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Bismuth Amides Mediate Facile and Highly Selective Pn–Pn Radical Coupling Reactions (Pn = N, P, As)

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Supporting information available

Abstract: The controlled release of well-defined radical species under mild conditions for subsequent use in selective reactions is an important and challenging task in synthetic chemistry. We show here that simple bismuth amide species $[\text{Bi}(\text{NAr}_2)_3]$ readily release aminyl radicals $[\text{NAr}_2]^{\bullet}$ at ambient temperature in solution. These reactions yield the corresponding hydrazines, $\text{Ar}_2\text{N}-\text{NAr}_2$, as a result of highly selective N–N coupling. The exploitation of facile homolytic Bi–Pn bond cleavage for Pn–Pn bond formation was extended to higher homologs of the pnictogens (Pn = N–As): homoleptic bismuth amides mediate the highly selective dehydrocoupling of HPnR_2 to give $\text{R}_2\text{Pn}-\text{PnR}_2$. Analyses by NMR and EPR spectroscopy, single crystal X-ray diffraction and DFT calculations reveal low Bi–N homolytic bond dissociation energies, suggest radical coupling in the coordination sphere of bismuth, and reveal electronic and steric parameters as effective tools to control these reactions.

The controlled release of radical species and their subsequent exploitation in selective bond forming events remains an outstanding challenge in synthetic chemistry.^[1] Recent progress in the chemistry of heavy p-block elements has allowed a glimpse of their potential in the development of controlled radical reactions.^[2,3] Examples include CH activation reactions by tin radicals,^[4] the activation of P_4 and S_8 by bismuth radicals,^[5] bismuth-catalyzed radical dehydrocoupling reactions,^[6] the radical cyclo-isomerization of iodoolefins,^[7] and controlled radical olefin polymerization.^[8] While recent developments in heavy p-block chemistry exploit isolable radical species^[9] and the homolytic cleavage of E–E bonds,^[3a, 3b] the homolysis of E–X bonds as a source of radicals X^{\bullet} without the need for a radical initiator is only little explored (E = heavy p-block element; X = C, N, O). For instance, the homolytic cleavage of E–C bonds has been exploited in the controlled radical polymerization of olefins, which includes the addition of a carbon-centered radical to the olefin monomer as the initiating step.^[8] Bi–O homolysis has been discussed as the rate-determining step in the industrially relevant

ammoxidation of propene to acrylonitrile at a $\text{Bi}_2\text{O}_3 \cdot \text{MoO}_3$ catalyst (SOHIO process).^[10]

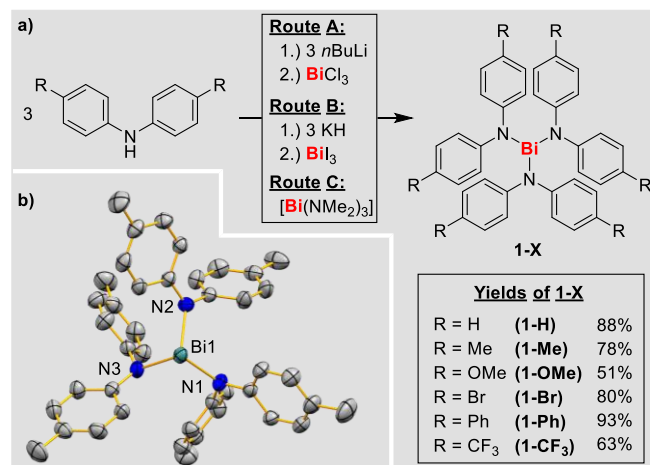
Aminyl radicals, $(\text{NR}_2)^{\bullet}$, play an important role in biological processes,^[11] and their emerging applications in synthetic chemical protocols have attracted increasing interest.^[12] However, their use is still limited due to their high reactivity and the lack of methods for their selective generation under mild conditions.^[12a] Thus, E–N bond homolysis would offer valuable prospects for the generation of aminyl radical species. Indeed, E–N homolysis has been suspected in applications such as the synthesis of highly monodisperse nanoparticles from $\text{Bi}(\text{N}(\text{SiMe}_3)_2)_3$ and CH activation / C–C coupling sequences with $\text{BiCl}_2(\text{N}(\text{SiMe}_3)(\text{Mes}^*))$ ($\text{Mes}^* = 2,4,6\text{-tBu}_3\text{C}_6\text{H}_2$).^[13] Pyrazolyl radicals have been generated by oxidation of the pyrazolide anion with BiCl_3 .^[14] However, the liberation of aminyl radicals from well-defined precursors through experimentally verified E–N homolysis under mild reaction conditions and their subsequent utilization in selective bond forming events has not been reported to date.

