Bismuth radical catalysis in the activation and coupling of redox-active electrophiles

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Abstract

Radical cross-coupling reactions represent a revolutionary tool to forge $C(sp^3)$–C and $C(sp^3)$–heteroatom bonds, by means of transition metals, photoredox or electrochemical approaches. This study demonstrates how a low-valent bismuth complex is able to undergo one-electron oxidative addition with redox-active alkyl radical precursors in an autonomous manner, mimicking the behavior of first-row transition metals. This reactivity paradigm for bismuth gives rise to unique radical-equilibrium complexes, which could be fully characterized in solution and solid state. The resulting $Bi(III)$–$C(sp^3)$ intermediates display divergent reactivity patterns depending on the α-substituents of the alkyl fragment. Mechanistic investigations on this reactivity led to the development of a bismuth-catalyzed $C(sp^3)$–N cross-coupling reaction that operates under mild conditions and accommodates synthetically relevant *N*-heterocycles as coupling partners.

Main text

Metal-catalyzed radical cross-coupling reactions represent a conceptual paradigm shift from the historical two-electron polar disconnections,[1] resulting in a completely new approach for the synthesis of organic molecules.[2] Particularly, disconnections based on the coupling of alkyl radical fragments have demonstrated to hold tremendous potential in making $C(sp^3)$–C and $C(sp^3)$–heteroatom bonds.[3,4] The evolution and application of such synthetic strategy is linked to advances in the fields of photoredox catalysis,[5,6,7] electrochemical synthesis[8,9] and, especially, their combination with first-row transition-metal catalysis.[10,11,12,13] Indeed, elements such as Fe, Co, Ni or Cu hold a preferential place when one-electron processes are required in cross-coupling cycles, resulting in redox events occurring via (n)/(n+1)/(n+2)

oxidation states (Fig. 1a, right). This particular chemical behavior leads to the facile generation of alkyl-radical fragments through single-electron-transfer (SET) oxidative addition from precursors such as redox-active esters (RAE) or Katritzky salts (KS). The recent years have witnessed significant efforts towards mimicking the redox behavior of transition metals by main-group elements.[14] For instance, pnictogens can take part in S_N2-type polar oxidative additions resulting in two-electron maneuvering throughout (n)/(n+2) redox catalytic cycles, emulating those of late transition metals (Fig. 1a, left).[15] However, the radical-activation of redox-active electrophiles is often restricted to first-row transition metals, and examples by a well-defined main group-element complex are rare.

Very recently, bismuth redox catalysis has been established as an emerging platform for organic synthesis.[16] In this context, our group has shown how polar Bi(III/V) or Bi(I/III) catalytic cycles can lead to the development of C–F,[17] C–O,[18] or C–H[19] bond-forming reactions, among others.[20] Nevertheless, even though persistent and stable radicals of heavier main-group elements are known,[21] the studies for bismuth are much more limited, and bismuth radical catalysis has been significantly underexplored.[22] Bi(II/III) catalytic cycles have been postulated for the living radical polymerization of alkenes,[23] or the cycloisomerization of 4-iodoalkenes.[24] This, together with further reports probing the existence of bismuth(II)-centered radicals,[25] prompted us to explore the behavior of the Bi(I/II) pair in SET-based oxidative additions of redox-active alkyl electrophiles. Here, we disclose how a well-defined bismuthinidene (**1**) reacts with alkyl phthalimide esters and alkyl Katritzky salts to give alkyl-bismuth(III) adducts, which were found to behave as Bi–C radical-equilibrium complexes (Fig. 1b, bottom). Additionally, we discovered that α-amino alkyl-radical fragments resulting from this process can be easily oxidized by Bi(II), giving rise to iminium ions[26,27] that can be trapped by N-nucleophiles. This observation led to the development of a Bi-catalyzed radical C–N cross-coupling reaction with a wide scope of both coupling partners (Fig. 1b, top). In spite of the vast number of alkyl-radical couplings developed during the past decade, seldom examples of $C(sp^3)$–N bond formation from redox-active radical precursors have been reported,[28] mainly relying on photoredox setups,[29,30,31,32] electrochemical synthesis,[33,34] or the use of an excess of chemical oxidant.[35] In this report, we demonstrate that catalytic amounts of a Bi(I) complex can promote this type of transformation in an autonomous manner,

