Diazonium Salts as Nitrogen-Based Lewis Acids

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Abstract
Aryldiazonium salts are widely used in many organic transformations with displacement of N₂ or through addition to the terminal nitrogen. Such aryldiazonium salts can be viewed as N-based Lewis acids that can react with Lewis bases to synthesize a wide variety of azo compounds. Additionally, diazonium salts are known to undergo single-electron transfer and release N₂, forming an aryl radical, which results in different reactivity. Herein, we provide a concise overview of the reactivity of aryldiazonium salts undergoing classical donor-acceptor reactivity or single-electron transfer.

Key words diazonium salts, donor–acceptor adducts, N-based Lewis acids, phosphines, carbenes, radicals

Introduction

Diazonium salts¹ are organic compounds with the general formula [R-N=N⁺][X]⁻, in which R can be an alkyl or aryl group. The general chemistry of diazonium salts has been reviewed recently,² so in this short review we describe selected examples of reactions of aryldiazonium salts, with a focus on those retaining the azo (N=N) moiety. [X]⁻ is typically an organic or inorganic anion such as a halide, [BF₄]⁻ or [PF₆]⁻. The reactivity of diazonium salts is often dominated by the loss of the N₂ moiety (Scheme 1).³ In the Sandmeyer reaction (I) the diazo group is replaced with a chlorine or bromine through the addition of the corresponding cuprous halide to a diazonium salt, forming an aryl halide.⁴ Formation of aryl chlorides or aryl bromides is also feasible using copper powder with HCl or HBr, referred to as the Gatterman reaction.⁵ Aryl cyanides can be formed via the Sandmeyer reaction with the use of CuCN, although here other metal complexes can be used.⁶ Aryl iodides can be prepared through the addition of hydroiodic acid or, more commonly, potassium iodide (II),⁷ and aryl fluorides are formed through thermal decomposition or photochemical induction of [BF₄]⁻ or [PF₆]⁻ with a diazonium salt in the Balz–Schiemann reaction (III).⁸ Mai showed that diazonium salts can be reduced by H₃PO₂ in water, forming the corresponding benzene analogue (IV).²,⁹

Scheme 1 Overview reactions of displacement of the N₂ group of diazonium salts. (I) Sandmeyer reaction; (II) replacement with iodide; (III) Balz–Schiemann reaction; (IV) reduction.
Thiols and thioethers can be formed in two steps from diazonium salts (Scheme 2). Addition of potassium xanthate and gentle warming promotes loss of $\text{N}_2$ and forms the intermediate shown. Subsequent pyrolysis forms the ArSR product, whereas alkaline hydrolysis yields the thio-phenol derivative. This reaction is called the Leuckart thio-phenol reaction (V).\(^1\,^3\,^10\)

![Scheme 2](image)

**Scheme 2** Representation of the Leuckart thiophenol reaction. The temperature is dependent on R-group and solvent used.

In the Gomberg–Bachmann reaction (VI; Scheme 3) an aryl group is coupled to the diazonium salt in basic media,\(^11\) and this can be carried out in an intramolecular fashion in the Pschorr cyclization. Addition of a hydroxyl group and thus formation of phenols proceeds upon heating a highly acidic aqueous solution of the diazonium salt, liberating an $\text{H}^+$ (VII).\(^7\) In the Meerwein arylation (VIII) an electron-poor alkene is coupled to the diazonium salt with use of a metal salt, commonly a copper(II) salt.\(^12\) The scope of the alkene as substrate has been extended to include a variety of olefins and even to electron-rich olefins.\(^3\)

![Scheme 3](image)

**Scheme 3** Overview reactions of displacement of $\text{N}_2$ group of diazonium salts. (VI) $\text{Ar}^\prime\text{O}^\prime$; (VII) $\text{H}_2\text{O}$, acidic condition, $\Delta$; (VIII) electron-poor alkene + catalyst.