Here we show that bismuth amides $[\text{Bi}(\text{NAr}_2)_3]$ readily release aminyl radicals, allowing for highly selective N–N coupling under mild conditions. The strategy of facile Bi–Pn homolysis could be extended to higher homologs with Pn = N, P, As.

A limited number of homoleptic bismuth amides bearing alkyl^[15] or silyl^[15b, 16] substituents is known. In addition, a few bismuth compounds with amide ligands that contain one aryl group, $(\text{NArR})^-$, have been reported and show unusual reactivity patterns that have not been rationalized in many cases (R = H, Si(alkyl)₃; Supp. Inf.). In contrast, only a single homoleptic bismuth amide of type $[\text{Bi}(\text{NAr}_2)_3]$ has been described, which also sticks out due to its simple substituents (Ar = Ph, **1-H**).^[17,18]

We targeted the synthesis of a series of homoleptic bismuth diaryl amides, $[\text{Bi}(\text{NAr}_2)_3]$ (**1-X**), with simple aryl substituents that do not impose extreme steric bulk on the overall complexes (Scheme 1a; X = H, Me, OMe, Br, Ph, CF_3). Different salt elimination protocols (Routes A, B) and transamination

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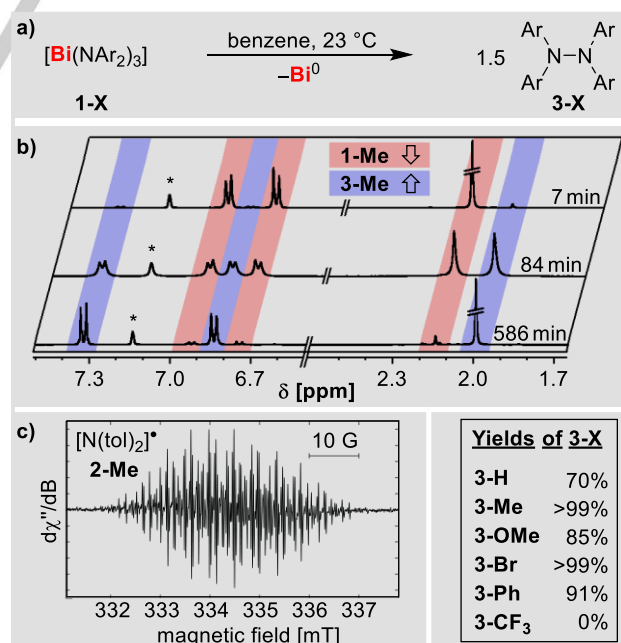
Scheme 1. a) Syntheses of aryl-substituted, homoleptic bismuth amides: Route A: **1-H**, **1-Me**, **1-OMe**; Route B: **1-OMe**, **1-Br**, **1-Ph**; Route C: **1-CF₃**. b) Molecular structure of **1-Me** in the solid state. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Bi1–N1, 2.1598(19); Bi1–N2, 2.158(2); Bi1–N3, 2.185(2); N1–Bi1–N2, 100.68(8); N1–Bi1–N3, 97.92(8); N2–Bi1–N3, 95.03(8).

