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Bismuth Chemistry

Bismuth in Radical Chemistry and Catalysis

*Mauro Mato and Josep Cornella**
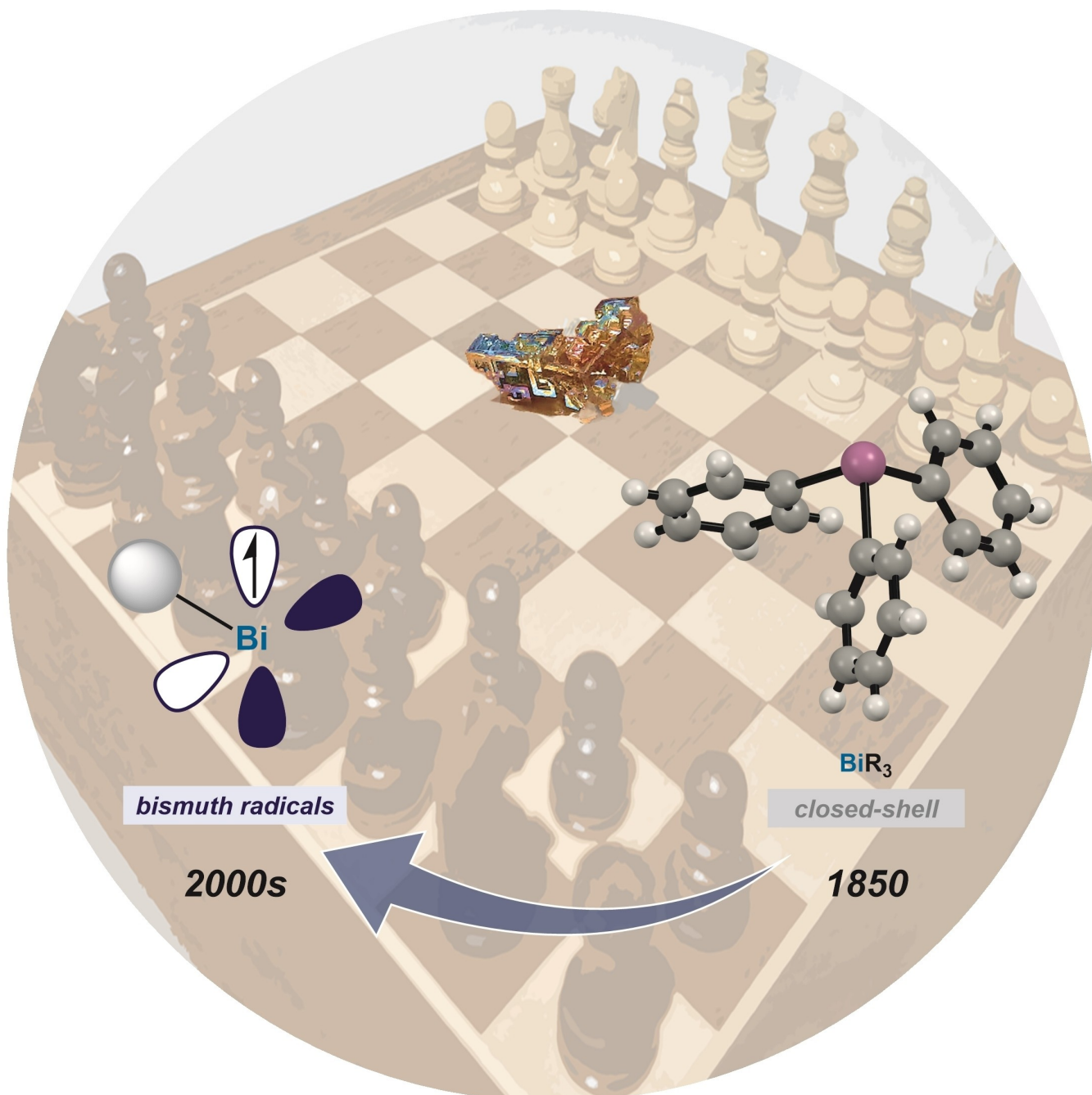
Abstract: Whereas indications of radical reactivity in bismuth compounds can be traced back to the 19th century, the preparation and characterization of both transient and persistent bismuth-radical species has only been established in recent decades. These advancements led to the emergence of the field of bismuth radical chemistry, mirroring the progress seen for other main-group elements. The seminal and fundamental studies in this area have ultimately paved the way for the development of catalytic methodologies involving bismuth-radical intermediates, a promising approach that remains largely untapped in the broad landscape of synthetic organic chemistry. In this review, we delve into the milestones that eventually led to the present state-of-the-art in the field of radical bismuth chemistry. Our focus aims at outlining the intrinsic discoveries in fundamental inorganic/organometallic chemistry and contextualizing their practical applications in organic synthesis and catalysis.

1. Introduction

Since ancient times, bismuth has fascinated chemists due to the beautiful brittle mirrors that form its characteristic crystals. With a half-life over a billion times longer than the estimated age of the universe, it is considered the heaviest stable element of the periodic table.[1] Bismuth has been claimed to have a remarkably low toxicity for a heavy metal;[2] hence, a significant portion of the global bismuth production is devoted to replacing toxic elements such as lead in various alloys.[3] Additionally, bismuth finds applications in cosmetics and pigments,[4] electronics,[5] and pharmaceuticals, such as bismuth subsalicylate or bibrocathol,[6] which are used to treat gastrointestinal diseases and eye infections, respectively.[7] Moreover, bismuth has found industrial applications such as the SOHIO process (Standard Oil Company of Ohio), where bismuth molybdate-based heterogeneous catalysts are essential in converting propene and ammonia to acrylonitrile.[8] Nevertheless, despite its low and stable price (fluctuating between 5 and 30 USD per kilogram from 1910 to 2010),[9] the use of bismuth in synthesis and catalysis remains limited.[10] The electron configuration of bismuth is [Xe] $4f^{14} 5d^{10} 6s^2 6p^3$ and, due to the inert pair effect, the $+3$ oxidation state is largely dominant. In addition, the weak shielding of the 4f electrons (lanthanide contraction),[11] results in Bi(III) compounds having a potent soft Lewis acidity. As a consequence, homogeneous bismuth catalysis has traditionally relied in the Lewis-acidic properties of Bi(III) salts, which can activate π-bonds or carbonyl compounds.[12] Though less prevalent in the literature, Bi(I)[13] and Bi(V)[12a] compounds —and their redox behavior—have also been studied over the last few decades.[14] Very recently, within the context of mimicking transition-metal reactivity with main-group elements,[15] novel redox processes where bismuth maneuvers through different oxidation states have been discovered. This led to the development of new synthetic method-

ologies based on bismuth redox catalysis.[16–18] Although the ability of bismuth to engage in radical redox processes has been postulated since as early as the late 19th century, the lack of modern synthetic or analytical techniques, such as NMR (nuclear magnetic resonance), EPR (electron paramagnetic resonance), SQUID (superconducting quantum interference device) or DFT (density functional theory),[19] prevented the identification of bismuth-radical intermediates.[20] It was not until the last few decades that the direct detection and characterization of well-defined bismuth-centered radicals has been achieved,[21] among many other main-group element counterparts.[22]

Bismuth compounds often display a distinct behavior compared to its lighter pnictogen congeners (N, P, As, Sb).[11,15c] Although common trends can be drawn for the Group 15, differences in structure and reactivity are often rationalized in terms of relativistic effects,[11,23] where spin-orbit coupling (SOC) plays a particularly important role for bismuth.[24] Due to the increasingly different size between the s and p orbitals down Group 15, bismuth has essentially non-hybridized orbitals, with the 6s and 6p as frontier orbitals.[25] The large and diffuse atomic orbitals of bismuth result in an inefficient overlap with the orbitals of other ligated atoms, leading to weaker (e.g.: Pn–H dissociation enthalpies in the PnH$_3$ series are P: 81.4; As: 74.6; Sb: 63.3; Bi: 51.8 kcal/mol)[26] and longer (e.g.: Pn–C distances in the PnPh$_3$ series are P: 1.93; As: 1.96; Sb: 2.15; Bi: 2.25 Å)[27,28] Bi–E bonds. The low dissociation enthalpies in Bi(III) compounds translate into a relatively facile homolytic cleavage, which can give rise to Bi(II) radical pairs under certain conditions.[29] Over the past years, various strategies have been elucidated in order to access the $+2$ open-shell oxidation state for bismuth. For example, the single-electron reduction of Bi(III), the one-electron oxidation of Bi(I) and the homolysis of weak Bi(III)–E bonds (see Section 3 for details). All in all, the rich variety of oxidation states available for bismuth makes it a promising element for developing new redox processes with potential applications in synthesis and catalysis.[30]

In this review, we aim to provide a general overview of the evolution of bismuth-radical chemistry throughout history; from anecdotal examples to the full characterization of bismuth-centered radical species. Our main goal is to contextualize the key discoveries in this field within the framework of organic synthesis and homogeneous catalysis, and therefore, we do not intend to provide an exhaustive and comprehensive account. Looking ahead, we hope that

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this article will serve as a bridge between fundamental inorganic chemistry and synthetic organic chemistry and catalysis, inspiring the development of new bismuth-based methodologies that operate through one-electron mechanisms.

2. Historical Perspective

The history of organobismuth chemistry dates back to 1850, when Löwig and Schweizer reported the synthesis of triethylbismuth.[31,32] Yet, the inflammability observed for trialkylbismuth compounds[33] limited further investigations on their properties. It was not until 1887, when Michaelis and Polis prepared the air-stable triphenylbismuth (**1**), that investigations in this area became more feasible.[34] In contrast to the modern approach which involves a polar ligand metathesis or transmetallation between a Grignard reagent and $BiCl_3$,[14,35] the seminal preparation of $BiPh_3$ involved the reaction of bromobenzene with a freshly prepared and grounded Bi/Na alloy (prepared by adding sodium to molten bismuth metal).[34] This approach is analogous to the prototypical first mechanistic step proposed in the Wurtz reaction or in the Wurtz–Fittig cross coupling (Scheme 1).[36] Nowadays, we rationalize this process through phenyl-radical intermediates generated upon single-electron transfer (SET) from sodium metal. Subsequent phenyl-radical recombination with Bi would lead to the observed Bi–Ph bond (Scheme 1, bottom). Later on, bismuth mirror was found to react with alkyl- or trifluoromethyl-radical fragments under different conditions (e.g.: pyrolysis or radiofrequency plasma) to afford organobismuth compounds; yet, the synthetic applicability of most of these methods was extremely limited and not well-explored.[34,37,38]

Besides reactions with metallic bismuth, significant but scattered examples of bismuth salts and organobismuth compounds reacting via one-electron mechanisms were reported throughout the course of the 20th century.[14] For example, Gilman and Yablunky proposed the formation of
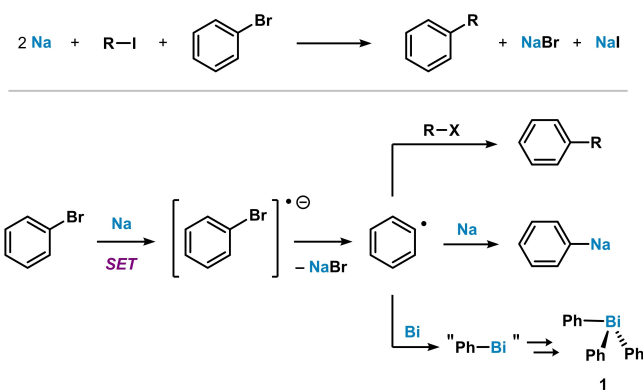

Scheme 1. The Wurtz–Fittig cross coupling and related processes.

sodium bismuthide Ph_2BiNa, upon reaction of Ph_2BiBr with 2 equiv. of sodium metal in liquid ammonia, where bismuth is in formal oxidation state +1 (Scheme 2, top left).[39] Years later, different groups showed that the same reaction using only 1 equiv. of sodium, at low temperature, allows the isolation and X-ray characterization of Bi_2Ph_4, a Bi(II) radical dimer (Scheme 2, top right).[40] Later, Suzuki, Matano and co-workers designed an alternative route to prepare sodium diarylbismuthides **7**, which were used as reagents to access mixed triarylbismuthines (Scheme 2, bottom).[41]