## 2 Azo Compounds

### 2.1 Retention of the Azo Moiety

As well as displacement of the $\text{N}_2$ group, diazonium salts are able to react with nucleophiles that add to the terminal nitrogen (Scheme 4).\(^3\) Such reactions have been known for several decades and they result in the formation of (di)azo compounds; for example arenediazooethers from alkoxide ions (IX),\(^13\) or triazenes from primary and secondary aliphatic and aromatic (or heterocyclic) amines with release of $\text{H}^+$ (X).\(^3\) Arenediazosulphonates are formed from sul-fite ions (XI);\(^2\) first the $Z$-isomer forms, which is slowly transformed into the $E$-isomer. Note, the $Z$-isomer is highly reactive and can rapidly decompose into the starting mate-

![Scheme 4](image)

**Scheme 4** Overview reactions of addition of nucleophiles that react as Lewis base to diazonium salts. (IX) alkoxide ions; (X) various primary and secondary amines; (XI) sulfite ion; (XII) anions of sulfinic acids; (XIII) thiolates; (XIV) cyanide ion.

Perhaps a more common and well-known reaction of a nucleophile that adds to the terminal nitrogen is through electrophilic aromatic substitution (XIV; Scheme 5). In this case the para-position of the phenyl group of aniline or phenol, containing strongly activating substituents, adds to the $\text{N}_2$ moiety of the diazonium salt.\(^3\)

![Scheme 5](image)

**Scheme 5** Electrophilic aromatic substitution of an amine or phenol to a diazonium salt.

### 2.2 Coupling of Imidazoles to Diazonium Salts

As the diazonium salt reacts as an electrophile, thermodynamically it can also be viewed as an N-based Lewis acid that can therefore react with Lewis bases. Compounds IX, XI, XII, XIII and XIV are examples of such reactivity, which is unusual reactivity for typical nitrogen-based molecules that contain a lone pair and are thus seen as Lewis bases. However, recent papers by Gandelman and Stephan demonstrated that nitrogen-based compounds can be tuned as useful Lewis acids.\(^17\) Generally, cationic azo dyes containing imidazolium groups are produced via the coupling of an aromatic diazonium compound with an imidazole, which acts as nucleophile, followed by alkylation (I; Scheme 6).\(^18\,^21\) This coupling is similar to the coupling of a diazonium salt to aniline or phenol (Scheme 5). Coupling followed by al-
alkylation was already patented in the end of the 1950s; Klingsberg and Lewis reported this reactivity as the quaternization of N-alkylated imidazolium azo dyes.18a The alkylation can be carried out in a stepwise manner, the first alkylation can be performed by dissolving the azomimidazolium salt in an alkaline solution and adding an alkylating agent. As the product is insoluble it precipitates out of the reaction mixture and is pure enough to be used directly in the second alkylation step. The second alkylation conveniently proceeds with alkyl halide, sulfate or arylsulfonate in an organic solvent. Through this route, the two groups on the imidazolium nitrogen centers can differ from each other.

Similar reactivity was described by Baumann and Dehnert (Scheme 7); they reacted para-chlorobenzenediazonium chloride with the imidazole at the 2-position of the ring, forming 2, and subsequent addition of dimethyl sulfate resulted in cationic product 3, which is alkylated at the 1- and 3-position of the imidazole.19 Along with the alkylation, the chloride counter-ion is exchanged for the methyl sulfane anion because the chloride is rather labile. Simov reported the one-pot process in water for obtaining such imidazolium cationic dyes and thus shortening the overall reaction time. Note, the coupling of the imidazole to the diazonium salt proceeds at pH values between 8.5 and 9.10

This overall reaction was expanded and the alkylation can proceed with NaH and excess alkyl iodide (MeI, EtI or PhCH2I) in anhydrous THF affording the desired compounds with an iodide as counter-ion. Besides their use as dyes, these compounds are able to act as N,N-bidentate ligands to a metal center such as Cu(I) and Ag(I).20

From a synthetic point of view, if after the initial coupling and alkylation, the azomimidazolium salt holds a suitably reactive group (e.g., NHAc in 4, Scheme 8), then (after deprotection if necessary) a second diazotization and subsequent coupling to an aryl compound is feasible (6; Scheme 8).21 This order may be reversed, thus first the aryl coupling to the diazonium salt and secondly the imidazole is coupled, followed by alkylation. This class of compounds is mostly used for dyeing keratin fibers such as hair.