approaches (Route C) were developed to account for differences in solubility, reactivity and stability of starting materials, products and by-products (Supp. Inf.). Compounds **1-X** were isolated as orange to violet solids in moderate (51%, X = OMe) to excellent (93%, X = Ph) yields. The molecular structures of **1-H**,^[17] **1-Me**, **1-Br**, and **1-Ph** in the solid state were determined by single-crystal X-ray diffraction, revealing isostructural relationships (triclinic space group *P* $\bar{1}$ in all cases). The compounds form typical molecular structures with trigonal pyramidal coordination geometries around the central Bi atoms (N–Bi–N, 94.2°–107.7°; see Scheme 1b for **1-Me** and Supp. Inf. for details). **1-Me** shows intermolecular Bi···Bi distances of 3.79 Å, suggesting weak Bi···Bi interactions in the solid state (Supp. Inf.).^[19] The Bi–N bond lengths in **1-H**, **1-Me**, and **1-Br** are virtually independent of the nature of the substituent X in *para*-position of the aryl groups (2.15–2.19 Å). Slightly elongated Bi–N bonds in **1-Ph** (2.16–2.23) were ascribed to intramolecular π -stacking between two [(N(C₆H₄Ph)₂)][–] ligands. The N atoms are only weakly pyramidalized (Σ C–N–C/Bi, 352°–360°). NMR spectroscopic analyses of compounds **1-X** are in agreement with six magnetically equivalent aryl groups in each complex without significant rotational barriers at ambient temperature in solution (for ¹H NMR spectrum of **1-Me** see top of Scheme 2b). However, it quickly became evident that compounds **1-X** only have a limited life-time in solution. At 23 °C in benzene, compounds **1-X** undergo a selective transformation with concomitant precipitation of a dark solid (the ¹H NMR spectroscopic monitoring of this process is shown in Scheme 2b for **1-Me**).^[20] The products of these reactions were identified as the hydrazines **3-X**, demonstrating that compounds **1-X** are precursors for selective N–N coupling reactions (Scheme 2a). The high (up to quantitative) yields indicate that the dark precipitate is mainly or exclusively Bi⁰ based on the atom balance of these reactions. Identical results were obtained when the reaction **1-Me** → **3-Me** was performed under exclusion of light, demonstrating that this transformation is thermally-induced. EPR spectroscopic monitoring of the reaction in the case of **1-Me** revealed the aminyl radical [N(tol)₂][•] (**2-Me**) as an intermediate of this reaction (tol = 4-Me-C₆H₄; Scheme 2c

and Supp. Inf.). In agreement with the literature, isolated **3-Me** was found to be EPR-silent under identical conditions.^[20b] This indicates homolytic Bi–N bond cleavage as the source of the aminyl radical and is, to the best of our knowledge, the first direct experimental evidence of facile Bi–N homolysis under mild conditions in the condensed phase. With different substituents X in the *para*-position of the aryl backbone of compounds **1-X**, the electronic influence on the properties of this class of compounds was examined. The half-life of each compound was determined by ¹H NMR spectroscopy and showed rapid reactions of electron-rich **1-Me** and **1-OMe** in solution (*t*_{1/2} = 1.2–1.4 h). In contrast, **1-H**, **1-Br**, and **1-Ph** with less electron density in the phenylene moieties reacted significantly slower (*t*_{1/2} = 63–84 h). Confirming this trend, the electron-poor compound **1-CF₃** is stable in solution at 23 °C for days. In an intermolecular reaction, addition of 3 equiv. HN(4-Me-C₆H₄)₂ to Bi(NMe₂)₃ (**4**) in benzene gave HNMe₂ and **3-Me** as the main benzene-soluble products (Supp. Inf.).

These findings on diaryl amides, [BiN(Ar₂)₃] (**1-X**), provide the first thorough understanding of the properties and spectroscopic data of this class of compounds. Closer investigation of the previously pioneered **1-H** showed exclusively the four expected signals in the ¹³C NMR spectrum in C₆D₆. Previously reported ¹³C NMR data in CD₂Cl₂ list seven signals,^[17] which are in fact due to a mixture of **1-H** (4 signals) and the N–N coupling product **3-H** (4 signals), with two resonances overlapping. Thus, a modified synthetic protocol allowed for the multi-gram-scale isolation of analytically pure material in 88% yield (improved from previously reported 30%).

Mechanistic aspects of the reaction of **1-Me** to give **3-Me** were investigated by DFT calculations (in this discussion, R = 4-Me-C₆H₄). Homolytic Bi–N bond cleavage in **1-Me** is clearly favored over heterolytic Bi–N bond cleavage by $\Delta\Delta G$ = 36.8 kcal·mol^{–1}, while the opposite is true for the protonated cationic derivative [Bi(NR₂)₂(HNR₂)]⁺ ($\Delta\Delta G$ = 24.1 kcal·mol^{–1}; for details see Supp.



Scheme 2. a) Selective formation of hydrazines **3-X** from bismuth amides **1-X** via N–N radical coupling (yields determined by ¹H NMR spectroscopy). b) NMR spectroscopic monitoring of the reaction **1-Me** → **3-Me** (asterisk denotes resonance of C₆D₆). c) EPR spectroscopic monitoring of the reaction **1-Me** → **3-Me** with detection of [N(tol)₂][•] (**2-Me**) (for details see Supp. Inf.).

