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Diazonium Salts

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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 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 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 N₂ σ 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).^[2c] Inspired by the recently reported interaction of boranes with metal–N₂ complexes enabling facile N protonation,^[3] borylation, and silylation,^[4] 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(C₆F₅)₃.^[5] While the direct interaction of dinitrogen with boranes has only been observed spectroscopically under forcing conditions,^[6] the use of transient borylenes afforded a stable bis(borylene)–N₂ complex as recently reported by Braunschweig and co-workers.^[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 C₆H₅⁺ activates N₂ by greatly lowering

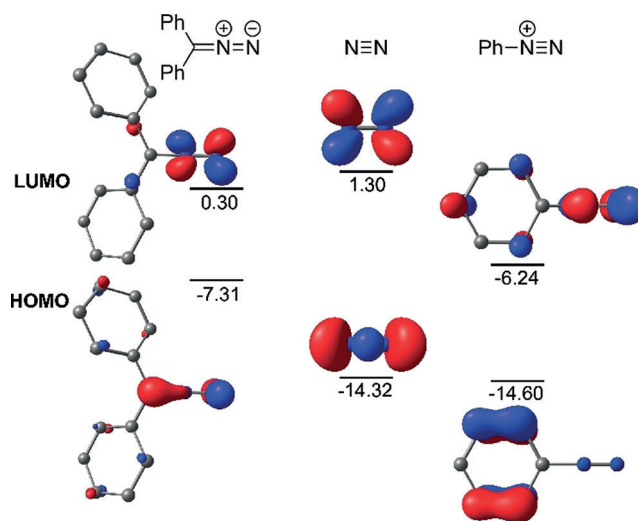


Figure 1. Lewis acid (C₆H₅⁺) and base (Ph₂C) augmented activation of N₂, including the HOMO (bottom) and LUMO (top) energies (in eV) calculated at the ωB97X-D/6–311 + G(d,p) level of theory.^[10]

its π* 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 [RN₂(NHC)][X] (X = Cl, BF₄, PF₆, etc.).^[11] Surprisingly, to date the corresponding azoammonium salts [RN₂(NR₃)]⁺[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 arylphosphonium salts [ArPPh₃][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 **B**, but only reported its ³¹P NMR resonance (δ³¹P{¹H} = 40 ppm; R = 6-naphthalen-2-ol),^[17] and Wokaun

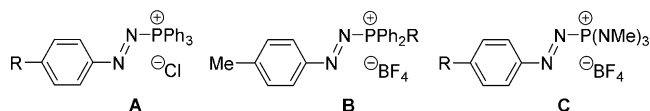


Figure 2. Reported aryldiazonium–phosphine adducts.

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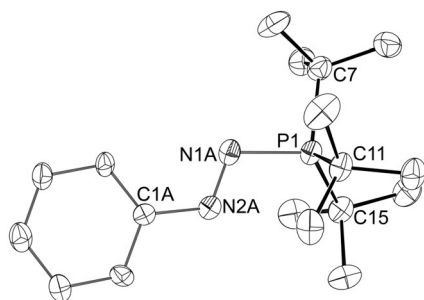
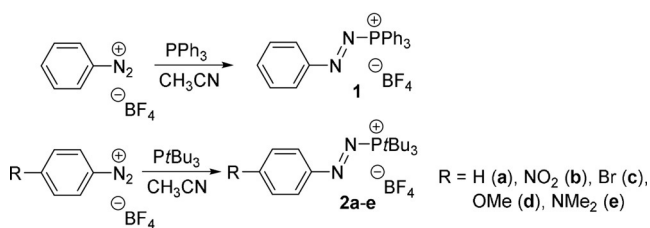
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and co-workers characterized **C** only spectroscopically (R = Cl, CN, SO₂NH₂, C(O)OEt; Figure 2).^[18] Herein, we report on the facile synthesis of readily tuneable azophosphonium salts simply from phosphines and aryldiazonium tetrafluoroborates in 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 [PhN₂][BF₄]^[19] with triphenylphosphine (1.0 equiv) in acetonitrile at 0 °C afforded the red azophosphonium salt [PhN₂(PPh₃)]⁺[BF₄]⁻ **1** ($\delta^{31}\text{P}\{^1\text{H}\} = 39.4$ ppm; Scheme 1; $\Delta E = -43.5$ kcal mol⁻¹ at the $\omega\text{B97X-D}/6-311+G(\text{d,p})$ 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%; $\delta^{31}\text{P}\{^1\text{H}\} = 43.9$ and 52.5 ppm, $^3J_{\text{PP}} = 18.8$ Hz),^[10] which we tentatively ascribed to the bis-phosphine adduct [PhN(PPh₃)N(PPh₃)]⁺[BF₄]⁻.^[20] As Horner and Stöhr had indicated^[13] 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 $\omega\text{B97X-D}/6-311+G(\text{d,p})$ level of theory, should provide a more stable product ($\Delta E = -53.2$ kcal mol⁻¹).^[10] The reaction of phenyldiazonium tetrafluoroborate with *t*Bu₃P (1.1 equiv) in acetonitrile resulted in an immediate colour change from colourless to pink and afforded azophosphonium salt [PhN₂(*t*Bu₃P)]⁺[BF₄]⁻ **2a** ($\delta^{31}\text{P}\{^1\text{H}\} = 69.4$ 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]