2.3 Coupling of N-Heterocyclic Carbenes to Diazonium Salts

Another way of accessing these azomimidazolium salts is by using carbenes as Lewis bases; specifically, N-heterocyclic carbenes (NHCs). This class of compound has made a significant impact as they are excellent σ-donor ligands for transition-metal complexes, they have been used in the stabilization of low-valent main group species, are used as organocatalysts, and are highly modular.22

Through the direct coupling of N-aryl or N-alkyl NHCs to diazonium salts, these strongly colored cationic azimidazolium dyes can be accessed in a straightforward manner and produced industrially (7; Scheme 9).23 This reaction is well described in the patent literature, which states various R-groups on the nitrogen atoms or backbone of the NHC are feasible as well as variations in the diazonium salt. Examples in patents describe various syntheses that reveal the in situ formation of the carbene through the use of an organic or inorganic base, once it is added to the diazonium salt.23 The imidazole derivative is added in slight excess (1.0 to 1.1 equiv) at 0 °C or room temperature and the azo compound is purified by column chromatography.23a
2.4 Coupling of Phosphines to Diazonium Salts

The analogous use of phosphines as Lewis bases in the addition to aryldiazonium salts is relatively underexplored, and only recently picked up interest. In 1953, Horner and Stöhr reacted triphenylphosphine with a variety of diazonium chlorides in an alcoholic solvent (methanol, ethanol or isopropanol) and obtained red azophosphonium chlorides \( A \) (\( R = H, Me, Cl, NO_2, CO_2H, OMe, OC(O)Me \); Scheme 10). Further reaction with water resulted in the formation of a triphenylaryl-hydrazyl phosphonium salt (\( 9 \)) and addition of hydrochloric acid resulted in the formation of aryl hydrazines (\( 10 \)) and triphenylphosphine oxide. Compound \( 8 \) is an unstable species, and Horner and Stöhr already noted that a second equivalent of triphenylphosphine is necessary to stabilize it. Compound \( 8 \) eliminates \( N_2 \) and decomposition results in substituted benzene (\( R-C_6H_5 \)), \( N_2 \), \( HCl \) and triphenylphosphine oxide (Scheme 10, a). A few years later Horner and Hoffmann reported the ratio between the diazonium salt and \( PPh_3 \), as well as the use of anhydrous solvents, turned out to be of importance (Scheme 10, bottom), as different products could be formed, not all of which are stable. It is noteworthy that the chemistry of the formation of compound \( 10 \) has only recently been described in the patent literature for its use in pharmacology.

Further research into the properties of the phosphine was performed by the group of Sutton in 1974 where they reacted not only \( PPh_3 \) but also tri(\( p \)-methoxyphenyl)phosphine and methyldiphenylphosphine with a range of diazonium salts (\( 11 \); Figure 1). The diazonium tetrafluoroborate salts were dissolved in acetone and added to \( PPh_3 \) at 0 \(^\circ\)C, yet only the electron-donating mesomeric substituents (\( NMe_2 \) and \( OMe \)) in the \( para \)-position resulted in the formation of isolable compounds, otherwise decomposition led to \([ArPPh_3][BF_4]\) with concomitant release of \( N_2 \). The benefit of the electron-donating groups leads to the formation of one large \( \pi \)-conjugated system, where the positive charge is not solely located on the phosphorus moiety but can also be found on the nitrogen or oxygen atom of the \( para \)-substituent, increasing the stability of the compound (Figure 1). A significant contribution of the delocalization of the positive charge can be observed in the crystal structure (Figure 1, X-ray structure). In the aryl ring \( C2-C3 \) and \( C5-C6 \) \((C2–C3 1.342(8), C5–C6 1.351(8) \text{ Å})\) are shorter compared to the other four bonds \((1.415(8) \text{ to } 1.429(8) \text{ Å})\). Also, the \( N1–N2 \) bond is longer than the typical \( N=N \) bond \((N1–N2 1.308(6), \text{ typical } N=N \text{ bond } 1.24 \text{ Å})\) and \( N3–C4 \) is shorter than the \( N3–Cethyl \) bonds \((N3–C4 1.336(7), N3–Cethyl1 1.490(9), N3–Cethyl2 1.473(8) \text{ Å})\), clearly showing the alternating long and short bonds throughout the crystal structure. Sutton and co-workers also reported on the improved stability for tri(\( p \)-methoxyphenyl)phosphine (\( (MeO)_3P \)), whereas with methyldiphenylphosphine (\( MePh_2P \)) the compounds proved to be more unstable. This is attributed
to the enhanced π-acceptor properties of phosphites relative to phosphines, leading to greater P–N multiple bonding character, and thus enhanced stability, in the former.27