In the late 1930s, Gilman and co-workers also reported the preparation of aryl Bi(III) complexes by reaction of Bi(III) halides with aryl radicals, generated from diazonium salts with copper powder as reducing agent.[43] Thus, triarylbismuth complex **13** could be prepared from **12** and $BiCl_3$, albeit in low yield. This was based on an earlier discovery by Nesmeyanov using $HgCl_2$,[44] a method that was eventually extended to metal halides of many main-group elements (Scheme 3).[45] A similar process could be carried out using aryl iodonium salts instead.[46] However, after the 1960s, this synthetic approach was for the most part
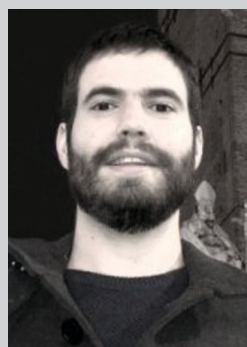
Dr. Mauro Mato completed his B.Sc. in chemistry at the University of A Coruña (Spain) in 2016 and his M.Sc. in synthesis and catalysis at the Rovirai Virgili University (Tarragona, Spain) in 2017. Then, he started his Ph.D. studies under the supervision of Prof. Antonio M. Echavarren at the Institute of Chemical Research of Catalonia (ICIQ, Spain), streamlining the generation and reactivity of metal carbenes. During this period, he carried out a short stay at Scripps Research (San Diego, CA) under the supervision of Prof. Phil S. Baran. Since 2021, he works as a Marie Curie Postdoctoral Fellow in the group of Dr. Josep Cornella at the Max-Planck-Institut für Kohlenforschung (Mülheim an der Ruhr, Germany), where he focuses on the development of radical bismuth chemistry.
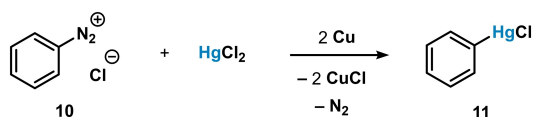
Dr. Josep Cornella (Pep) was born in La Bisbal del Penedès, a small town in south Catalunya. He studied chemistry at the University of Barcelona (2008) and carried out Ph.D. studies at Queen Mary University (UK), under the supervision of Prof. Igor Larrosa. After graduating in 2012, he carried out postdoctoral studies in the groups of Prof. Ruben Martin (ICIQ, Spain) as a Marie Curie Postdoctoral Fellow and Prof. Phil S. Baran (The Scripps Research Institute, California, USA) as a Beatriu de Pinos Fellow. In 2017, he was appointed as a Max Planck Research Group Leader in the Department of Organometallic Chemistry at the Max-Planck-Institut für Kohlenforschung in Mülheim an der Ruhr, Germany.
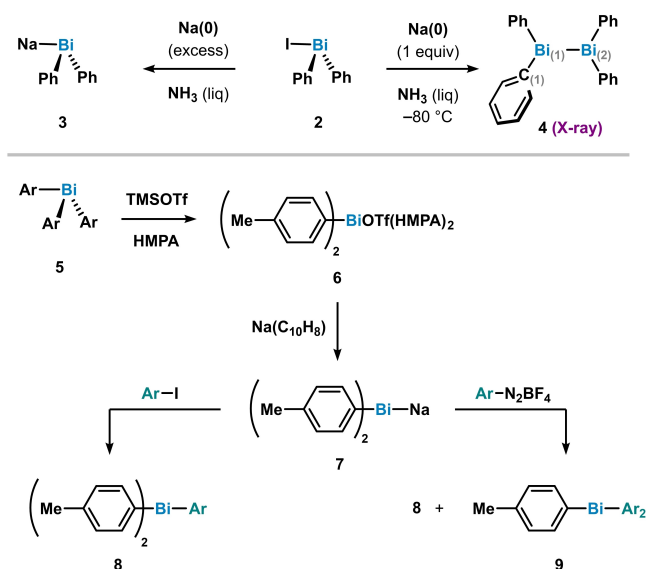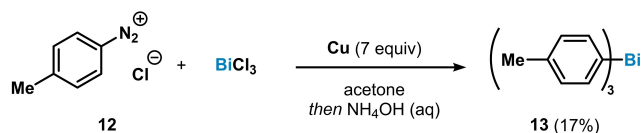
Scheme 2. Early reports on the single-electron reduction of Bi(III) complexes. Application of sodium diarylbismuthides in synthesis. Bond distances (Å) and angles (°) from X-ray analysis of **4**: Bi(1)–Bi(2): 2.990; Bi(1)–C(1): 2.28; C(1)–Bi(1)–Bi(2): 91.6.[42]
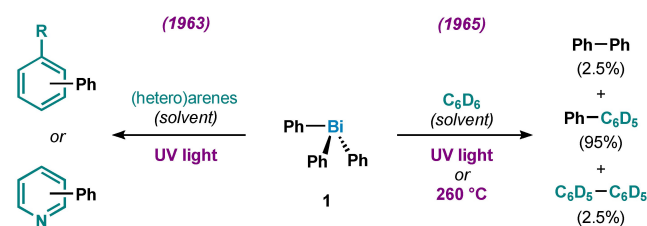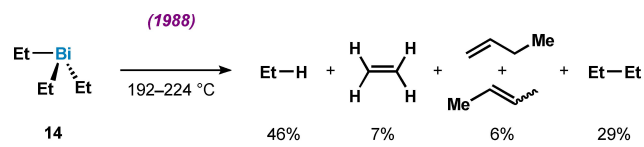
Scheme 3. The Nesmeyanov reaction and its extension to bismuth by Gilman.

Scheme 4. Homolysis of Bi(III)–C bonds upon heating or under light irradiation.

abandoned in favor of the more convenient use of Grignard reagents.[14,35,47]

As mentioned, simple trialkylbismuth compounds react violently with oxygen from air, leading to bismuth alkoxides and a variety of free organic products.[48] This process can be slowed down by increasing the steric encumbrance around the bismuth-alkyl bond; for example, bis(2,4,6-tri-iso-propylphenyl)methyl Bi(III) can even be purified by flash column chromatography under air.[49] The thermal decomposition of triethylbismuth at 200 °C leads to the formation of ethylene, butane and butenes as major gaseous products, suggesting the formation of ethyl radicals via homolysis of the Bi–C(sp^3) carbon bonds (Scheme 4, top).[50] Besides thermal homolysis, early work in the 1960s showed that the Bi–C(sp^2) bond in BiPh$_3$ can also be homolyzed under UV light irradiation, releasing phenyl radicals. These ensuing radicals were subsequently trapped by (hetero)aromatic toluene and pyridine, giving products of phenylation,

benzene and metallic bismuth (Scheme 4, bottom).[51] UV-light photolysis of BiPh$_3$ in C$_6$D$_6$ (or ^{14}C$_6$H$_6$) led mostly to biphenyl-d_5. Interestingly, a similar result was observed after heating the same solutions at 260 °C for several days.[52]

In the early 1970s, Davies and co-workers studied bimolecular homolytic substitution reactions (S$_H$2) in a broad range of metal centers using EPR spectroscopy.[53] In these studies, they proposed that organobismuth compounds undergo S$_H$2-type reactions with oxygen- or sulfur-centered radicals (e.g.: tBuO$^•$ or PhS$^•$).[54] For example, the reaction of BiPh$_3$ with PhSH in the presence of a radical initiator such as **15** gave PhBi(SPh)$_2$ upon mild heating, whereas radical inhibitors slowed down the process. The mechanistic rationale proposed by the authors for this activation is shown in Scheme 5, invoking the homolysis of Bi–O bonds.[55]

Although overlooked in the context of modern organometallic chemistry and catalysis, the history of radical bismuth chemistry is rich and diverse, most likely dating back to the very first processes involving the preparation of organobismuth compounds >150 years ago. The limited attention given to this reactivity can be ascribed to the common belief that radical chemistry was uncontrollable (hence the name) and unpredictable, thus resulting in enormous difficulties for its study and application. Nevertheless, thanks to the evolution of analytical and synthetic techniques, as well as novel concepts in catalysis, the scientific community has recently witnessed a reemergence
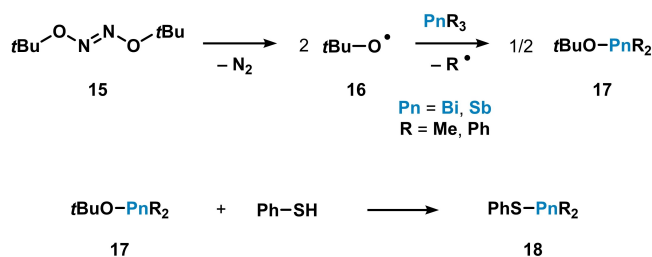
Scheme 5. Radical substitution reactions in organopnictogen compounds.

of fundamental radical bismuth chemistry. In the next sections, we will provide examples of these advancements, which pave the way for bismuth to join the explosively developing field of radical synthetic chemistry and catalysis.[56]

3. Generation, Characterization and Properties of Bismuth Radicals

Within Group 15, many nitrogen-centered radicals such as NO and NO$_2$ have been known for a long time.[57] On the other hand, the characterization of well-defined long-lived radicals of the heavy pnictogens remained largely unexplored until the last few decades.[58] This is a rather surprising dichotomy, since the first Group 15 organometalloid in the divalent oxidation state, Me$_2$AsAsMe$_2$ (cacodyl), was unknowingly prepared by Cadet already in 1757 and later characterized by Bunsen during the 1830s—a discovery regarded by some as the origin of organometallic chemistry.[59] Despite this, it was not until two centuries later that the preparation of Sb(II) and Bi(II) compounds was reported, reflecting the increasing difficulty for isolating radicals of the heavier pnictogens, due to their propensity to disproportionation.[37,40] However, recent years have witnessed a significant progress in the generation and characterization of relatively stable bismuth-centered radicals and, in this section, we present an overview of the landmark discoveries in this field.

3.1. Generation of Bismuth Radicals by Reduction of Bi(III)

The vast majority of known bismuth complexes present a +3 oxidation state. Thus, an intuitive method for accessing Bi(II) radical species is the single-electron reduction of Bi(III) compounds. Indeed, in 2014, Iwamoto and co-workers successfully reported the generation of a persistent Bi(II) radical by single-electron reduction of Bi(III) **19** with KC$_8$. Complex **20** was found to be a dimer in the solid state (**20a**), but in equilibrium with **20b** in solution, via reversible dissociation of the Bi–Bi bond (Scheme 6).[60] Besides characterization of the radical species by NMR and UV-Vis spectroscopy, they found that **20** could engage in a radical-radical coupling with the nitroxyl radical TEMPO (2,2,6,6-tetramethylpiperidin-1-yl)oxy) to give adduct **21**. It was also revealed that the Bi–O bond in **21** can dissociate back to **20** and TEMPO. The same group also reported the generation of compounds analogous to **20** but with lighter pnictogens, which showed significantly different behaviors.[61] It is worth mentioning that similar R$_2$Pn(II) (Pn = Sb, Bi) radicals had been previously identified in chemical vapor deposition processes, but not in solution.[62] Other compounds of the R$_4$Bi$_2$ family were already known at the time, but their dissociation or radical character was not explored in detail.[40,63]

In 2015, Coles and co-workers reported the isolation and characterization of the first monomeric Bi(II) radical that is
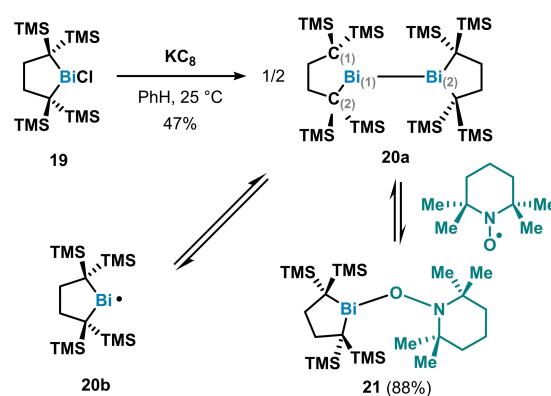

Scheme 6. Generation of persistent bismuth(II)-Centered radicals in solution. Bond distances (Å) from X-ray analysis of **20a**: Bi(1)–Bi(1): 3.182; Bi(1)–C(1): 2.237; Bi(1)–C(2): 2.370.

stable in the solid state.[64] Supported by an *N,O,N* backbone, **23** was obtained as a red solid via single-electron reduction of **22** with Mg(0). Monomeric radical **23** could be characterized by single-crystal X-ray diffraction, SQUID magnetic measurements (consistent with a paramagnetic compound with a single unpaired electron) and EPR spectroscopy. Exposure of **23** to excess Mg(0) for a longer time eventually led to over-reduction, giving metallic Bi(0) and Mg(II) complex **24** (Scheme 7).