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Inf.). An energy decomposition analysis of the Bi–N bond in **1-Me** (homolytic fragmentation) revealed similarly stabilizing contributions by orbital interactions (45%) and electrostatic interactions (46%) to the Bi–N bond, while dispersion interactions contribute significantly (9%), but not decisively to the stability of the Bi–N bond. As an initiating step of the reaction $2 \text{ 1-Me} \rightarrow 2 \text{ Bi}^0 + 3 \text{ 3-Me}$, the elimination of **3-Me** from **1-Me** with formation of the triplet-bismuthinidene $^3[\text{Bi}(\text{NR}_2)]$ is highly unlikely ($\Delta G = 46.3 \text{ kcal}\cdot\text{mol}^{-1}$), with the corresponding singlet bismuthinidene and its solvent adducts being even higher in energy (Scheme 3 and Supp. Inf.).^[3c] In contrast, the formation of a dibismuthane according to $2 \text{ 1-Me} \rightarrow [\text{Bi}_2(\text{NR}_2)_4] + 3 \text{ 3-Me}$ is thermodynamically more reasonable ($\Delta G = 12.7 \text{ kcal}\cdot\text{mol}^{-1}$).^[21] From $[\text{Bi}_2(\text{NR}_2)_4]$, the two-step elimination of two equivalents of **3-Me** to give dibismuthene $[\text{Bi}_2(\text{NR}_2)_2]$ ($\Delta G = 36.4 \text{ kcal}\cdot\text{mol}^{-1}$) and finally Bi_2 ($\Delta G = 21.4 \text{ kcal}\cdot\text{mol}^{-1}$) is not energetically viable. Instead, the ratio of $\text{Bi}:\text{NR}_2$ is most likely increased by formation of bismacrocyclic compounds according to reactions such as $2 [\text{Bi}_2(\text{NR}_2)_4] \rightarrow [\text{Bi}_4(\text{NR}_2)_4] + 2 \text{ 3-Me}$ ($\Delta G = 18.0 \text{ kcal}\cdot\text{mol}^{-1}$), which may further proceed through bismuth clusters^[22] to finally give Bi^0 . Indeed, our calculations suggest that the formation of bismuth metal is an important driving force in these reactions (e.g.: $[\text{Bi}_4(\text{NR}_2)_4] \rightarrow 4 \text{ Bi}^0(\text{bulk}) + 2 \text{ 3-Me}$ ($\Delta G = -62.1 \text{ kcal}\cdot\text{mol}^{-1}$)). The net reaction $2 \text{ 1-Me} \rightarrow 2 \text{ Bi}^0(\text{bulk}) + 3 \text{ 3-Me}$ is exergonic by $\Delta G = -9.4 \text{ kcal}\cdot\text{mol}^{-1}$. We suggest that the single steps outlined above may well proceed through catalysis by radicals such as $(\text{NR}_2)^\bullet$ (Supp. Inf.). Homolytic Bi–N bond dissociation of **1-Me** ($\Delta G = 25.4 \text{ kcal}\cdot\text{mol}^{-1}$) or $[\text{Bi}_2(\text{NR}_2)_4]$ ($\Delta G = 28.9 \text{ kcal}\cdot\text{mol}^{-1}$) would readily provide sufficient concentrations of such radicals, which were detected by EPR spectroscopy (*vide supra*). Investigations into the kinetics of the formation of **3-Me** from **1-Me** confirmed the complexity and suggest a concentration-dependency of the mechanism of this radical reaction (Supp. Inf.).

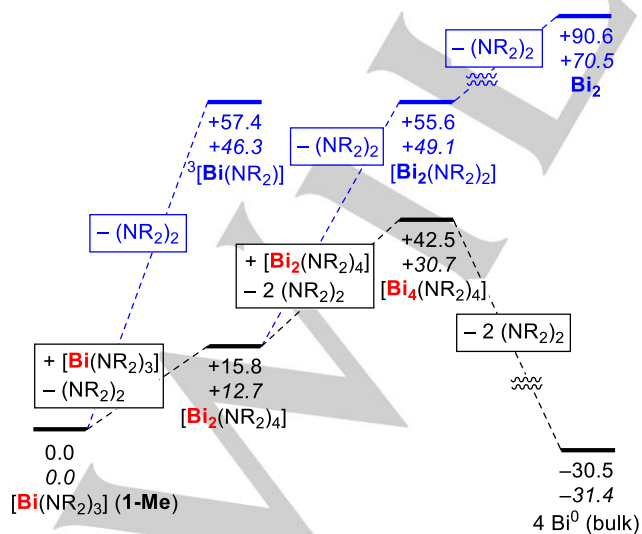
To expand the utilization of well-defined bismuth precursors for selective homo-coupling reactions of lighter group 15 species, we turned our attention to secondary phosphanes as substrates. Dehydrocoupling of secondary phosphanes to give diphosphanes, $\text{R}_2\text{P}-\text{PR}_2$ (important building blocks for the synthesis of bidentate phosphane ligands)^[23] have so far mostly relied on the use of transition metal complexes.^[24] Only recently, the first reports on

Table 1. Reactions of bismuth amides with secondary phosphanes and arsane proceed with highly selective P–P and As–As bond formation (R' : see table).