A few decades later in 1997, Wokaun and co-workers reacted tris(dimethylamino)phosphine with equimolar amounts of various diazonium tetrafluoroborate salts in acetonitrile (R = Cl, CN, SO2NH2, C(O)OEt; Figure 2) affording the corresponding azophosphonium tetrafluoroborates 12 [p-R-PhN2(P[NMe2])3][BF4] in good yields (80–95%), which can be handled in air.28 In 1999, Flower and co-workers obtained the azophosphonium salt 13 [R = 6-naphthalen-2-ol; Figure 2] in anhydrous THF, which they only characterized spectroscopically by 31P NMR spectroscopy (31P{1H} NMR: δ = 40 ppm).30 Furthermore, Matsuda and co-workers obtained [p-(R-C6H4)N2(PR3)][BF4] (R = H, CH3, MeO, F) upon reaction of the corresponding diazonium salt with (PPh3)3Pd; they reported it as a side-product in their reaction.31

![Figure 2](https://example.com/figure2.png)

**Figure 2** Examples of azophosphonium salts

We expanded this little knowledge about azophosphonium salts by addition of the bulky, electron-donating tri-tert-butylphosphine to various aryldiazonium salts with para-substituents ranging from electron-withdrawing to electron-donating groups (14; Scheme 11).32 Addition of a slight excess of tBu3P (1.1 equiv) to the para-substituted phenyldiazonium salts [(p-R-C6H4)N2][BF4] (R = NO2, Br, H, OMe, NMe2) in acetonitrile at 0 °C resulted in the formation of intensely colored compounds 14 ranging from purple to pink to red/brown (R = NO2 to NMe2; Scheme 11), respectively, which can be used as dyes. Removal of the solvent and subsequent addition of CH2Cl2 and n-pentane resulted in the precipitation of the desired solids, [(p-R-C6H4)N2(tBu3P)][BF4], which were obtained in high yields (92–96%). X-ray crystallography of the tetraphenylborate analogue confirmed the formation of [(p-H-C6H4)N2(tBu3P)][BPPh3]. These azophosphonium salts are air-stable and experiments in D2O and 2 M HCl, in which they dissolve poorly, revealed, over time, only hydrolisis of the tetrafluoroborate anion, leaving the azophosphonium cation intact. The high tuneability of the diazonium salt directly relates to the color of the azophosphonium salt, which can be substantiated by UV/Vis spectroscopy, revealing two absorption bands from λabs = 303–464 nm (π→π*) and λabs = 453–523 nm (n→π*).

Simultaneously, Stephan and co-workers reported the synthesis of new azophosphonium salts (Scheme 12) by reacting diazonium salt [(p-Cl-C6H4)N2][BF4] with the bulky phosphines tBu3P or Mes3P in CH2Cl2 at room temperature, affording the azophosphonium salts 15 [(p-Cl-C6H4)N2(tBu3P)][BF4] (R = tBu, Mes), which are purple and red colored, respectively.33 Further reaction of [(p-Cl-C6H4)N2(Mes3P)][BF4] with addition of 1 equivalent of tBu3P resulted in the liberation of Mes3P and showed clean addition of tBu3P, presumably because of the greater Lewis basicity of the latter. Note, addition of 1 equivalent of the less bulky Ph3P leads to the unstable species [(p-R-C6H4)N2(PPh3)][BF4] (R = H,32 Cl33) and, upon addition of 2 equivalents, bis-addition is observed, resulting in the addition of the phosphine to both nitrogen atoms in a pseudo-transoid disposition forming [(p-Cl-C6H4)N2(N(PPh3)N(PPh3))[BF4]],33 highlighting the necessity of bulky groups on the phosphine for controlled mono-addition.

![Scheme 11](https://example.com/scheme11.png)

**Scheme 11** Reaction of aryldiazonium salt [(p-R-C6H4)N2][BF4] (R = NO2, Br, H, OMe, NMe2) with tBu3P; isolated yield in parentheses.

![Scheme 12](https://example.com/scheme12.png)

**Scheme 12** Top: reaction of aryldiazonium salt [(p-Cl-C6H4)N2][BF4] with tBu3P or Mes3P, isolated yield in parentheses. Bottom: product of the bis-addition.