Scheme 1. Synthesis of aryazophosphonium tetrafluoroborates **1** and **2a–e** and molecular structure of [(C₆H₅)N₂(*t*Bu₃P)][BPh₄] (**2a**-BPh₄; displacement ellipsoids are set at 30% probability, hydrogen atoms and the noncoordinating BPh₄ 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)].

determined by X-ray crystal-structure analysis of suitable crystals of its tetraphenylborate analogue (obtained after anion exchange with NaBPh₄ in DCM),^[10] displays an almost planar (P1–N1–N2–C1 173.4(7)°) *trans* aryazophosphonium 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 aryazoimidazolium borates [ArN₂(IMes)][BPh₄] (Ar = Mes, *o/p*-ClC₆H₄) 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),^[11e] illustrating that in these cationic azo dyes, phosphines behave similar to carbenes.

As the colour of the aryazophosphonium salts can be readily tuned by changing the donor ligand (**1** (L = PPh₃): red; **2a** (L = *t*Bu₃P): pink), we next investigated the influence of the *para* substituent on the arene ring on the photophysical properties of **2**. Treatment of the 4-substituted phenyldiazonium salts [(*p*-R-C₆H₄)N₂][BF₄] (R = NO₂ (**b**), Br (**c**), OMe (**d**), NMe₂ (**e**))^[19] with tri-*tert*-butylphosphine (1.1 equiv) in acetonitrile afforded the intensely coloured (from purple to red/brown) aryazophosphonium salts [(*p*-R-C₆H₄)N₂(*t*Bu₃P)]⁺[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–**

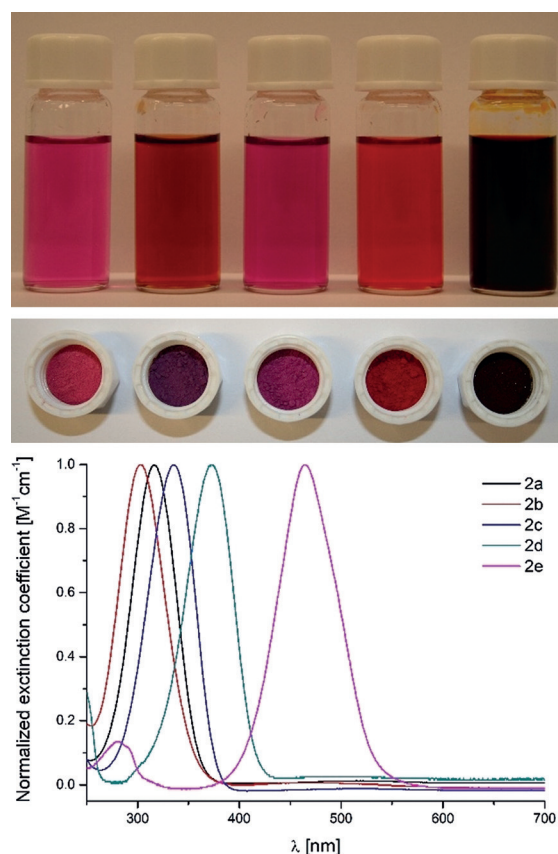


Figure 3. UV/Vis spectra and colours of azophosphonium salts **2a–e** in solution (0.006 M in CH₃CN) and in the solid state (from left to right: **2a**, **2b**, **2c**, **2d**, and **2e**).