In 2018, Schulz and co-workers reported the synthesis and solid-state structures of another Bi(II) radical (**26**) supported by two Lewis-acidic Ga(III) centers, which allow for a significant delocalization of the unpaired electron (Scheme 8A).[65] Reaction of Cp*BiI$_2$ with 2 equiv. of Ga(I) **25** led to the formation of Bi(II) radical-complex **26** upon release of 0.5 equiv. of decamethylfulvalen. The description of **26** as a predominantly metal-centered radical was consistent with the results of NMR, EPR, SQUID and DFT studies.[66] Later on, the same group used a similar redox strategy to access a variety of bismuth clusters containing a variable number of metal centers.[67] They also reported the in situ generation of Bi(II) biradical species **28** upon double single-electron reduction of **27** with Mg(0). This transient Bi(II) biradical could be trapped via [2+2] cycloaddition with alkynes (Scheme 8B).[68] It is worth mentioning that closed-shell *N,C,N*-Bi(I) complexes such as **61** (see Section 3.3) also undergo cycloadditions with alkynes, giving formal hetero Diels–Alder products.[69]
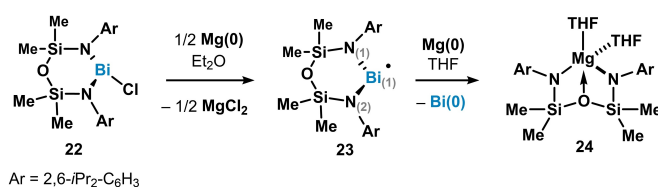

Scheme 7. Generation of a persistent and stable Bi(II) radical by reduction with Mg(0). Bond distances (Å) and angles (°) from X-ray analysis of **23**: Bi(1)–N(1): 2.173; Bi(1)–N(2): 2.172; N(1)–Bi(1)–N(2): 94.7.

A.

B.
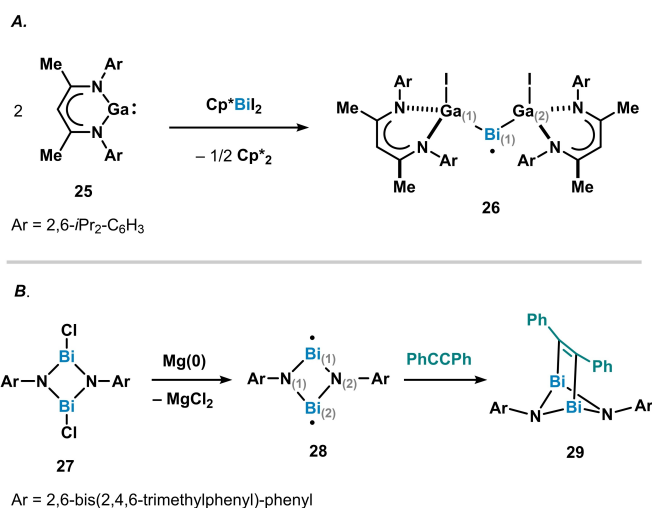
Scheme 8. A) Generation of a stable bis-gallium(III)-stabilized bismuth-(II) radical. B) Trapping of transient Bi-centered biradicals with an alkyne. Bond distances (Å) and angles (°) from X-ray analysis of **26**: Bi(1)–Ga(1): 2.664; Bi(1)–Ga(2): 2.666; Ga(1)–Bi(1)–Ga(2): 106.7; **28**: Bi(1)–N(1): 2.177; Bi(1)–N(2): 2.213; Bi(1)–Bi(2): 3.276; N(1)–Bi-(1)–N(2): 75.3; Bi(1)–N(1)–Bi(2): 97.0.

In 2019, Turner reported the reactivity of presumably transient Bi(II) **34** (Scheme 9).[70] Whereas the reaction of **30** with Mg(0) led to over-reduction of bismuth (giving Mg(II) complex **31** as main product), 1,4-bis(trimethylsilyl)-1,4-diaza-2,5-cyclohexadiene **32** in THF led to the exclusive formation of ring-opened product **36** upon release of tetramethylpyrazine **35** and TMS iodide.

It was rationalized that reduction of Bi(III) complex **30** with 1 equiv. of **32** leads to the transient generation of Bi(II)
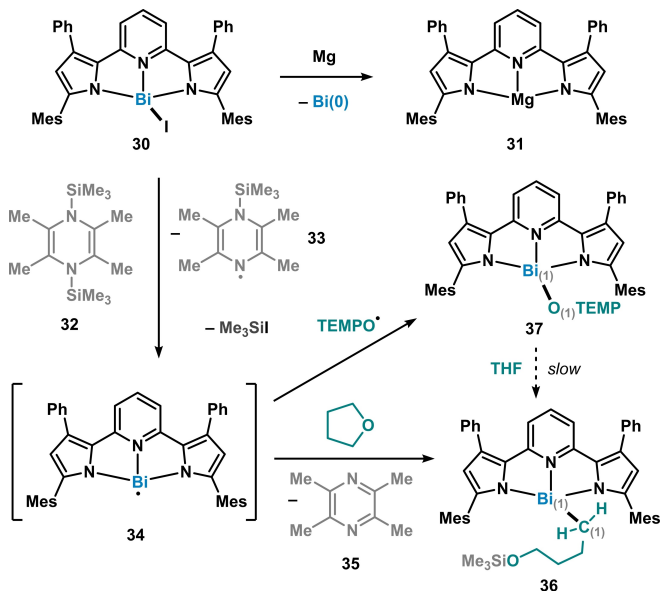
radical **34**, TMS iodide, and organic radical **33**.[71] Subsequently, bismuth radical **34** reacts with THF, which after ring opening leads to a Bi(III)(CH$_2$)$_4$O$^\bullet$ intermediate. At this point, the O-centered radical reacts with the Si in **33** to form the strong Si–O bond in **36**, with concomitant release of tetramethylpyrazine **35**. Under the same reaction conditions, Bi(II) radical **34** could be intercepted with TEMPO, giving adduct **37**. Interestingly, **37** also evolved slowly to give alkyl Bi(III) **36**, suggesting the reversibility of this radical recombination via Bi–O bond homolysis (Scheme 9).

3.2. Generation of Bismuth Radicals via Homolysis of Bi(III)–E bonds

As described in the first two sections, Bi–E bonds have been established for a long time to be relatively weak.[38,50–52,72] This weakness arises from the minimal overlap of the large and diffuse orbitals of bismuth, and hence, results on facile homolytic cleavages that can happen under both thermal or photochemical conditions. Indeed, many Bi(III) compounds have been identified as photosensitive or unstable at room temperature, such as BiCp$_3$,[73] and Bi(NMe$_2$)$_3$,[74] among others.[75] As a consequence, the homolysis of Bi(III)–E bonds has emerged as a viable tool for the generation and study of transient Bi(II) radical species. For example, in the context of studying the mechanism of the SOHIO process,[8] Hanna and co-workers reported the homolysis of the Bi–O bond in Bi(III) phenolates **39**,[76] prepared by reaction of Bi(III) halides or Bi(III) amides with lithium phenolate or phenols, respectively.[77] Importantly, the stability of the resulting adducts depends on the substitution pattern of the phenolate group (Scheme 10).

Bi(III) phenolates derived from 2,4,6-tri-*tert*-butyl-phenol were found to be relatively stable (Scheme 10, R = *t*Bu); however, upon standing in solution, homolysis to give
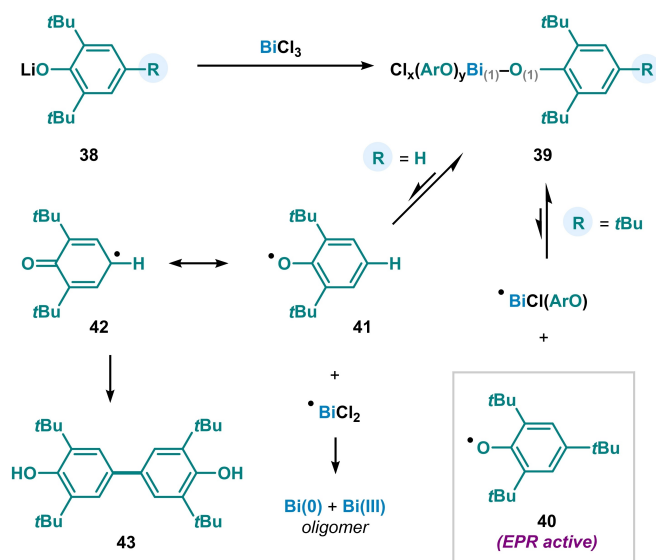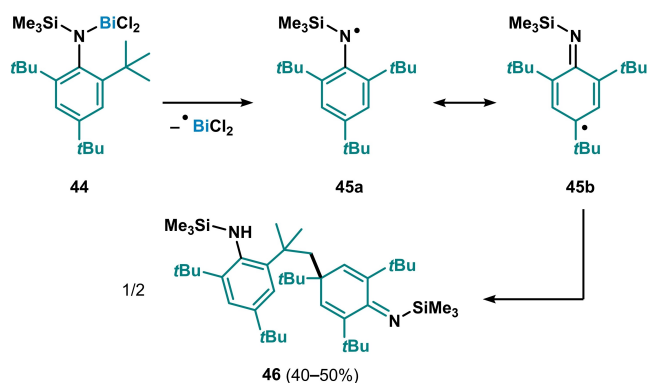

Scheme 9. A transient Bi(II) species that can ring-open THF. Bond distances (Å) from X-ray analysis of **36**: Bi(1)–C(1): 2.175; **37**: Bi(1)–O(1): 2.086.
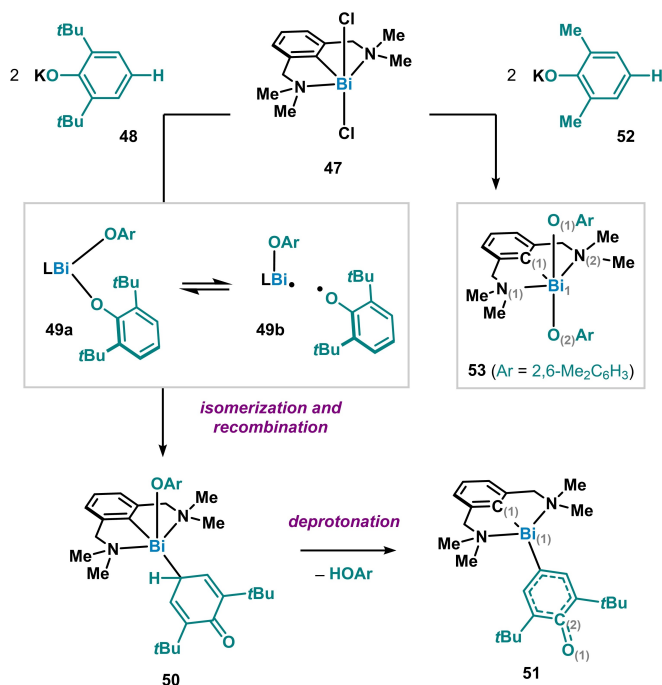

Scheme 10. Bi(II) radicals via Bi(III)-O homolysis. Bond distances (Å) from X-ray analysis of **39** (ArO$_2$BiCl): Bi(1)–O(1): 2.093.

persistent radical **40** occurred. Diamagnetic **39** could be observed by NMR, and the corresponding O-centered radical **40** was successfully detected by EPR. However, evidence of a well-defined paramagnetic signal for the putative Bi(II) radical could not be obtained.[78] On the other hand, when the *para* position of the phenolate was not blocked (Scheme 10, R=H), **39** is not stable, and the ensuing phenoxy radical **41** evolves to give biphenol **43** after dimerization of **42** and tautomerization (diphenoquinone is also obtained after final oxidation). The unstable Bi(II) fragment is proposed to engage in a series of disproportionation events ultimately leading to Bi(0) and Bi(III). In view on these findings, and based on precedents on the thermal radical formation in bismuth complexes, the authors suggest that this type of Bi–O bond homolysis could be analogous to the one proposed in the rate-determining step of the SOHIO oxidation and ammoxidation of propene at high temperatures.[79] In 2016, a similar dimerization was reported by Schulz and co-workers through the homolytic cleavage of the Bi–N bond in complex **44** (Scheme 11).[80]

In 2011, W. Evans and co-workers provided another example of this concept using *N,C,N*-supported Bi(III) dichloride **47** (Scheme 12).[81] Reacting **47** with 2 equiv. of 2,6-dimethyl substituted potassium phenoxide **52** led to the exclusive formation of bismuth(III) diphenoxide **53**. On the other hand, 2 equiv. of bulkier 2,6-di-*tert*-butyl-substituted potassium phenoxide **48** led to the formation of Bi(III) complex **51**, which contains an unusual oxyaryl dianion as ligand. Upon homolysis of the Bi–O bond of **49a**, the resulting phenoxy radical undergoes isomerization to a carbon-centered radical in the *para* position, which would subsequently recombine with the Bi(II) center to give **50**. Finally, the second basic phenoxide unit in **50** accepts the proton in α-position to the bismuth, giving **51** with concomitant formation of the corresponding phenol.