without the need of a photoredox system, a chemical oxidant, an external base, or an electrochemical set-up.
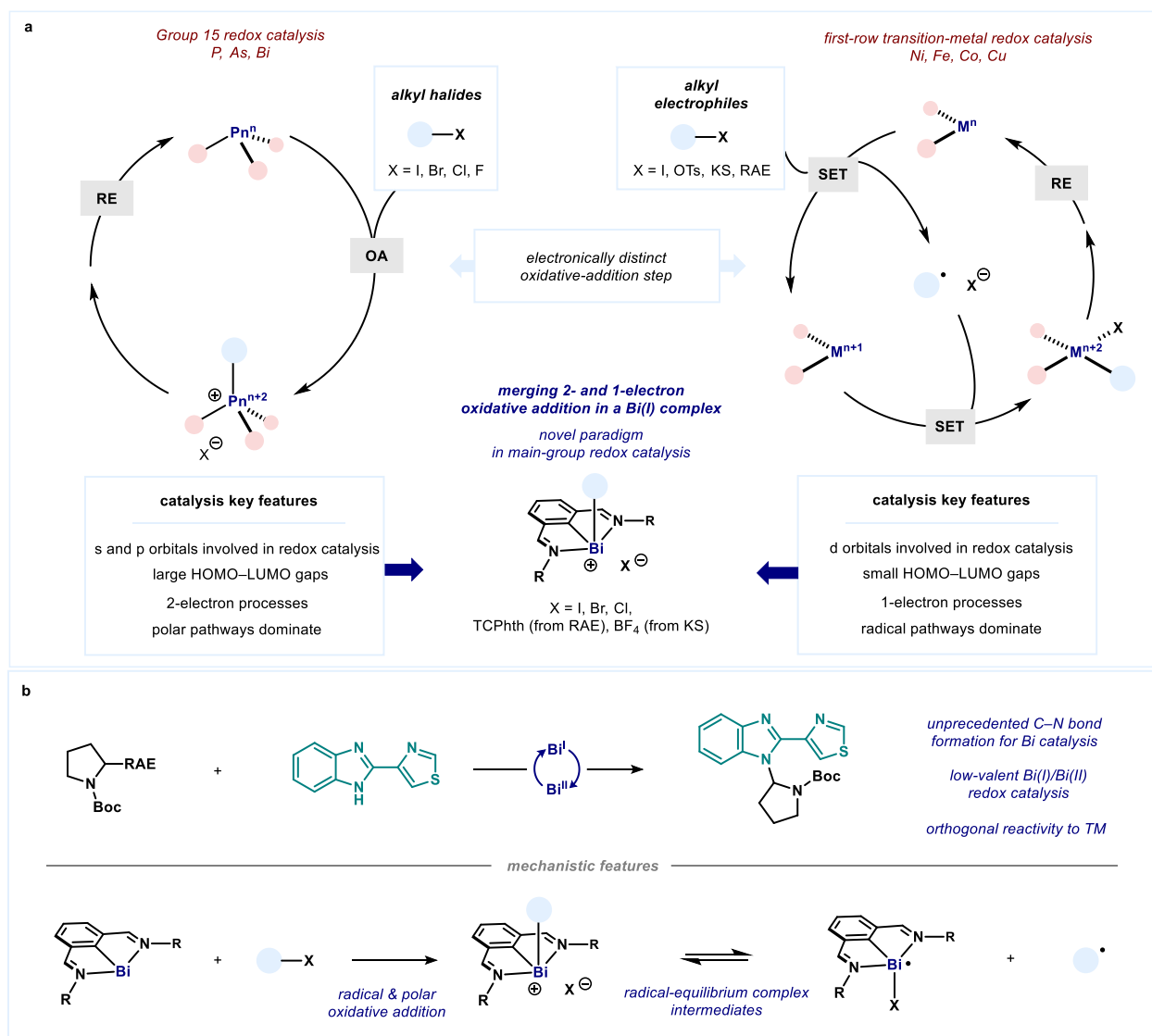

Fig. 1. Unlocking single-electron oxidative-addition processes for bismuth. a, Merging pnictogen reactivity (left) with first-row transition metal behavior (right) to unveil the oxidative addition of redox-active alkyl-radical precursors into bismuth(I) via single-electron transfer (SET). **b**, Development of a bismuth-catalyzed C–N cross-coupling reaction through the study of the behavior of alkyl-bismuth radical-equilibrium complexes. OA = oxidative addition. RE = reductive elimination. KS = Katritzky salt. RAE = redox-active ester.