The scope of azophosphonium salts was extended by our group by altering the aryl ring as well as the phosphine, demonstrating the readily tunability of this synthetic protocol (Figure 3).34 For the use of tri-tert-butylphosphine a wide range of stable adducts (16) can be synthesized in various shades of purple, pink and red ([[(p-R-C6H4)N2(tBu3P)][BF4] (R = CN, CF3, Cl, F, Ph, OC(O)CH3, tBu, CH3, OPh, OIPh, NH2)]). With the addition of trimesitylphosphine to selected aryldiazonium salts (17 [(p-R-C6H4)N2(Mes3P)][BF4] (R = NO2, Br, H, OMe, NMe2)), a difference in color was ob-
served as lighter shades of color are formed. Compounds 17 have reduced thermodynamic stability owing to the less donating ability of PMes₃ compared with PtBu₃.

2.5 Coupling of Tertiary Amines to Diazonium Salts

Notably, the use of tertiary amines as nucleophiles for the formation of azoammonium salts are still elusive as they can undergo electrophilic aromatic substitution with aromatic amines (18) or undergo Hofmann elimination if β-hydrogen atoms are present (19), as found in triisopropylamine, and thus form a triazene. Nevertheless, the formation of the triazene goes via the azoammonium intermediate (Scheme 13).

3 Use of Radicals with Diazonium Salts

For the aromatic amines, if the reactive para positions are blocked off, nucleophilic attack by the nitrogen could be envisioned, yet instead single-electron transfer occurs. Besides the reactivity of diazonium salts as a Lewis acid with a Lewis base, which is classical donor-acceptor reactivity, they can undergo single-electron transfer (SET) from a reducing agent. The diazonium ion is a useful oxidant that can undergo irreversible reduction in which it forms the intermediate diazenyl radical (ArN=N·), which is a rather labile species and readily releases dinitrogen forming the aryl radical Ar· (also referred to as dediazoniation, Scheme 14).

There are various ways of generating such an aryl radical: through thermal decomposition, reduction at an electrode, photoinduction, radiolysis with γ-radiation, through reduction by metal cations, or through anion-induced dediazoniation. Yet, the most essential element in all cases is that the redox potential of the reducing agent is strong enough to supply a single electron to the diazonium salt. Consequently, for the anion-induced case there is a fine line between coupling of the nucleophile (the anion) to the diazonium salt forming the azo-coupled product, or formation of the aryl radical via ArN₂⁺ + Y⁻ → ArN⁺ + Y⁻ (Y⁻ is a nucleophile and can be the solvent). The oxidation potential of the nucleophile and the solvent features plays an important role, still the azo-coupled product may cleave into the aryl radical photochemically or thermally.

3.1 Tertiary Nitrogen as Radical Species

Horner and Stöhr reported in 1953 the reaction of p-chloro- or p-nitrodiazonium salt with triethylamine in methanol and observed the release of N₂ (about 80% of product had released N₂; Scheme 15). Only a small amount of product could be isolated containing chloro- or nitrobenzene (20) and formaldehyde (21), suggesting it reacted via a radical pathway. The authors noted that when a drop of triethylamine was added to anhydrous diazonium salt it may explode.

We observed that reaction of [PhN₂][BF₄] with tri-p-tolylamine leads to the formation of a blue color, which is evidence of the tri-p-tolylamine radical cation ([p-tol₃N⁺]) and can be confirmed by EPR spectroscopy. This notion stands in contrast to the reaction of a diazonium salt with NPh₃ (Section 2.4), which undergoes two-electron chemistry. We illustrated that the more electron-rich tri-p-tolylamine is more prone to one-electron oxidation compared to triphenylamine as the oxidation potential is shifted to more negative potentials (p-tol): E_p = 0.78V vs. Fe/Fc'. Ph₃N:
3.2 Tertiary Phosphines as Radical Species