		$n \text{ Bi}(\text{NR}_2)_3$		$\xrightarrow[3 \text{ HNR}_2]{3 \text{ HPnR}'_2}$	$1.5 \text{ R}'_2\text{Pn}-\text{PnR}'_2$
				$-\text{Bi}^0$	$5\text{-R}': \text{Pn} = \text{P}$
				-3 HNR_2	$6\text{-R}': \text{Pn} = \text{As}$
		1-Me : $\text{R} = 4\text{-Me-C}_6\text{H}_4$			
		4 : $\text{R} = \text{Me}$			
#	Reagent	Substrate	n	Conditions	Yield [%]
1	1-Me	HPPPh ₂	1	RT, <7 min	>99
2	1-Me	HP(Xyl) ₂ ^[a]	2	RT, 3 h	90
3	4	HPMeS ₂	2	RT, 16 h	>99
4	1-Me	HP(4-OMe-C ₆ H ₄) ₂	1.5	RT, <2 h	92
5	1-Me	HP(4-Cl-C ₆ H ₄) ₂	1.2	RT, <2 h	97
6	1-Me	HP(4-CF ₃ -C ₆ H ₄) ₂	2	RT, <3 h	>99
7	1-Me	HPCy ₂	1	RT, 1.5 h	>99
8	1-Me	HP <i>i</i> Pr ₂	1.2	RT, <6 h	99
9	4	HP(cyclo-pentyl) ₂	2	RT, <3 h	94
10	4	HP <i>t</i> Bu ₂	2	60 °C, 1 d	>99
11	4	HPAd ₂ ^[b]	6	60 °C, 2 d	>99
12	1-Me	HASPh ₂	1	–78 °C, 0.5 h	80

Yields were determined by ¹H and/or ³¹P NMR spectroscopy. [a] Xyl = 3,5-Me₂-C₆H₃. [b] Ad = adamantyl.

main group species in the context of this reaction have been published. Carbenoids, NHCs, tri(aryl)boranes, the radical starter “Vazo 88”, and KO*t*Bu in the presence of different hydrogen acceptors generate diphosphanes from secondary phosphanes, but are all limited to substrates bearing at least one aryl group.^{[25],[26],[27],[28]} Only the organotin species $\text{Sn}(\text{C}_5\text{Me}_5)_2\text{Cl}_2$ has been reported to also dehydrocouple HPCy₂ as a single example of a dialkylphosphane (Cy = cyclohexyl).^[29] These reactions proceed even in a catalytic manner (10 mol% $\text{Sn}(\text{C}_5\text{Me}_5)_2\text{Cl}_2$), but require long reaction times of 3 d, elevated temperatures of 60 °C, tedious protocols (periodical removal of H₂), and result in low yields of 40% $\text{Cy}_2\text{P}-\text{PCy}_2$. Reports on heavy main group element compounds $\text{L}^1\text{Bi}-\text{PPh}_2$ (suggested) and $\text{L}^2\text{Pb}-\text{PPh}_2$ (isolated) leading to the formation of the coupling product $\text{Ph}_2\text{P}-\text{PPh}_2$ (**5-Ph**) spurred us to test the potential of bismuth amides as reagents for dehydrocoupling reactions of secondary phosphanes ($\text{L}^1/\text{L}^2 =$ bulky mono-/dianionic ligand).^[5a, 30] Indeed, reaction of **1-Me** with three equiv. HPPPh₂ at 23 °C resulted in the instant and quantitative formation of the coupling product **5-Ph** (Table 1, entry 1). A dark solid (presumably Bi^0) precipitated, and $\text{HN}(4\text{-Me-C}_6\text{H}_4)_2$ was observed as the only benzene-soluble by-product. Sterically more demanding phosphanes HP(Xyl)₂ and HPMeS₂ also underwent coupling in high to quantitative yields at 23 °C, albeit 2 equiv. $\text{Bi}(\text{NMe}_2)_3$ (**4**) as the bismuth amide were needed and the latter case required extended reaction times (entries 2,3). Diarylphosphanes with *e*[–]-donating or -withdrawing substituents (OMe, Cl, CF₃) in the *para*-position of their phenyl substituents were well tolerated (yields: 92–99%, entries 4–6). The synthetically challenging coupling of dialkyl phosphanes was also successful: reaction of **1-Me** with three equivalents of HPCy₂ at 23 °C resulted in quantitative formation of **5-Cy** in 1.5 h (entry 7). Similarly,



Scheme 3. Potential steps in the formation of **3-Me** from **1-Me** (unfavourable [more favourable] steps shown in blue [black]; energy levels scaled to ΔG); Values for ΔH (regular font) and ΔG (italic) are given in $\text{kcal}\cdot\text{mol}^{-1}$.