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

	$^{31}\text{P}\{^1\text{H}\}$ [ppm]	λ_{abs} [nm] ^[b] ($\log \epsilon_{\text{max}}$)	λ_{abs} [nm] ^[c] ($\log \epsilon_{\text{max}}$)	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) ^[d]	-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

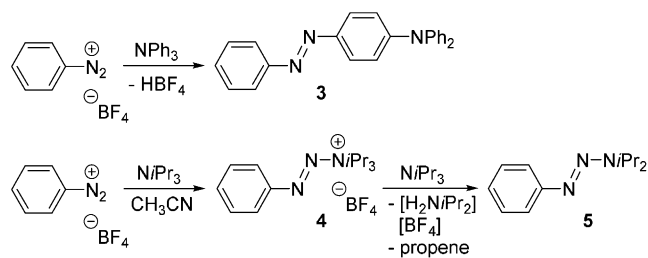
[a] Absorption wavelength corresponding to the lowest-energy transition (λ_{abs}); molar extinction coefficients (ϵ , $\text{M}^{-1}\text{cm}^{-1}$, solvent: CH_3CN); HOMO, HOMO-1, and LUMO energies at $\omega\text{B97X-D/6-311+G(d,p)}$.

[b] $\pi \rightarrow \pi^*$ transition. [c] $n \rightarrow \pi^*$ transition. [d] The initially yellow solution becomes pink after a few hours and purple after a few days, indicating secondary interactions, [e] $n \rightarrow \pi^*$ 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^[10,24] reveal two low-lying excitations for **2a–e** with $n \rightarrow \pi^*$ (E-S_1) and $\pi \rightarrow \pi^*$ (E-S_2) character. The first excitation corresponds to the HOMO \rightarrow 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 due to the admixture of π -orbitals from the aromatic ring (TD-DFT: 508 nm, $f = 0.0005$ for **2a**). The change in colour is determined by the *para* substituents, which have a stabilizing effect on 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**, $R = \text{NMe}_2$). The π and π^* orbitals involved in these two excitations are bonding/antibonding orbitals centred mostly on the $\text{N}=\text{N}$ moiety (Figure S10).

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_2^{\cdot}).^[25] Subsequent radical coupling with the concomitantly formed phosphine radical cation ($\text{R}_3\text{P}^{\cdot+}$) presents an alternative pathway to afford these readily tuneable azophosphonium salts. As N-based Lewis bases, such as arylamines, are known to undergo one-electron oxidation by Lewis acids to generate the corresponding radical cations,^[26] we also included triphenylamine and triisopropylamine (*t*Bu₃N is still elusive)^[27] in our mechanistic study.

In contrast to the reaction with triphenylphosphine, treatment of phenyldiazonium tetrafluoroborate with triphenylamine yields azobenzene **3** (Scheme 2)^[28] by electrophilic aromatic substitution of the arylamine.^[29] Blocking the *para*

**Scheme 2.** Reaction of $[\text{PhN}_2][\text{BF}_4]$ with tertiary amines.

position resulted in a different outcome. We discovered that treatment of $[\text{PhN}_2][\text{BF}_4]$ with tri-*p*-tolylamine in CH_3CN afforded an immediate colour change to deep blue, characteristic of the formation of the radical cation $[\text{p-tol}_3\text{N}^{\cdot+}]$, which was confirmed by EPR spectroscopy (Figure S6).^[30] Compared to the cyclic voltammogram of triphenylamine ($E_p^{\text{ox}} = 0.97$ V vs. Fc/Fc^+), the oxidation potential of the more electron-rich *p*-tolylamine is shifted to more negative potentials ($E_p^{\text{ox}} = 0.78$ 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^{-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.

	HOMO [eV] ^[a]	LUMO [eV] ^[a]	$E_p^{\text{ox}}(\text{LB}/\text{LB}^{\cdot+})$ vs. Fc/Fc^+ ^[b]	$\Delta G^0 = (E_p^{\text{ox}}\text{F}) - (E_p^{\text{red}}\text{F})$ ^[c]
Ph_3N	-7.10	0.95	0.97 V	24.7
<i>p</i> -tol ₃ N	-6.80	1.04	0.78 V	20.3
<i>i</i> Pr ₃ N	-7.33	1.69	1.20 V	30.0
Ph_3P	-7.97	0.92	1.23 V	30.7
<i>t</i> Bu ₃ P	-7.69	1.53	0.90 V	23.1

[a] Calculated at $\omega\text{B97X-D/6-311+G(d,p)}$. [b] CH_3CN , 0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$, glassy carbon working electrode, $\nu = 100$ mV s^{-1} .