Tertiary phosphines are also able to undergo single-electron transfer. In 1991, Ohno and co-workers reported on the reaction of p-nitrobenzenediazonium tetrafluoroborate ([p-N02-PhN2][BF4]) with triphenylphosphine (Ph3P) or triethylphosphate ((EtO)3P) in an alcoholic solvent at room temperature in air in the dark (Scheme 16).42 First the aryl radical 22 and the phosphine radical cation 23 are formed, which subsequently react to give the benzene derivative 24 (major) with trace amounts of the coupled biaryl compound 25. Evidence for a radical mechanism was provided with deuterium experiments and varying the ratio between the two starting materials. Deuterium experiments with CH3OD and CD3OD showed the hydrogen atom was abstracted from the methyl group of the alcohol solvent, and not from the OH group. Upon hydrogen abstraction, the solvent methanol, CH3OH, gets oxidized by another equivalent of the diazonium salt, ultimately affording formaldehyde. Subsequently, the radical cation R3P+ (23) also reacts with the solvent, forming R3POR (the alcohol releases H+ which adds to the counter-ion), which, upon release of R+, forms R3P=O (26). Further investigations on the mechanism, supported by EPR spectroscopy, were conducted under nitrogen or argon atmosphere because performing the reaction in air suppresses the formation of 24.43–45

For reaction with the phosphite (EtO)3P additionally a coupled product (29) of the aryl radical with the phosphine radical cation was observed. This was described as being formed by analogy with the Arbuzov reaction (Scheme 17).42

Follow-up chemistry by the same group showed expansion of the scope of the diazonium salt to [p-CH3-PhN2][BF4] and the phosphines with trimethylphosphite (P(OMe)3), dimethyl phenylphosphonite (PhP(OMe)2) and methyl diphenylphosphinite (Ph3P(OMe)) to investigate the influence of the phenyl groups on the phosphine.43 No phenyl groups on the phosphorus leads to the largest amount of coupled product 29, as the electron pair is mostly centered on the phosphorus atom and not delocalized over the phenyl groups.

Comparing [p-NO2-PhN2][BF4] to [p-CH3-PhN2][BF4] or [p-CH3-O-PhN2][BF4] revealed comparable yields to the reaction with the nitro-substituent, indicating little influence of the electron-donating or withdrawing abilities of the para substituent.44 Furthermore, changing the solvent methanol to a 1:1 mixture methanol/acetonitrile lowers the product formed through coupling with methanol (24) and increases the amount of coupled product 29. Variation of the alcohol solvent (methanol, ethanol, cyclohexanol or propan-2-ol) influences the stability of the hydroxylalkyl radical and thus influences the ratio between the formed products, with increased formation of 24 for less stable hydroxylalkyl radicals.
Additionally, we investigated the reactivity, one- or two-electron transfer, of triphenylphosphine and tri-tert-butylphosphine and confirmed that both undergo a two-electron Lewis acid–base coupling with the phenyldiazonium tetrafluoroborate. Investigations of the stronger oxidant nitrosium tetrafluoroborate (\([\text{NO}]\text{[BF}_4\text{]}\); NO\(^+\): 0.87 V vs. Fc/Fc\(^+\)), PhN\(^2\text{-Cl}\)-C\(_6\text{H}_4\)N\(_2\text{)(PR}_3\)]\([\text{BF}_4\text{]}\), detected by \(\text{^31P NMR spectroscopy}\), is a result of quenching by subsequent reaction with acetoni trile of the radical species (Scheme 18). The major product \([\text{Bu}_3\text{P}]\text{[NO]}\text{[BF}_4\text{]}\), detected by \(\text{^31P NMR spectroscopy}\), is a result of quenching by subsequent reaction with acetoni trile as small amounts of a radical species could be detected by EPR spectroscopy. We propose the nitrosyl-phosphate radical species \([\text{Bu}_3\text{P}]\text{NO}\), formed by the capture of the generated NO\(^+\) with residual \([\text{Bu}_3\text{P}]\text{P}\) (Scheme 18). The nitrosyl-phosphate radical species \([\text{Bu}_3\text{P}]\text{NO}\), formed by the capture of the generated NO\(^+\) with residual \([\text{Bu}_3\text{P}]\text{P}\) (Scheme 18). The major product \([\text{Bu}_3\text{P}]\text{[NO]}\text{[BF}_4\text{]}\), detected by \(\text{^31P NMR spectroscopy}\), is a result of quenching by subsequent reaction with acetoni trile of the reactive radical cation intermediate \([\text{Bu}_3\text{P}]\text{NO}\).

Scheme 18 Generation of the radical species of the nitrosium cation with tri-tert-butylphosphine.