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HP*i*Pr₂ and HP(*cyclo*-pentyl)₂ underwent dehydrocoupling in excellent yields (entries 8,9). Not only electron-donating substituents at P (alkyl vs aryl), but also increased steric bulk around the phosphorus atom tend to complicate P–P coupling reactions.^[25b, 25d, 28-29] Thus, it is remarkable that not only the aryl species HPMes₂ (entry 3), but even HP*t*Bu₂ and HPAd₂ with their extremely bulky alkyl groups could quantitatively be transformed into the coupling products **5-*t*Bu** and **5-Ad** with modified experimental conditions (entries 10,11). Reactions of the secondary arsane HAsPh₂ with **1-Me** (or **4**) were performed as a proof of principle and resulted in the selective formation of the dehydrocoupling product **6-Ph** in 80% yield (entry 12 and Supp. Inf.). In the formation of Ph₂P–PPh₂, literature reports suggest homolytic splitting of L¹Bi–PPh₂ and L²Pb–PPh₂ bonds (*vide supra*).^[5a, 30] Indeed, we detected a weak EPR spectroscopic signal in reactions of **4** with HPMes₂, which was tentatively assigned to a P-centered radical (*g*_{iso} = 2.007, *a*(³¹P) = 270 MHz (96 G))^[31] and thus suggests a radical nature of this reaction step (for details and full discussion see Supp. Inf.). In contrast, polar mechanisms have been discussed for most main group compounds in phosphane dehydrocoupling.^[25a-c, 26b, 28-29] Notably, the only other main group species that has been reported for the challenging dehydrocoupling of dialkylphosphanes has also been suggested to operate via polar reaction pathways.^[29] Transition-metal-based catalytic protocols for phosphane dehydrocoupling require elevated temperatures, longer reaction times, and/or show limitations in their substrate scope (see Supp. Inf.).^[24]

In summary, we have re-investigated the fundamental bismuth diarylamide [Bi(NPh₂)₃] and provided data for the thorough understanding of this class of compounds. As a striking feature, they can easily release aminyl radicals under mild reaction conditions and mediate highly selective N–N bond formation. The first experimental proof of facile Bi–N bond homolysis has been delivered, electronic parameters controlling aminyl radical formation have been revealed, and fundamental mechanistic aspects have been uncovered. Simple homoleptic bismuth amides efficiently mediate highly selective dehydrocoupling of HPnR₂ to give R₂Pn–PnR₂ (Pn = N–As). These findings reveal the potential of well-defined bismuth compounds to be exploited for the controlled generation and synthetic utilization of radicals such as [PnR₂]*. The ability of bismuth to readily release radical species and to easily accommodate very bulky ligands due to its large atomic radius sets bismuth-based methodologies apart from previously reported reagents in the field.

Keywords: bismuth amide • aminyl radical • radical coupling • heavier pnictogens • diphosphanes

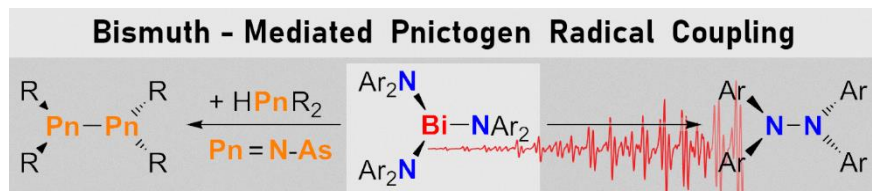
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Bismuth radical chemistry: the first series of bismuth amides of type [Bi(NAr₂)₃] has been synthesized and characterized. Remarkably, they readily release aminyl radicals (NAr₂)• and facilitate highly selective radical coupling to give (NAr₂)₂. Bismuth amides mediate the selective dehydrocoupling of HPnR₂ (Pn = N, P, As), including very challenging substrates. Conditions, mechanisms, and substrate scopes are complementary or superior to those of more established procedures.

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