In 2022, the concept of Bi–O homolysis with bulky phenoxide ligands was applied by Cornella and co-workers for the radical activation of strong N–H and O–H bonds (Scheme 13).[82] Homolytic dissociation of the Bi–O bond in **54** gives a phenoxy radical and a highly reactive Bi(II) intermediate. According to DFT calculations, coordination of the lone pair on N–H and O–H bonds to the Bi(II) center results in a decrease of the bond-dissociation free energy (BDFE_{X-H}), which enables its cleavage by the phenoxy radical. This allows the activation of ammonia and water to give amido-Bi(III) complex **55a** and hydroxy-Bi(III) complex **55b**, respectively, upon release of 2,4,6-tri-*tert*-butyl-phenol. These products could be characterized both in

Scheme 11. Bi(II) radicals via Bi(III)-N homolysis.
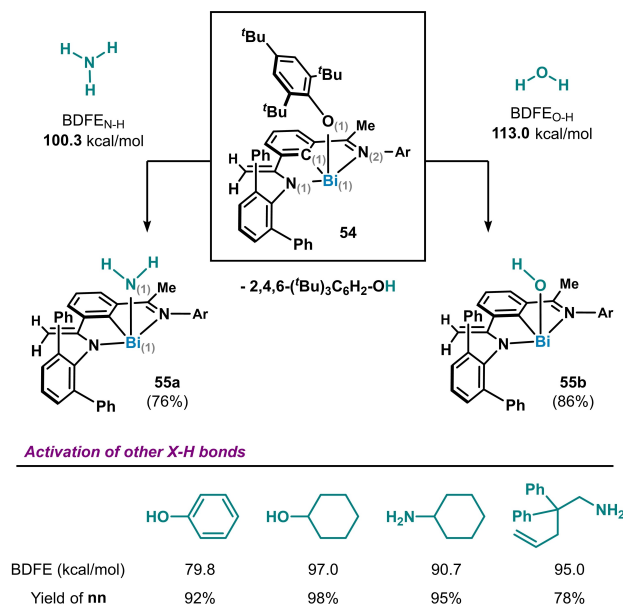

Scheme 12. Divergent radical reactivity in Bi(III) phenoxides supported by an *N,C,N* ligand. Bond distances (Å) from X-ray analysis of **53**: Bi(1)–O(1): 2.307; Bi(1)–O(2): 2.297; Bi(1)–N(1): 2.518; Bi(1)–N(2): 2.522; Bi(1)–C(1): 2.183; **51**: Bi(I)–C(1): 2.191; C(2)–O(1): 1.278.

Activation of other X-H bonds

|			
BDFE (kcal/mol)	79.8	97.0	90.7	95.0
Yield of **nn**	92%	98%	95%	78%

Scheme 13. Radical activation of strong N–H and O–H bonds with Bi(II) radical pairs. Bond distances (Å) from X-ray analysis of **54**: Bi(1)–C(1): 2.199; Bi(1)–N(1): 2.213; Bi(1)–N(2): 2.793; Bi(1)–O(1): 2.178; **55a**: Bi(1)–N(1): 2.177.

solution and in the solid state by single-crystal X-ray diffraction. Besides ammonia and water, the same concept was successfully extended to the activation of phenol, cyclohexanol and primary amines. (Scheme 13, bottom). In 2021, Lichtenberg and co-workers demonstrated that simple bismuth amides $Bi(NAr_2)_3$ undergo facile homolytic cleavage, releasing aminyl radicals under mild conditions (Scheme 14).[83] By themselves, these aminyl radicals (observed by EPR monitoring) evolve very selectively into hydrazines **57**, ultimately leading to Bi(0). In the presence of R_2PnH-type compounds (Pn = P, As), the same bismuth amides mediate a clean dehydrocoupling reaction, leading to the formation of $R_2Pn\text{-}PnR_2$ products **58**, upon release of $HNAr_2$.

As described in earlier sections, the homolysis of Bi–C bonds has also been reported, and its study has recently gained momentum in the context of catalysis (for details, see Section 5). Furthermore, it is also worth mentioning that several examples of complexes containing transition metal-bismuth bonds have been reported, which could, in principle, deliver bismuth-centered radicals upon M–Bi bond scission.[84] Similarly, an extensive variety of homometallic or heterometallic bismuth clusters (from 2 to more than 10 bismuth atoms) have been reported, and could also display radical character.[85] For example, the simplest Bi_2^{2-} anion (the only Pn_2^{2-} anion known to date) could in theory be described as isoelectronic to O_2. However, it was found to be diamagnetic with a singlet ground state, due to the strong spin-orbit coupling.[86] For the sake of conciseness, the literature on transition metal-bismuth complexes and bismuth-based metal clusters is not covered in this review since it has been recently reviewed elsewhere.[84,85]

3.3. Generation by Oxidation of Bi(I)

The single-electron oxidation of Bi(I) complexes is a much less explored alternative for the generation of Bi(II) radical intermediates. While low-valent bismuth compounds have been known for decades, the scarce availability and high reactivity of well-defined monomeric Bi(I) complexes has
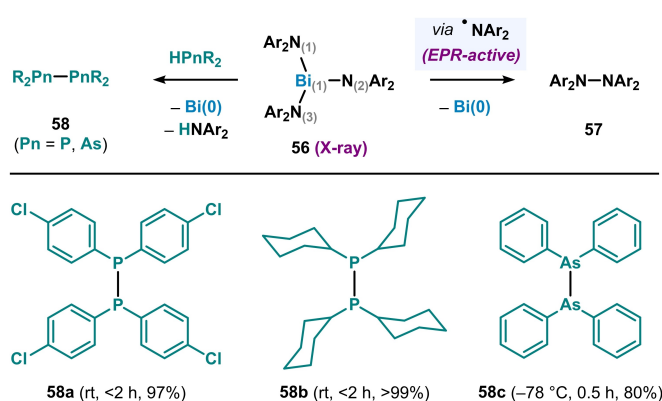
limited their study until recent years.[13,39] Some of these older scattered examples include the solid-state synthesis of BiCl from $BiCl_3$ and Bi(0),[87] or the laser-ablated generation of BiH in the gas phase.[88] Interestingly, a similar protocol based on the laser-ablation of Bi atoms in the presence of CH_4 could be employed to detect MeBiH, a Bi(II) radical generated through the activation of methane.[89] A breakthrough discovery in Bi(I) chemistry was made by Dostál and co-workers in 2010, with the synthesis of monomeric *N,C,N*-stabilized singlet bismuthinidenes such as **61** by reduction of the corresponding Bi(III) dihalides. This process can be accomplished through either polar or radical mechanisms. For example, treatment of **59** with 2 equiv. of K-Selectride allows for a simple and scalable preparation of bismuthinidene **61**. The reaction is proposed to proceed via polar ligand metathesis and subsequent reductive elimination of hydrogen gas from **60** (Scheme 15A).[13,30] In this context, diaryl-Bi(III) monohydrides have been characterized, and they were also found to release H_2 upon formation of the corresponding diaryl-Bi(I) dimers (see Section 3.4 for more details).[90] Alternatively, Bi(III) precursors can be reduced through a radical mechanism using single-electron

A. *Polar reduction of bismuth(III) to bismuth(I)*
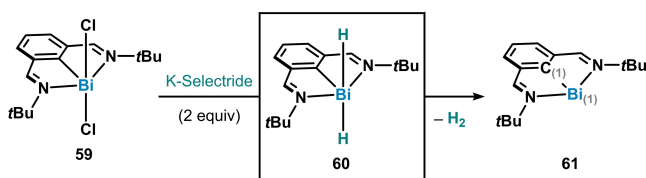
B. *Radical reduction of bismuth(III) to bismuth(I)*
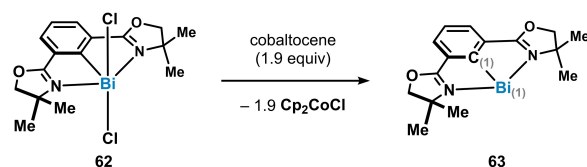
C. *In-situ coordination and radical reduction of bismuth(III)*
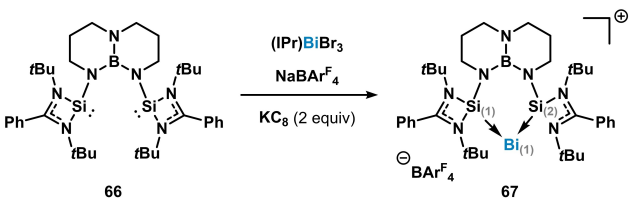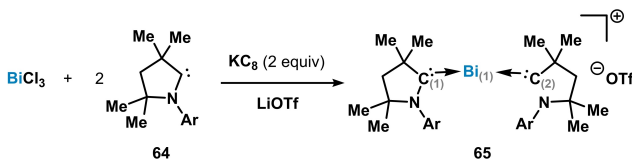
Scheme 15. Synthesis of Bi(I) complexes via polar (A) or one-electron mechanism (B and C). Bond distances (Å) and angles (°) from X-ray analysis of **61**: Bi(1)–C(1): 2.146; **63**: Bi(1)–C(1): 2.193; **65**: Bi(1)–C(1): 2.270; Bi(1)–C(2): 2.314; C(1)–Bi(1)–C(2): 111.9; **67**: Bi(1)–Si(1): 2.561; Bi(1)–Si(2): 2.557; Si(1)–Bi(1)-Si(2): 82.1.

Scheme 14. Pn–Pn (Pn = N, P, As) homocoupling via Bi–N homolysis. Bond distances (Å) from X-ray analysis of **56** (Ar = 4-methylphenyl): Bi(1)–N(1): 2.159; Bi(1)–N(2): 2.158; Bi(1)–N(3): 2.185.

reductants. For example, Cornella and co-workers reported the synthesis of Phebox-supported bismuthinidene **63** (among other complexes) by homogeneous radical reduction of **62** using cobaltocene (Scheme 15B).[17c,91] Heterogeneous single-electron reductant KC_8 can also be employed to access *N,C,N*-bismuthinidenes, among other complexes, such as CAAC- or silylene-stabilized Bi(I) cations **65** and **67**, as reported by the group of Roesky and by Mo and co-workers, respectively (Scheme 15C).[92] It is worth mentioning that highly reducing KC_8 can also be employed in some instances to reduce Bi(I) dimers to the corresponding radical anions.[93]

In 2023, Cornella and co-workers reported the synthesis and characterization of stable Bi(II) radical cations generated by single-electron oxidation of *N,C,N*-Bi(I) complexes (Scheme 16).[94] Treatment of bismuthinidenes **68** with 1 equiv. of ferrocenium cation allowed the isolation of Bi(II) radical cations **69**. These complexes were found to be highly sensitive to air, but they could be stored under argon atmosphere at −35 °C for several weeks. X-ray analysis revealed that they exist as monomeric Bi(II) structures in the solid state, while a combination of SQUID magnetometry and NMR/EPR spectroscopy suggests a paramagnetic S = 1/2 state. Multifrequency EPR allowed the observation

of Bi(II) with an unprecedented resolution, and the accurate assignment of the *g*- and ^{209}Bi *A*-tensors could be performed.