3.3 Azophosphonium Salt as Radical Species

Stephan and co-workers demonstrated that the formed azophosphonium salt could be used in follow-up chemistry forming a radical species (Scheme 19). Dissolving the azophosphonium salt \([\text{Bu}_3\text{P}]\text{N}\text{[NO]}\text{[BF}_4\text{]}\) with (SPh)\(_2\) and P\(_3\text{Bu}\), detected by \(\text{^31P NMR spectroscopy}\), is a result of quenching by subsequent reaction with acetoni trile of the reactive radical cation intermediate \([\text{Bu}_3\text{P}]\text{NO}\).

Cyclic voltammetry revealed a reversible reduction potential of the compounds \([p\text{-Cl-C}_6\text{H}_4\text{N}(\text{Mes})\text{[PhSP}_3\text{Bu}_3\text{])[BF}_4\text{]}\) (R = \([\text{Bu}_3\text{P}\), Mes]) at the potentials of –0.91 and –0.93 V vs. Fc/Fc\(^+\), respectively. K, \([\text{Cp}_2\text{Co}\) and PhSN\(_3\) all revealed to be strong enough reductants to reduce the azophosphonium salts. This reduction is a reversible reaction; the radical species can be oxidized back with \([\text{Cp}_2\text{Fe}]\text{[BF}_4\text{]}\) to the azophosphonium tetrafluoroborate salt.

Scheme 19 Reaction of azophosphonium salt \([p\text{-Cl-C}_6\text{H}_4\text{N}(\text{Mes})\text{[PhSP}_3\text{Bu}_3\text{])[BF}_4\text{]}\) with (SPh)\(_2\) and \([\text{Bu}_3\text{P}\). Note, an unidentifiable product was also formed.

3.4 Azoimidazolium Salt as Radical Species

Like the azophosphonium salts, the azoimidazolium salts are able to form a radical species. Severin and co-workers investigated various azoimidazolium salts (Scheme 20) given that, upon irradiation of 32 with UV-light, the \(^1\text{H NMR signals were no longer observable, indicating a paramagnetic species.}\) Cyclic voltammetry of 32 in acetoni trile revealed a reversible one-electron reduction (\(E^\text{°'} = –0.89\) V vs. Fc/Fc\(^+\)) and, synthetically, addition of potassium to the azoimidazolium salt in THF revealed the formation of a neutral radical (Scheme 20), which, upon oxidizing with I\(_2\), proved to be reversible. The phenyl analogue 33, with mesityl groups on the nitrogen, turned out to be remarkably stable under inert conditions and, even after exposure to air, only relatively slow decomposition was observed. Severin commented on the importance of the N-aryl substituents on the imidazole (Mes 33, 34 or Dipp 35) as the reduction of compounds containing N-methyl or N-isopropyl substituents were not successful. Computational studies and X-ray crystallography indicated 50% of the spin density is located on the N\(_2\) moiety, with the largest value on the nitrogen linked to the aryl group; thus, the radical can be described as an aminyl radical.

Note the azoimidazolium salt precursors applied in this study were synthesized via a new route, addition of AlCl\(_3\) to NhC-N\(_2\text{O}\) and the corresponding arene, and not the coupling of a diazonium salt with a carbene.

Scheme 20 Top: reduction of the azoimidazolium salt to the neutral radical; Bottom: Two additional neutral radicals through reduction of corresponding azoimidazolium salts. Counter-ion omitted for clarity, Dipp = 2,6-diisopropylphenyl.

Stephan and co-workers reported on the analogy of their azophosphonium radical species to these azoimidazolium radical species, indicating both class of compounds have similar EPR spectra. Moreover, both azo compounds can be reversibly reduced to their corresponding aminyl radical species and both reductions can be performed with potassium as reducing agent.
4 Summary and Outlook

Diazonium salts are important intermediates and can undergo various reactions, some of which are well-established, like the Sandmeyer reaction or electrophilic aromatic substitution with aniline. Two mechanisms for reactivity are identified in this research, firstly donor-acceptor reactivity and thus adduct formation where the diazonium salts react like a Lewis acid, and secondly where the diazonium salts act as an oxidant and hence undergo single-electron transfer. Direct addition of Lewis bases towards aryl diazonium salts offers a facile approach to azo compounds that can find applications as one-electron acceptors and form stable organic radicals. This overview shows great potential for the formation of a wide variety ofazo compounds and their use in radical chemistry.

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