Results and discussion

As a result of the high nucleophilicity of the $6p^2$ lone pair on the Bi(I) center, bismuthinidene **1** has recently been shown to engage in polar S_N2-type reactions with alkyl halides and triflates.[36] Similarly, **1** reacted quantitatively with a range of benzyl (pseudo)halides (Cl, Br, I, OMs) to give benzyl bismuth(III) complexes **5–8** (Fig. 2b). Cyclic voltammetry analysis of **1** ($E_{1/2} = -0.85$ vs $Fc^{0/+}$) evidences that such C–X cleavages should proceed through a classical S_N2 pathway ($E_{p/2} < -2.0$ V vs $Fc^{0/+}$). On the other hand, the electrochemical behavior observed suggested that **1** could potentially engage in SET oxidative addition processes with alkyl redox-active electrophiles (Fig. 2a). Accordingly, reaction of **1** with 1 equivalent of tetrachlorophthalimide ester **2** ($E_{p/2} = -1.1$ V vs $Fc^{0/+}$) cleanly afforded benzyl bismuth(III) complex **9**, after SET and fragmentation upon release of CO_2, followed by radical recombination.[37] The resulting alkyl bismuth(III) adduct could be fully characterized by NMR, HRMS and single-crystal X-ray diffraction. Furthermore, Katritzky salt **4** ($E_{p/2} = -1.2$ V vs $Fc^{0/+}$) also underwent radical oxidative addition with **1** to give **10**. As expected, non-chlorinated phthalimide ester **3** ($E_{p/2} = -2.0$ V vs $Fc^{0/+}$) remained unreacted when mixed with **1**. Besides benzyl groups, the same process occurs with primary (**11**), or secondary (**13**) RAEs, leading to stable alkyl-bismuth(III) complexes.[38] Interestingly, the process is orthogonal to classical polar transition-metal oxidative additions, as it could be performed in the presence of an aryl bromide, giving **12** as the sole product in 93% yield (Fig 2b). This reactivity is a rare example where bismuth, besides emulating the redox behavior of first-row transition metals during oxidative addition, allows the isolation and characterization of the corresponding alkyl–metal species resulting from radical recombination. Furthermore, when **13** was analyzed by EPR spectroscopy a weak but steady signal of the carbon-centered radical could be observed (see Supplementary Materials), which points to **13** being a radical-equilibrium complex.[39,40] Based on this, the reaction of bismuthinidene **1** with cyclopropylmethyl iodide was monitored by NMR at low temperature in the dark (Fig. 2c). Complete conversion to cyclopropylmethyl adduct **14** was observed within one hour at –20 °C. When the mixture was warmed to 50 °C, a slow but steady conversion to ring-opening compound **16** was observed (35% after 12 h). This indicates that homolysis of the Bi–C bond in **14** takes place, and the complex is in equilibrium with its corresponding in-cage radical pair (**18**).

Furthermore, subjecting a solution of **14** to blue-LED irradiation for 5 min resulted in complete conversion to open product **16**, showing that light can be used to shift this radical equilibrium, accelerating the radical ring-opening process.[24]
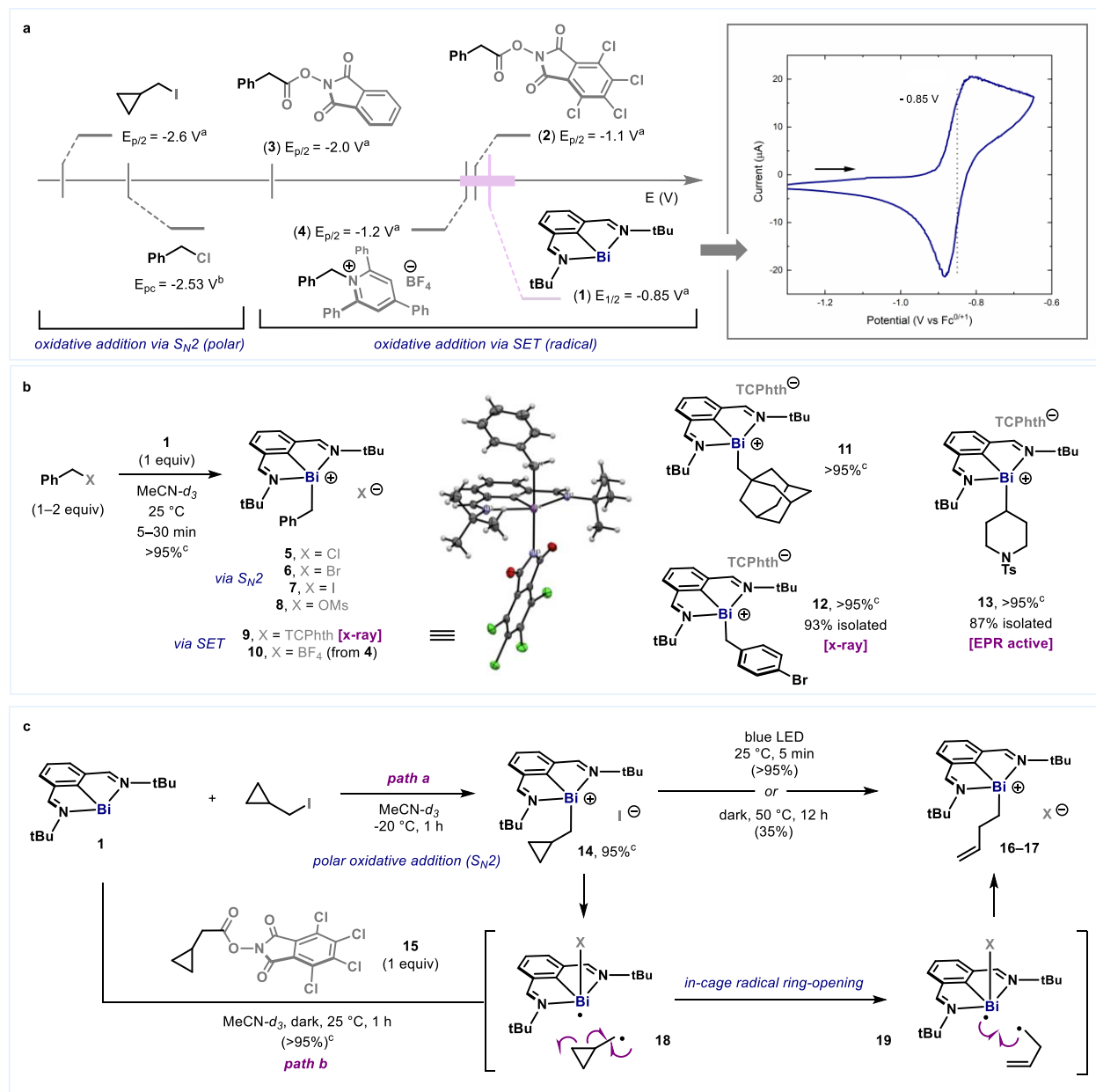