3.4. Mono-Coordinated Bismuthinidenes: Bismuth Diradical Species

In contrast to Lewis base-stabilized bismuthinidenes,[13,17] which are often described to be in a singlet ground state (with two paired electrons in the 6p orbital), recent reports have described the generation and characterization of bismuthinidenes with a diradical-type electronic structure (Scheme 17A). In 2020, Lichtenberg and co-workers reported the generation, spectroscopic characterization and computational analysis of BiMe, the first non-stabilized bismuthinidene. BiMe was generated by controlled, stepwise abstraction of methyl radicals from $BiMe_3$ in the gas phase by flash pyrolysis (Scheme 17B).[95] Out of the three possible structural descriptions of BiMe (**72a–c**), theoretical analysis suggests a triplet (diradical) ground state (**72b**). Furthermore, besides gas-phase generation, radical trapping experiments in the condensed phase revealed the feasibility of a Me-$BiMe_2$ homolytic cleavage under relatively mild reaction conditions (60–120 °C).

However, attempts to synthesize and isolate non-stabilized bismuthinidene diradicals often lead to the formation of dimeric species, with the two unpaired electrons in the 6p orbital forming a double bond with the 6p orbital of another Bi(I) center. For example, inspired by the work on lighter pnictogens,[96] the groups of Tokitoh[97] and Power[98] reported the synthesis and characterization of stable dibismuthenes **74** and **75**, respectively, providing evidence, for the first time, of a Bi=Bi double bond (Scheme 18, top). In 2023, Cornella, Neese and co-workers reported the first non-stabilized monocoordinate bismuthinidene (**77**, Scheme 18, bottom),[99] in contrast to previously reported lighter-pnictogen analogs stabilized by π-donation.[100] The use of a rigid and bulky ligand was of key importance, as reduction of the steric effects led to a dimeric structure (**76**). All magnetic and spectroscopic measurements point to a diamagnetic compound; however, due to the large SOC on Bi, theoretical analysis suggests that the ground state is mainly conformed of a triplet (diradical) state. The apparent diamagnetism is rationalized by the presence of an extremely large axial zero-splitting: as a result of the large spin-orbit contribution, the $m_s = 0$ is thermally isolated by 4500 cm^{-1} from the subsequent $m_s = +1$ and $−1$ magnetic sublevels. This type of ligand backbone allowed the preparation of analogous triplet stibinidines, which display a higher tendency to dimerize and to activate small molecules than the Bi-based counterparts. Nevertheless, a more forcing steric environment could be used to stabilize the Sb(I) diradical as a monomer in the solid state.[101]

3.5. Elusive Bi(IV) Radicals

Monomeric Sb(IV) radical cations [Sb(Ar)₃]X have been successfully prepared and fully characterized after single-
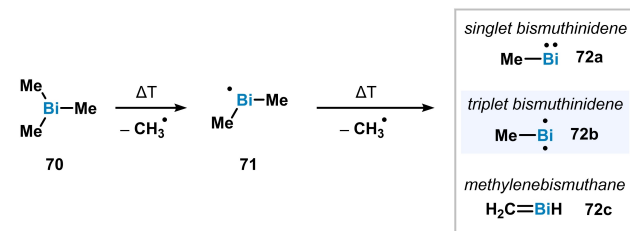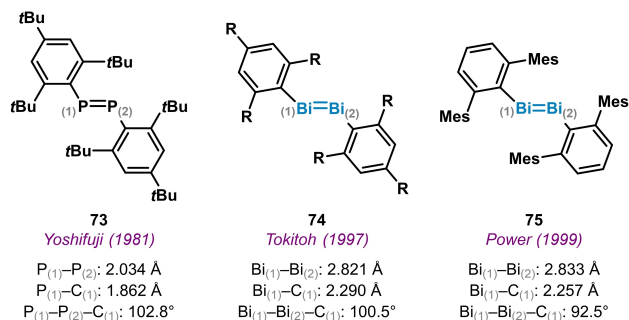
Scheme 16. Preparation of a stable monomeric Bi(II) radical cation by single-electron oxidation of a bismuthinidene. Bond distances (Å) from X-ray analysis of **68a**: Bi(1)−C(1): 2.149; Bi(1)−N(1): 2.460; Bi(1)−N(2): 2.507; **69b**: Bi(1)−C(1): 2.177; Bi(1)−N(1): 2.423; Bi(1)−N(2): 2.505.

Scheme 17. A) Neutral Lewis-base stabilized bismuthinidenes vs mono-coordinated bismuthinidenes (the 6 s² lone pair of electrons was omitted for clarity). B) Generation of the methylbismuth diradical.

Dimeric bismuthinidenes

73
Yoshifuji (1981)
$P_{(1)}$–$P_{(2)}$: 2.034 Å
$P_{(1)}$–$C_{(1)}$: 1.862 Å
$P_{(1)}$–$P_{(2)}$–$C_{(1)}$: 102.8°

74
Tokitoh (1997)
$Bi_{(1)}$–$Bi_{(2)}$: 2.821 Å
$Bi_{(1)}$–$C_{(1)}$: 2.290 Å
$Bi_{(1)}$–$Bi_{(2)}$–$C_{(1)}$: 100.5°

75
Power (1999)
$Bi_{(1)}$–$Bi_{(2)}$: 2.833 Å
$Bi_{(1)}$–$C_{(1)}$: 2.257 Å
$Bi_{(1)}$–$Bi_{(2)}$–$C_{(1)}$: 92.5°

A monomeric triplet bismuthinidene with a quenched magnetic response

76
$Bi_{(1)}$–$Bi_{(2)}$: 2.846 Å
$Bi_{(1)}$–$C_{(1)}$: 2.290 Å

77
$Bi_{(1)}$–$Bi_{(2)}$: >4.3 Å
$Bi_{(1)}$–$C_{(1)}$: 2.278 Å
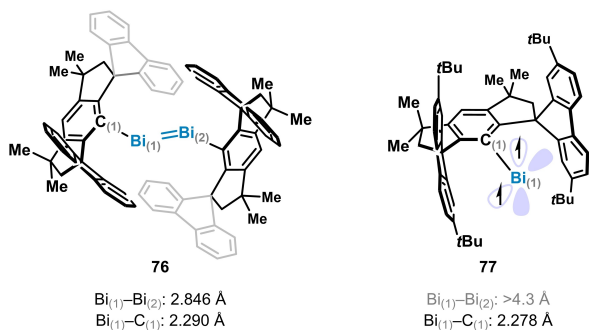
Scheme 18. From dimeric bismuthinidenes to a monomeric triplet Bi(I) complex with a quenched magnetic response. Selected bond lengths and angles from X-ray diffraction analysis.

electron oxidation of the corresponding SbAr$_3$ precursor.[102] On the other hand, the selective one-electron oxidation of Bi(III) compounds is much more challenging, due to the harsher conditions required (inert-pair effect) and the lower stability (i.e.: lower BDE) of the resulting products. As a consequence of this, no well-defined monomeric Bi(IV) species has been reported to date.[21] The transient formation of Bi(IV) species has been proposed under harsh conditions in different contexts. For example, the presence of Bi(II) and Bi(IV) species has been postulated upon low-temperature radiolysis of BiCl$_3$ solutions in concentrated HCl, as suggested by UV/Vis absorption and EPR spectroscopy.[103] In 2009, the [BiMe$_3$]$^{·+}$ radical cation could be generated in the gas phase (and detected by mass spectroscopy) by photoionization of BiMe$_3$ using a monochromatic photon beam in the vacuum UV range from 7 to 14 eV.[104] Furthermore, it is worth mentioning that, besides Bi(II) intermediates, Bi(IV) species have also been postulated as intermediates in the SOHIO process.[8,76,77] In 2000, the synthesis and electrochemical characterization of a Bi(III) complex with a tri-anionic *N,N,N,N* corrole ligand was reported. The first reversible oxidation was assigned to the formation of a corrole π radical cation, whereas the second one was tentatively associated with the generation of a Bi(IV) species in solution.[105] Subsequent analysis of a similar system suggested both oxidation processes to be centered on the macrocyclic ligand, instead of on the bismuth center.[106] In 1998, Fuchigami and co-workers showed that anodic oxidation of BiPh$_3$ gave rise to Bi(III)–C

bond-cleavage products such as biphenyl or amide **79**. The authors invoked Bi(IV) radicals **78** as reactive intermediates (Scheme 19).[107]

Similarly to Bi(III)–E bonds (see Section 3.2), Bi(V)–E bonds are significantly weak and can undergo homolytic cleavage, a behavior that might explain the dramatic instability of compounds such as BiMe$_5$ and, to some extent, BiPh$_5$.[108] However, due to the limited availability of Bi(V) compounds and to the aforementioned instability of the resulting Bi(IV) species, this homolysis has been much less studied.[109] The intermediacy of aryl radicals was initially considered in the context of the C–C arylation of phenols and enols with arylbismuth(V) complexes pioneered by Barton and co-workers (Scheme 20, top).[110,111] Although the mechanism responsible for the main aryl-transfer pathway was polar in nature (as the reaction also proceeds in the presence of radical traps, such as nitrone **83**, nitrosobenzene or 1,1-diphenylethylene), the presence of aryl radicals under these reaction conditions was also confirmed by EPR and trapping studies (Scheme 20, bottom).[112]

Further scattered observations supporting the homolysis of Bi(V)–C bonds were later reported in similar contexts.[113] In 2008, Matano and co-workers showed that triaryl(1-pyrenyl) bismuthonium salts such as **106** led to the rapid formation of pyrene upon irradiation at 365 nm, suggesting a Bi(V)–C bond homolysis.[114] The corresponding Bi(IV) species arising from this cleavage has been proposed as intermediate in the initiation step of polymerization reactions (see Scheme 25 in Section 5 for details).
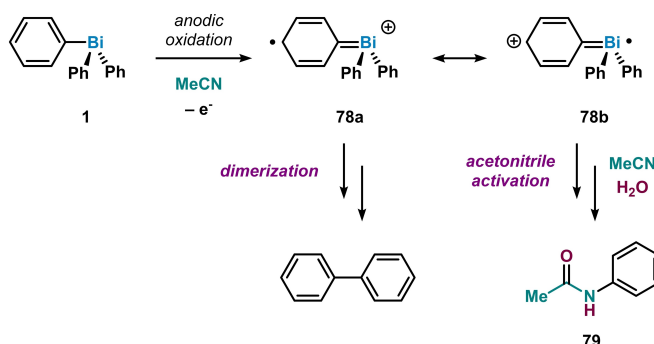
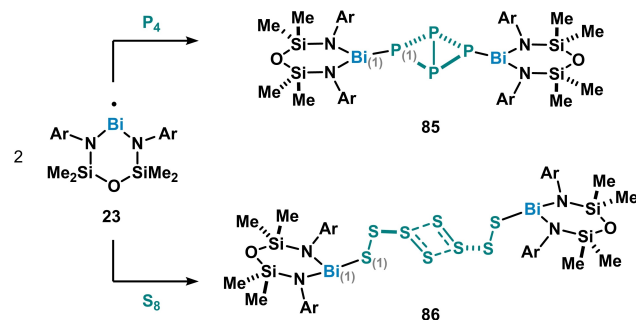**Scheme 19.** Anodic oxidation and subsequent reactivity of BiPh$_3$.
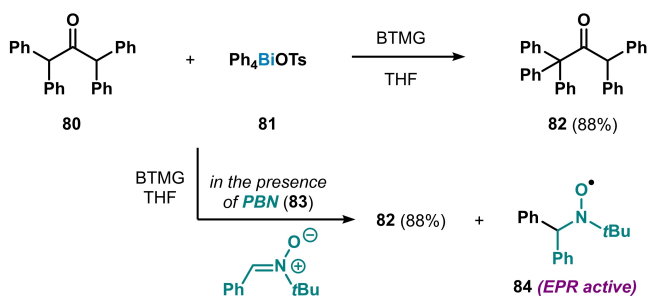
Scheme 20. Arylation and generation of aryl radicals with Ph$_4$BiOTs. BTMG = 2-*tert*-butyl-1,1,3,3-tetramethylguanidine.