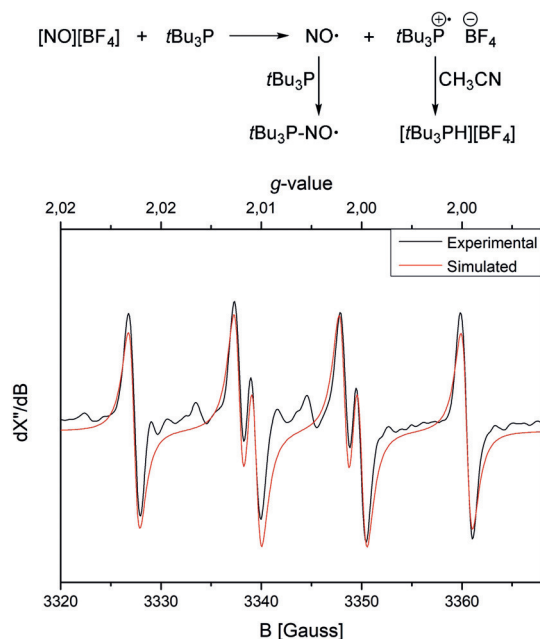
[c] $\Delta G^0 = -nFE_{\text{cell}}^0 = -RT \ln K_{\text{eq}}$, $F = \text{Faraday constant}$; $E_p^{\text{red}}(\text{PhN}_2^{\cdot+}/\text{PhN}_2) = -0.10$ V vs. Fc/Fc^+ .

Interestingly, the bulky triisopropylamine^[31] provided a different reaction course. Treatment of phenyldiazonium tetrafluoroborate with *i*Pr₃N (2 equiv) in CH_3CN resulted in the formation of triazene $\text{PhN}=\text{NNiPr}_2$ **5** (72%),^[12b] diisopropylammonium borate $[\text{H}_2\text{NiPr}_2][\text{BF}_4]$ (2 equiv; 92%), and propene (2 equiv; detected by MS), instead of the anticipated amine–diazonium Lewis adduct $[\text{PhN}_2(\text{NiPr}_3)][\text{BF}_4]$ **4** ($\Delta E = -24.9$ kcal mol^{-1} ; Scheme 2).^[10] Cyclic voltammetry shows that the reaction of triisopropylamine with $[\text{PhN}_2][\text{BF}_4]$ is, for thermodynamic reasons, unlikely to be initiated by single-electron transfer ($E_p^{\text{ox}}(\text{iPr}_3\text{N}/\text{iPr}_3\text{N}^{\cdot+}) = 1.20$ V vs. Fc/Fc^+ ; $\Delta G^0 = 30.0$ kcal mol^{-1} ; Table 2). 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 triphenylphosphine ($E_p^{\text{ox}} = 1.13$ V vs. Fc/Fc^+) and tri-*tert*-butylphosphine ($E_p^{\text{ox}} = 0.80$ V vs. Fc/Fc^+) in acetonitrile (0.1 M $[\text{nBu}_4\text{N}][\text{PF}_6]$) and compared them to the reduction potential of the

phenyldiazonium cation ($E_p^{\text{red}}(\text{PhN}_2^+/\text{PhN}_2) = -0.10$ V vs. Fc/Fc^+).^[32] Based on the sizable free energy change for radical cation formation by one-electron oxidation of the phosphines ($\Delta G^0 > 23$ kcal mol⁻¹; Table 2) and the facile formation of **1** and **2** at low temperatures (even at -20°C),^[10] 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*Bu₃P with the nitrosonium salt $[\text{NO}][\text{BF}_4]$ ($E_p^{\text{red}}(\text{NO}^+/\text{NO}^\bullet) = 0.87$ V vs. Fc/Fc^+)^[32] in acetonitrile resulted in the formation of $[\text{tBu}_3\text{PH}][\text{BF}_4]$ as the major product ($\delta^{31}\text{P} = 56.1$ ppm, $^1J_{\text{PH}} = 445.6$ Hz; Scheme 3),^[10,33]



Scheme 3. Reaction of *t*Bu₃P with $[\text{NO}][\text{BF}_4]$ together with the experimental (black) and simulated (red) EPR spectra of *t*Bu₃P-NO[•]. Simulated *g* value and hyperfine coupling constants (A): $g_{\text{iso}} = 2.0071$, $A_{\text{iso}}^{\text{N}} = +29.55$ MHz, $A_{\text{iso}}^{\text{P}} = -34.10$ MHz.

which could be attributed to H atom abstraction from the solvent by the reactive $[\text{tBu}_3\text{P}^{\bullet+}]$ radical cation intermediate ($\Delta G^0 = 0.7$ 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 ($A_{\text{iso}}^{\text{N}} = +29.55$ MHz) and an $I = 1/2$ nucleus, likely phosphorus ($A_{\text{iso}}^{\text{P}} = -34.10$ MHz; Scheme 3).^[10] We postulate this to be the nitrosyl–phosphine adduct *t*Bu₃P-NO[•] ($\Delta E = -0.5$ kcal mol⁻¹),^[10] which can be formed by the capture of the in situ generated NO[•] by residual *t*Bu₃P.

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 $[\text{RN}_2(\text{NR}_3)][\text{X}]$ are still

elusive, but should be accessible with strongly donating tertiary amines that lack β -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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