO}^- + [t\text{Bu}_3\text{P}][\text{BF}_4] \text{ (1)} \\
\text{[NO][BF}_4\] + t\text{Bu}_3\text{P} & \rightarrow \text{NO}^- + [t\text{Bu}_3\text{P}][\text{BF}_4] \text{ (2)} \\
\text{[NO][BF}_4\] + t\text{Bu}_3\text{P} & \rightarrow \text{CH}_2\text{CN} + [\text{BF}_4] \\
\end{align*}
\]

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

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

which could be attributed to H atom abstraction from the solvent by the reactive \([t\text{Bu}_3\text{P}^+\) 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 \(\text{g}_\text{e} = 2.0071\), which is consistent with an organic doublet with hyperfine coupling interactions \((A)\) with nitrogen \((A_{\text{iso}}^\text{N} = +29.55 \text{ MHz})\) and an \(I = \frac{1}{2}\) nucleus, likely phosphorus \((A_{\text{iso}}^\text{P} = -34.10 \text{ MHz}; \text{ Scheme 3})^{[10]}\). We postulate this to be the nitrosyl–phosphine adduct \(t\text{Bu}_3\text{P}^-\text{NO}^-\) \((\Delta E = -0.5 \text{ kcal mol}^{-1})^{[30]}\), which can be formed by the capture of the in situ generated NO by residual \(t\text{Bu}_3\text{P}\).

In summary, in acetonitrile, aryldiazonium salts react as nitrogen-based Lewis acids with phosphines, enabling the facile synthesis of tuneable azophosphonium salts. The corresponding azosazmonium salts \([\text{RN}_2(\text{NR}_2)]^+\) 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.

Acknowledgements

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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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