4. Radical Bond Activation Mediated by Bismuth

Due to the interesting one-electron chemistry displayed by Bi, several approaches to activate small molecules in a radical fashion have recently evolved. While some of these examples have already been covered in Section 3, in this section we highlight radical activations using stable, well-defined low-valent bismuth complexes. For example, Coles and co-workers reported that isolated Bi(II) radicals **23** (see Section 3.1, Scheme 7) react with white phosphorus (P_4) via reversible and selective single P–P bond activation, affording bimetallic compound **85** (Scheme 21).[115] The same type of Bi(II) radicals react also with sulfur (cyclo-S_8) to afford similar bimetallic complexes containing bridging polysulfide anions (**86**).[116] The selective activation of only one bond in these processes is rationalized by the influence of the steric hindrance provided by the ligand backbone. Dimeric Bi(II) compounds (Ar_2Bi–$BiAr_2$) have also been reported to engage in this type of reactivity.[117]

Besides elemental sulfur and phosphorus, a wide range of bismuth compounds have been reported to activate various small inorganic molecules, although in most cases the radical or polar nature of the involved process has not been studied in detail.[118] For example, Lichtenberg and co-workers reported the radical insertion of CO into a Bi–N bond,[119] and several groups revealed the ability of different bismuth complexes to activate CO_2.[120] Both the insertion[121] and extrusion[122] of SO_2 on Bi–C bonds have been reported, and the insertion of CO_2, COS and NO was also accomplished using highly polarized complex **51** (see Section 3.2, Scheme 12).[123] Besides Bi(II) and Bi(III) compounds, *N,C,N*-bismuthinidenes have also been employed for the catalytic activation of greenhouse gas N_2O.[124] Importantly, this type of Bi(I) complexes has recently emerged as a main-group platform to carry out and study transition-metal-like oxidative additions of organic electrophiles. In 2013, Dostál and co-workers reported the activation of diphenyl-dichalcogenides PhEEPh (E=S, Se, Te) with *C,N*- or *N,C,N*-bismuthinidenes, leading to $LBi(EPh)_2$ complexes.[125] In 2020, the same group reported the S_N2-type oxidative addition of alkyl iodides and triflates into bis-amino or bis-imino bismuthinidenes **87**, giving alkyl-Bi(III) complexes **88** (Scheme 22, top).[126] Shortly after, Cornella and co-workers revealed that *N,C,N*-bismuthinidenes can also engage in
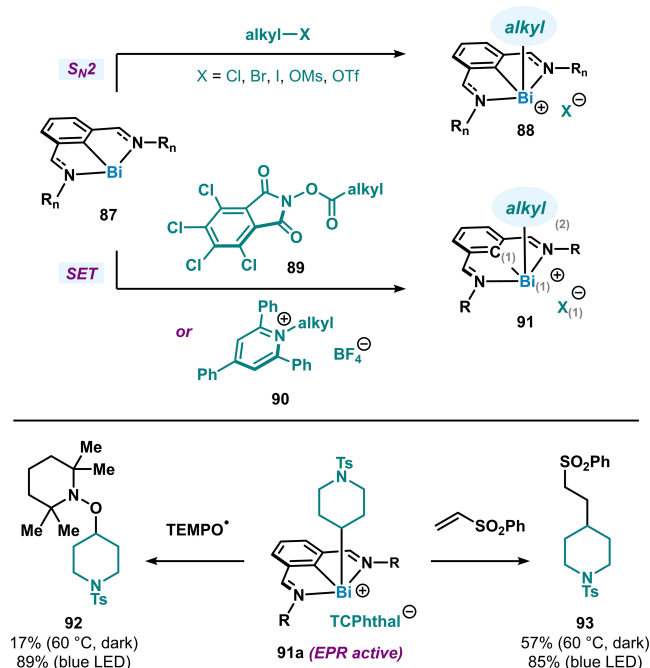
radical oxidative-addition processes, activating redox-active electrophiles (such as phthalimide esters **89** or Katritzky salts **90**) via single-electron transfer, followed by fragmentation and recombination of the organic radical with Bi(II) (Scheme 22, middle).[127] The resulting alkyl-Bi(III) complexes **91** display alkyl-radical-type reactivity, as evidenced by trapping and radical-clock experiments, as well as EPR analysis. This behavior is consistent with a facile Bi–C bond homolysis, which can be triggered either thermally or photochemically (Scheme 22, bottom).

In 2023, Cornella and co-workers disclosed a general approach for the oxidative addition of various aryl electrophiles into *N,C,N*-bismuthinidenes, a rare process for well-defined main-group-element complexes.[128,129] Bi(I) complex **61** is mildly reducing in the ground state and it can activate, in the absence of light, highly oxidizing (hetero)aryl electrophiles, such as diazonium and iodonium salts, leading to oxidative addition complexes **94** and **95**, respectively (Scheme 23, top). The intermediacy of open-shell intermediates was supported by radical-trapping experiments. More interestingly, **61** was identified as a photochemically active species. Upon red-light irradiation, **61** underwent oxidative addition with more challenging aryl electrophiles, such as aryl thianthrenium salts or aryl iodides, giving complexes **96** and **97**, respectively (Scheme 23, bottom). It is worth noting that, even though bismuthinidene **61** can absorb light all along the visible range, low-energy red light led to selective oxidative-addition processes, due to the absence of degradation pathways originating from high-energy irradiation.

Scheme 22. Polar and radical activation of alkyl electrophiles with a Bi(I) complex. Reactivity of alkyl-Bi(III) adducts. Bond distances (Å) from X-ray analysis of **91** (alkyl = benzyl, X = tetrachlorophthalimide): Bi(1)–C(1): 2.183; Bi(1)–C(1) (CH_2 from benzyl): 2.362; Bi(1)–N(1) (tetrachlorophthalimide): 2.908.
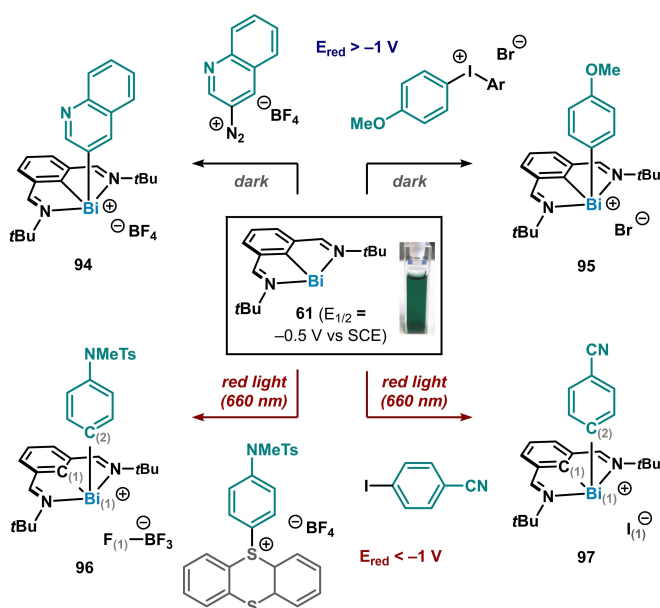
Scheme 21. Radical activation of P_4 and S_8 with Bi(II). Bond distances (Å) from X-ray analysis of **85**: Bi(1)–P(1): 2.675; **86**: Bi(1)–S(1): 2.599.
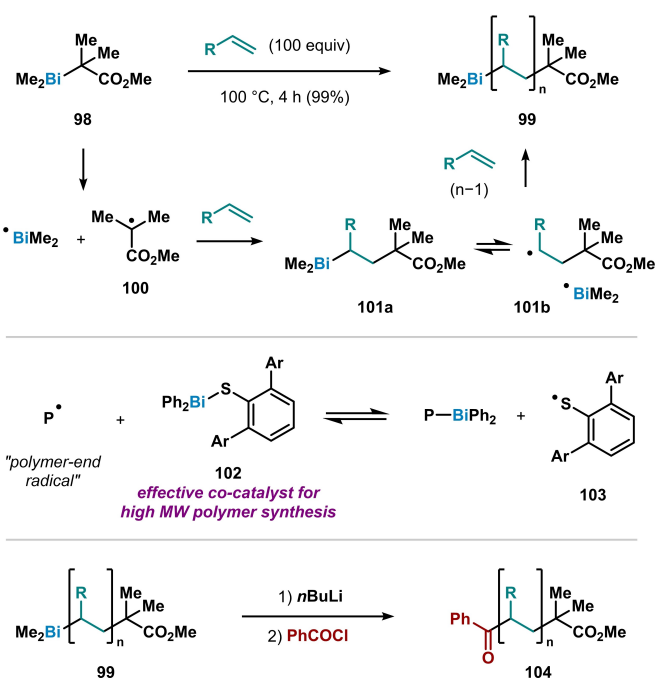
Scheme 23. Oxidative addition of aryl electrophiles into a red-light-active bismuthinidene. Bond distances (Å) from X-ray analysis of **96**: Bi(1)—C(1): 2.199; Bi(1)—C(2): 2.236; Bi(1)—F(1): 3.192; **97**: Bi(1)—C(1): 2.195; Bi(1)—C(2): 2.258; Bi(1)—I(1): 3.969.

Scheme 24. Controlled living radical polymerization via bismuth-radical activation.

5. Bismuth Radical Catalysis

As described in the introduction, throughout the history of homogeneous catalysis, bismuth has been employed almost exclusively in the form of Lewis-acid catalyst.[12] Present times are witnessing the unfolding of bismuth redox catalysis as a viable tool for organic synthesis.[13–16] However, in spite of all the scattered (but varied) observations suggesting the generation of radical species from bismuth compounds, limited examples of bismuth-catalyzed or initiated radical reactions have been reported. In fact, it was not until 2007 that an organobismuth compound was employed as radical catalyst or initiator.[130] In this section, we present an overview of the key findings that have contributed to the understanding and development of the emerging field of bismuth radical catalysis.

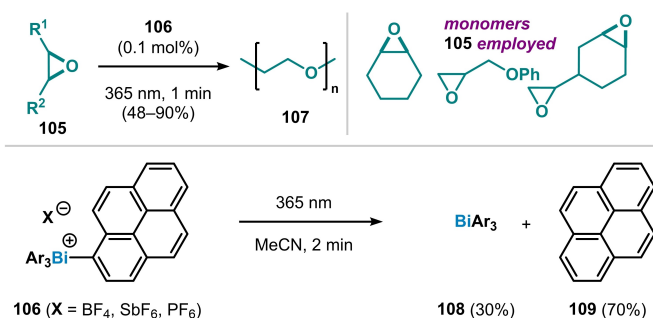### 5.1. Polymerization Reactions

In 2007, Yamago and co-workers reported the use of organobismuth(III) compounds such as **98** as initiators and mediators for the highly controlled living radical polymerization of styrenes, acrylates and other related activated alkenes (Scheme 24, top).[130] Although analogous reactivity was already known for other organo-pnictogen compounds,[131] to the best of our knowledge, this represents the first synthetically relevant example where catalytic species of bismuth are involved in radical activation processes.[132] Two years later, the same group reported that arylthiobismuthines **102** are excellent co-catalysts (together with **98**) for the synthesis of high molecular weight polymers. The ability of **102** to react reversibly with alkyl radicals[133]

allowed for a much more controlled polymerization process (Scheme 24, middle).[134] Later on, other Bi(III) complexes such as the bis(allyl)bismuth cation were also employed as initiators for similar controlled radical polymerizations.[135] Interestingly, the bismuth-based ω-polymer capping of some of these products could be employed as a handle for further functionalization. While the reaction of **99** with tributyltin hydride afforded the corresponding reduced product, a bismuth-metal exchange could also be carried out with organolithium, among other organometallic reagents. The resulting carbanions reacted efficiently with electrophiles (e.g.: CO₂, aldehydes, acyl chlorides, alkyl halides) to give the corresponding functionalized polymers (e.g.: **104**) with >99% of end-group incorporation (Scheme 24, bottom).[136]

In 2008, Matano and co-workers identified triaryl(1-pyrenyl)bismuthonium cations **106** as active pre-catalysis for the cationic polymerization of oxiranes **105** under UV-light irradiation (Scheme 25, top).[114] They proposed a light-induced homolysis of the Bi(V)–C bond, giving a transient Bi(IV) radical cation and a pyrenyl radical (isolated as pyrene after hydrogen-atom transfer, from stoichiometric homolysis experiments, Scheme 25, bottom) as key step of the activation mechanism. The authors highlight the importance of the counteranion in the process (SbF₆ > PF₆ ≫ BF₄). In 2023, Chitnis and co-workers showed that Bi(III) complexes supported by an *N,N,N* trianionic ligand are active in the ring-opening polymerization of cyclic esters such as ε-caprolactone and *rac*-lactide, although the mechanism of activation was not investigated in detail.[137]

Scheme 25. Triaryl(1-pyrenyl)bismuthonium cations: photoinitiators for cationic polymerization via Bi(V)−C homolysis.

5.2. Cycloisomerization Reactions

Due to their behavior as a Lewis acids,[12] Bi(III) salts have been explored significantly in the cycloisomerization of enynes and related compounds,[138] which can be rationalized by classical π-activation polar mechanisms.[139] In contrast, in 2019, Lichtenberg and co-workers reported how transition-metal-based bismuthanes such as **111** can catalyze the cycloisomerization of 5-iodoalkenes **110** via radical activation (Scheme 26).[140] Whereas this reactivity has been largely explored using other photocatalytic systems,[141] it is important to highlight that the reaction proceeds in the absence of light with catalyst **111**. The authors could identify **114** (together with manganese iodide **113**) as a competent reaction intermediate. Stoichiometric alkylbismuth(III) **114** reacted with further equivalents of **110** to give the cyclized product, presumably via Bi−C bond homolysis and radical cyclization followed by iodination of the cyclized alkyl-radical fragment. Persistent-radical adduct **115** could be observed upon EPR monitoring of the catalytic reaction in the presence of spin-trap **83**.
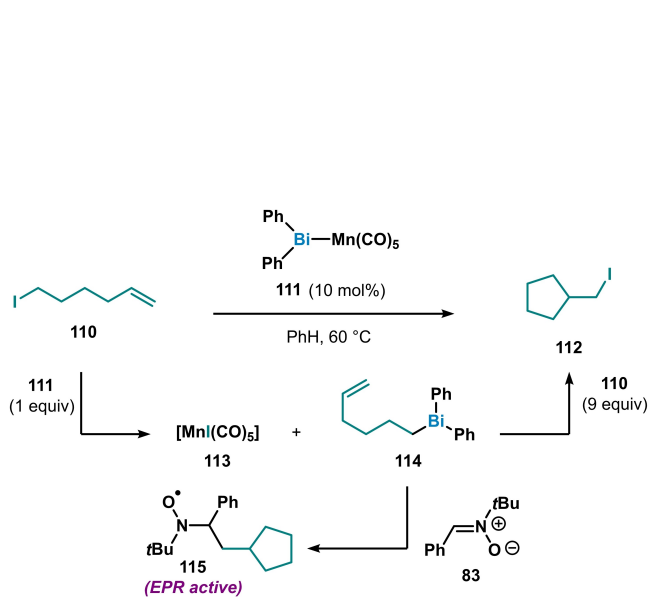
5.3. Coupling Reactions

Radical cross-coupling reactions are a revolutionary tool that has been widely exploited in modern synthetic chemistry to construct a variety of bonds.[142] While some of the findings described throughout this review hint at the potential of low valent-bismuth to promote this type of transformation, the field of bismuth-catalyzed radical couplings is still on its infancy. Some oxidative homocoupling reactions have been recently suggested to proceed via bismuth-radical mechanisms. For example, as described in Section 3.2 (see Scheme 14), stoichiometric amounts of bismuth amides Bi(NAr$_2$)$_3$ promote the dehydrocoupling of Pn−H bonds via Bi−N bond homolysis.[83] In 2017, Pârvulescu and co-workers showed how the dehydrocoupling of PhSH to give PhSSPh under air was accelerated dramatically in the presence of catalytic amounts of Bi(III) complexes containing weak Bi−O bonds. The authors suggest that a radical initiation to give Bi−S intermediates could be involved in the activation mechanism.[143] In 2023, Cornella and co-workers reported a bismuth-catalyzed formal C(sp^3)-N cross-coupling reaction based on the radical activation of redox-active electrophiles via single-electron transfer from a Bi(I) complex.[127] While unbiased alkyl redox-active electrophiles led to stable alkyl-Bi(III) complexes (see Section 4, Scheme 22), α-amino alkyl radicals **119** rapidly undergo oxidation to give iminium ions such as **120**, upon regeneration of Bi(I). These highly electrophilic intermediates can be trapped by external N-nucleophiles **117**, giving products of formal cross coupling **118**, through an overall Bi(I/II) or Bi(I/II/III) catalytic manifold (Scheme 27).

Scheme 26. Bi-Mn-catalyzed radical cycloisomerization of alkenyl iodides.
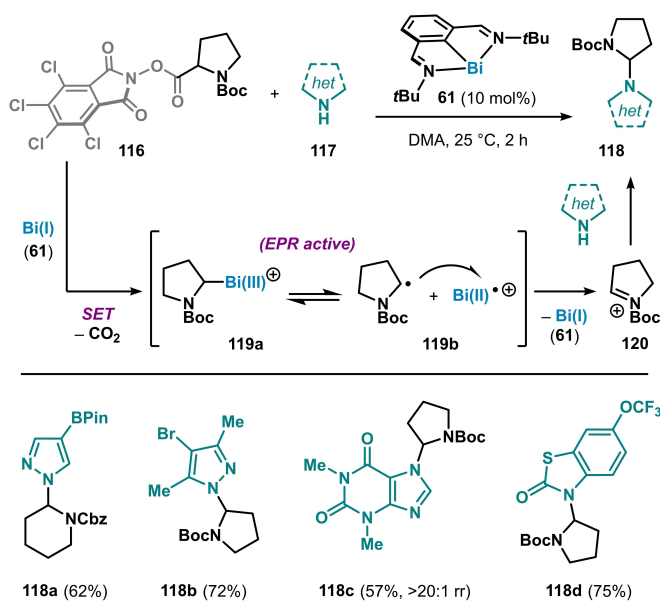
Scheme 27. Bi(I)-Catalyzed formal C(sp^3)-N cross-coupling by radical activation of α-amino redox-active esters.

5.4. Bismuth Catalysis under Light

As explained throughout previous sections, the photochemical activity of some bismuth complexes is a phenomenon that has been known for decades. For example, light absorption has been proved to have a positive effect in the homolysis of Bi–E bonds.[51,52,127] Furthermore, properties as the large spin-orbit coupling associated with heavy elements enable UV-Vis transitions that would not be feasible for lighter elements. These features have recently resulted in several methodologies based on the photochemistry of bismuth complexes.[129,144] In 2020, Lichtenberg and co-workers showed that diarylbismuth(III) thiophenolate **121** can be used to promote the intermolecular dehydrocoupling between silanes and TEMPO under UV light irradiation (mercury-vapor lamp), through a Bi(III/II) catalytic cycle (Scheme 28).[145] It is worth mentioning that this type of reactivity was first studied with radical bismuth by Coles and co-workers,[146] who demonstrated the feasibility of such coupling albeit in low TOF (Scheme 28, bottom left).[147] The activation mechanism using **121** as catalyst was proposed to proceed by a light-promoted Bi–S bond homolysis (Scheme 28, top). The resulting Bi(II) intermediate (**122**) would react with TEMPO to form Bi(III) TEMPOxide **123**, which gets reduced by a silane, releasing reaction product **124** upon generation of transient Bi(III) hydride **125**. This intermediate collapses into Bi(II) radical dimer **126** (characterized by X-ray diffraction) with concomitant release of hydrogen gas. Bi(II) radical **126** closes up the catalytic cycle by reaction with more TEMPO.
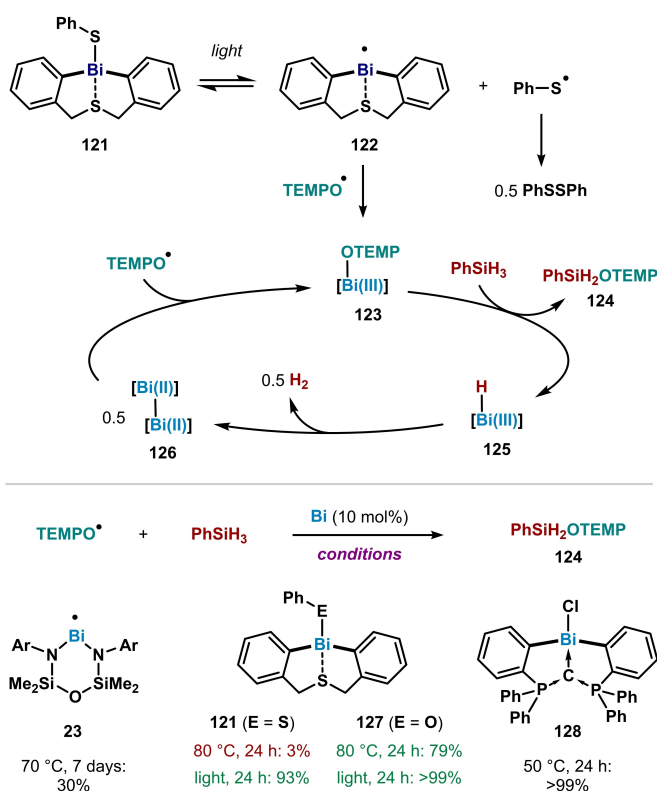
The same group disclosed that an analogous catalyst with a phenolate ligand instead of a thiophenolate (**127**) was also able to promote the same transformation under either thermal or photochemical conditions (Scheme 28, bottom center).[148] Furthermore, this complex was also catalytically active in the coupling of silanes with phenol (instead of TEMPO), presumably operating through a polar mechanism. At the same time, Gilliard and co-workers reported that carbone-stabilized diarylbismuth(III) halide complexes such as **128** are very active in this transformation under thermal conditions, giving full conversions to **124** upon mild heating, or even at room temperature (Scheme 28, bottom right).[149] These findings might suggest a favorable Bi–Cl homolysis, as a consequence of a weaker bond that results from the *trans* effect exerted by the carbone donor. A similar Bi(III)–Cl homolysis was later proposed by König and co-workers, albeit high-energy light was required.[150] They found that BiCl₅²⁻ (generated in situ) is able to activate simple alkanes upon absorption of 385-nm light (Scheme 29). Thus, a combination of 5 mol% of BiCl₃ and 10 mol% of TBACl catalyzed the Giese-type coupling between a variety of alkanes and Michael acceptors under light irradiation, giving products **131** in moderate to excellent yields. The authors suggest that pentachloride coordination to Bi(III) is the photoactive species absorbing purple light. The bands at 385 or 400 nm were associated to a ligand-to-metal charge transfer (LMCT) process. Presumably, upon absorption of light, BiCl₅²⁻ is able to release chlorine radicals, which would engage in hydrogen-atom transfer (HAT) processes with alkanes such as cyclohexane. The resulting alkyl radicals would undergo Giese-type

Scheme 28. Bismuth-catalyzed radical dehydrocoupling.
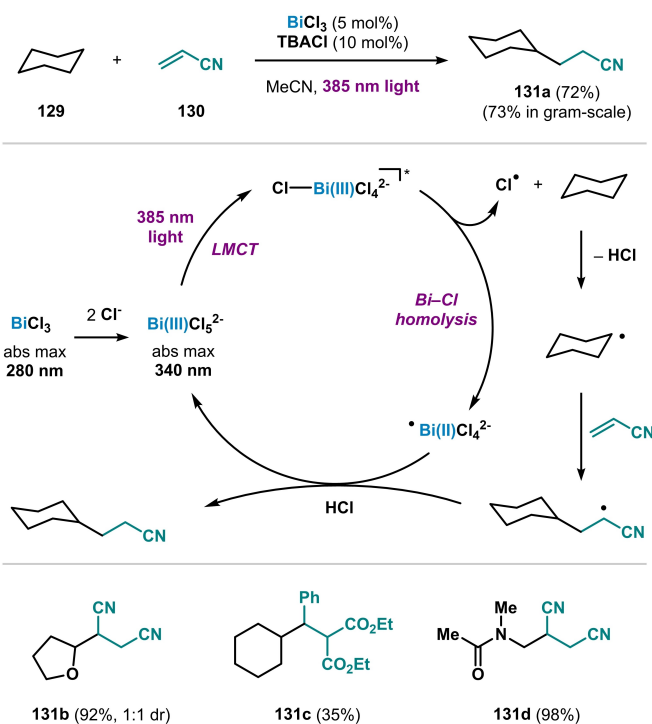
Scheme 29. Bismuth photocatalysis via ligand-to-metal charge transfer. TBACl = tetrabutylammonium chloride.

addition with Michael acceptors, giving reaction-products **131** upon re-oxidation of Bi(II) to Bi(III) and subsequent protonation.

Pericàs and co-workers unveiled the use of Bi_2O_3 as photocatalyst in the α-alkylation of aldehydes (**132**) with alkyl bromides (**133**), using second-generation MacMillan imidazolidinone **134** as co-catalyst, to give products such as **135** in high enantiomeric excess (Scheme 30, top).[151] Later, they also showed Bi_2O_3 to be active in the photocatalytic atom-transfer radical addition (ATRA) between alkyl bromides and alkenes,[152] a process which was subsequently developed in a flow set-up.[153] Their original mechanistic proposal involved a light-induced promotion of one electron from the valence band to the conduction band of semiconductor Bi_2O_3, which would be transferred to the alkyl bromide to generate an alkyl radical (for an analogous step, see Scheme 31, bottom). However, further investigations on the system showed that Bi_2O_3 actually acts as a pre-catalyst. In the presence of alkyl bromides, suspensions of Bi_2O_3 lead to yellow homogeneous solutions under light irradiation (Scheme 30, bottom). This corresponds to the generation of
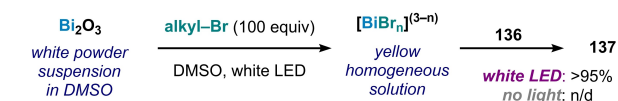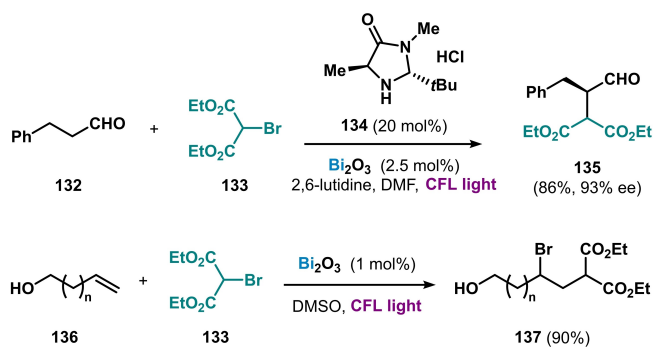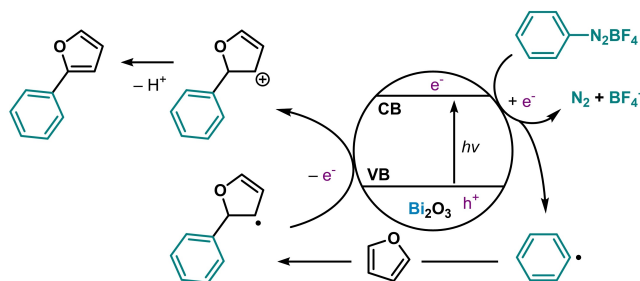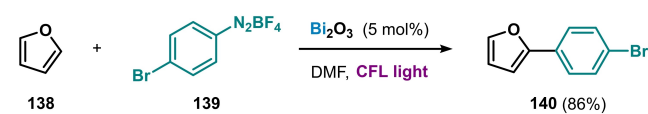
blue-light-absorbing (i.e.: yellow-colored) $BiBr_n^{(3-n)}$ species, which were then suggested to be the actual photocatalytic species in solution.[154] A similar observation was later made by König and co-workers during the work summarized in Scheme 29.[150]

In 2015, the same group also revealed that Bi_2O_3 is able to promote photocatalytic arylation reactions with aryl diazonium salts (Scheme 31).[155] Contrarily to the aforementioned findings on the in situ formation of photoactive $BiBr_n^{(3-n)}$ species, the absence of halide sources on this system suggests the original mechanistic proposal involving a semiconductor-type activation mechanism as a feasible rationale.

Very recently, Cornella and co-workers disclosed a C–H trifluoromethylation by means of bismuth radical catalysis under blue-light irradiation.[156] Thus, the reaction of (hetero)aromatic substrates such as **141** with trifluoromethanesulfonyl chloride **142** in $CHCl_3$ in the presence of 10 mol% of a bismuthinidene (**61**) gave the corresponding direct C–H trifluoromethylation products, under blue-LED irradiation (Scheme 32). The reaction mechanism was proposed to start by the oxidative addition between the Bi(I) complex and **142**, giving adduct **144** which could be structurally characterized by X-ray diffraction. The radical trifluoromethylation reaction was confirmed to proceed in a stoichiometric fashion when complex **144** was irradiated in the presence of an excess of **141**, affording 71% of **143**. This suggests a process involving a light-induced homolysis, subsequent fragmentation and release of SO_2. The ensuing CF_3 radical would engage with the corresponding arene and a HAT process would deliver the product and close the catalytic cycle.

Scheme 30. Radical photocatalysis with Bi_2O_3.
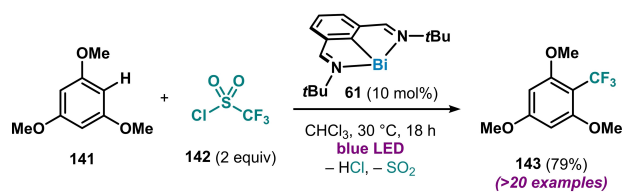

Scheme 31. Radical photo-activation of aryl diazonium salts with Bi_2O_3 via semiconductor photocatalysis. CB = conduction band; VB = valence band.

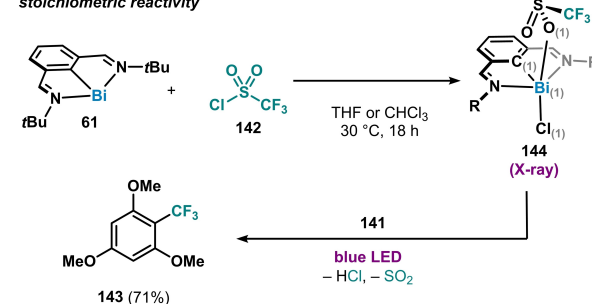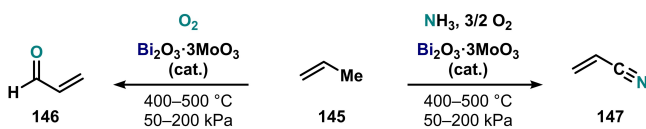**Scheme 32.** Bismuth-catalyzed trifluoromethylation of arenes under blue-light irradiation. Bond distances (Å) from X-ray analysis of **144**: Bi(1)–C(1): 2.199; Bi(1)–O(1): 2.562; Bi(1)–Cl(1): 2.565.
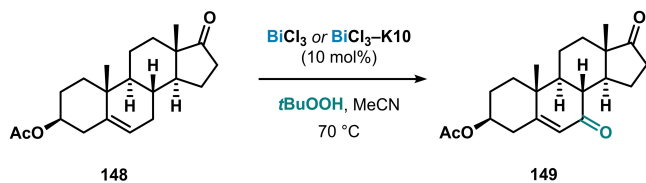
5.5. Heterogeneous Catalysis

As briefly introduced in the previous section, a broad range of inorganic bismuth compounds have found applications as heterogeneous catalysts—or, more often than not, photocatalysts.[10] While the focus of this review is centered on homogeneous catalysis, a concise overview of some key developments in bismuth heterogeneous (photo)catalysis that can involve radical intermediates is offered in this section.[157] Arguably, the best known and most used heterogeneous process that involves bismuth is the SOHIO process (Scheme 33).[158] The SOHIO process is the ammoxidation or oxidation of propene over bismuth molybdate catalysts (e.g.: $Bi_2O_3 \cdot 3MoO_3$) to give acrylonitrile or acrolein, respectively. Studies in the heterogeneous system show that bismuth is involved in the rate-determining hydrogen abstraction from propene in both cases.[159] Model studies in homogeneous systems support a Bi–O bond homolysis to form transient Bi(II) radicals, analogously to a fundamental step suggested to intervene in the SOHIO process (see Section 3.2 for details).[76,77,82]

Different bismuth(III) salts have also found applications in heterogeneous or homogeneous catalytic oxidations with t-BuOOH.[160] For example, the allylic oxidation of steroid dehydroepiandrosterone acetate (**148**) was achieved by Salvador and co-workers using either homogeneous $BiCl_3$ or the heterogeneous $BiCl_3/K$-10 system (i.e.: $BiCl_3$ supported on a clay adsorbent material, Scheme 34).

While the aforementioned processes are initiated thermally, photochemically induced reactions represent the majority of processes involving heterogeneous bismuth catalysis. Besides the examples of Section 5.4 where Bi_2O_3 was used as a precursor of soluble active species, this semiconductor (among a variety mixed oxides) was used directly as heterogeneous photocatalyst in different contexts, such as alkene polymerization.[161] Bismuth titanates (e.g.: $Bi_4Ti_3O_{12}$) have been employed in the degradation of organic dyes such as methyl orange.[162] Bismuth vanadates (e.g.: $BiVO_4$) or bismuth-vanadium oxide clusters have also been applied in the degradation of tetracycline antibiotics[163] or organic dyes,[164] respectively. Bismuth halide perovskites (e.g.: $Cs_3Bi_2Br_9$) were employed in the C–H activation of aliphatic and aromatic hydrocarbons.[165] A bismuth oxybromide $Bi_{24}O_{31}Br_{10}(OH)_\delta$ was found to accelerate the hydrogen-transfer step in both the light-induced reduction and oxidation of different redox pairs (ketones/alcohols, thiones/thiols, quinones/hydroquinones, etc.).[166] These and many other examples of the use of bismuth in heterogeneous photocatalysis have been recently reviewed in detail elsewhere,[167] and go beyond the intent of this overview.

6. Conclusions and Outlook

In conclusion, this review outlines how the field of bismuth radical chemistry has started to reemerge during the past two decades, after laying dormant for more than a century. This renaissance was enabled by the progress in synthetic and spectroscopic techniques, allowing the preparation and full characterization of both transient and persistent bismuth-radical species. Beyond fundamental discoveries, this emergence has revealed the vast potential of bismuth compounds in the realm of redox catalysis. Several research groups have uncovered catalytic processes, such as polymerization or coupling reactions, which proceed through open-shell intermediates, forging the path to establish the novel field of bismuth radical catalysis. We firmly believe that this discipline remains a fertile ground for discovery, and many possibilities await exploration. For example, whereas some examples of monomeric and dimeric Bi(II) complexes have been characterized, well-defined open-shell Bi(0) or Bi(IV) species still remain elusive and unexplored in catalysis. Furthermore, the synergy between bismuth radical chemistry and photocatalysis, as well as its potential application in synthetic electrocatalysis, have yet to be investigated in depth. All in all, we hope that this review provides a broad perspective of the richness of bismuth in open-shell chemistry, and is able to bridge the realm of fundamental inorganic/organometallic bismuth chemistry with the field of organic synthesis. We believe that this review will spur the development of novel transformations based on bismuth radical catalysis.[168]

Scheme 33. The SOHIO oxidation (left) and ammoxidation (right) of propene.

Scheme 34. Allylic oxidation catalyzed by bismuth-based homogeneous or heterogeneous systems.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: Bismuth · Radical Chemistry · Radicals · Redox Catalysis · Synthesis

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[42] The geometries shown to depict structures in the Schemes throughout the manuscript are a simplified representation of each compound and do not reflect accurately the X-ray structural data. Nevertheless, for reference, we have included values for relevant bond lengths and angles of some bismuth compounds (taken from X-ray data on the original publications) in the caption of the corresponding schemes. The atoms involved in these distances and angles are highlighted on the schemes with subscript numbers in parenthesis.

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