Fig. 2. Oxidative additions into bismuth(I). a, Evaluating electronically different (polar vs radical) oxidative additions to bismuthinidene **1**. **b**, Stable oxidative-addition complexes accessed via S_N2 (**5–8**) or SET (**9–13**) mechanisms. **c**, Evidences for radical-equilibrium complexes after oxidative addition. [a] Cyclic voltammetry recorded in MeCN, potential in V vs $Fc^{0/+}$. [b] Cyclic voltammetry recorded in MeCN (ref. [41]); potential in V vs $Fc^{0/+}$ converted from V vs SCE (-2.13 V). [c] Yields and conversions determined by ^{1}H NMR, unless noted otherwise. TCPhth = tetrachlorophthalimide.

Conversely, when cyclopropylmethyl redox-active ester **15** was reacted with bismuthinidene **1**, a complex analogous to **14** was not observed. Instead, radical ring-opening product **17** was immediately obtained, even in the dark. This is consistent with the two distinct mechanistic scenarios for the oxidative addition. On one hand, polar S_N2-type reaction of cyclopropylmethyl iodide with **1** initially leads to **14**, which eventually ring-opens via radical equilibrium. On the other hand, SET and fragmentation of RAE **15** leads to an in-cage bismuth(II)/alkyl radical pair (**18**), for which cyclopropane ring-opening is faster than radical recombination, resulting in the formation of **17** (Fig. 2b). The radical-equilibrium hypothesis is consistent with the reactivity displayed by these complexes: the secondary alkyl radical derived from **13** reacts with Michael acceptors such as phenylvinylsulfone giving Giese addition product **21**, either in the dark (57%) or under blue-light irradiation (85%) (Fig. 3a, left). The alkyl-radical fragment of several complexes was successfully trapped with TEMPO leading to $C(sp^3)$–OTEMP adducts. Moreover, we observed that catalytic amounts of **1** can promote Giese-type reactions, among others, upon blue light irradiation (for these catalytic examples, and for TEMPO trapping experiments, see Supplementary Information).[42] Interestingly, when attempting the isolation of α-amino alkyl-bismuth(III) adduct **23** derived from proline, we observed the exclusive formation of the product of decarboxylative amination **24**, with recovery of bismuthinidene **1** (Fig. 3a, right).[29,32] It was speculated that product **24** would arise from the oxidation of the corresponding α-amino alkyl radical by a highly reactive bismuth(II) species. This would lead to the formation of an electrophilic iminium ion,[27] which ultimately reacts with the tetrachlorophthalimide (TCNPhth) anion to forge the C–N bond (for details, see Fig. 4b and Supplementary Information).
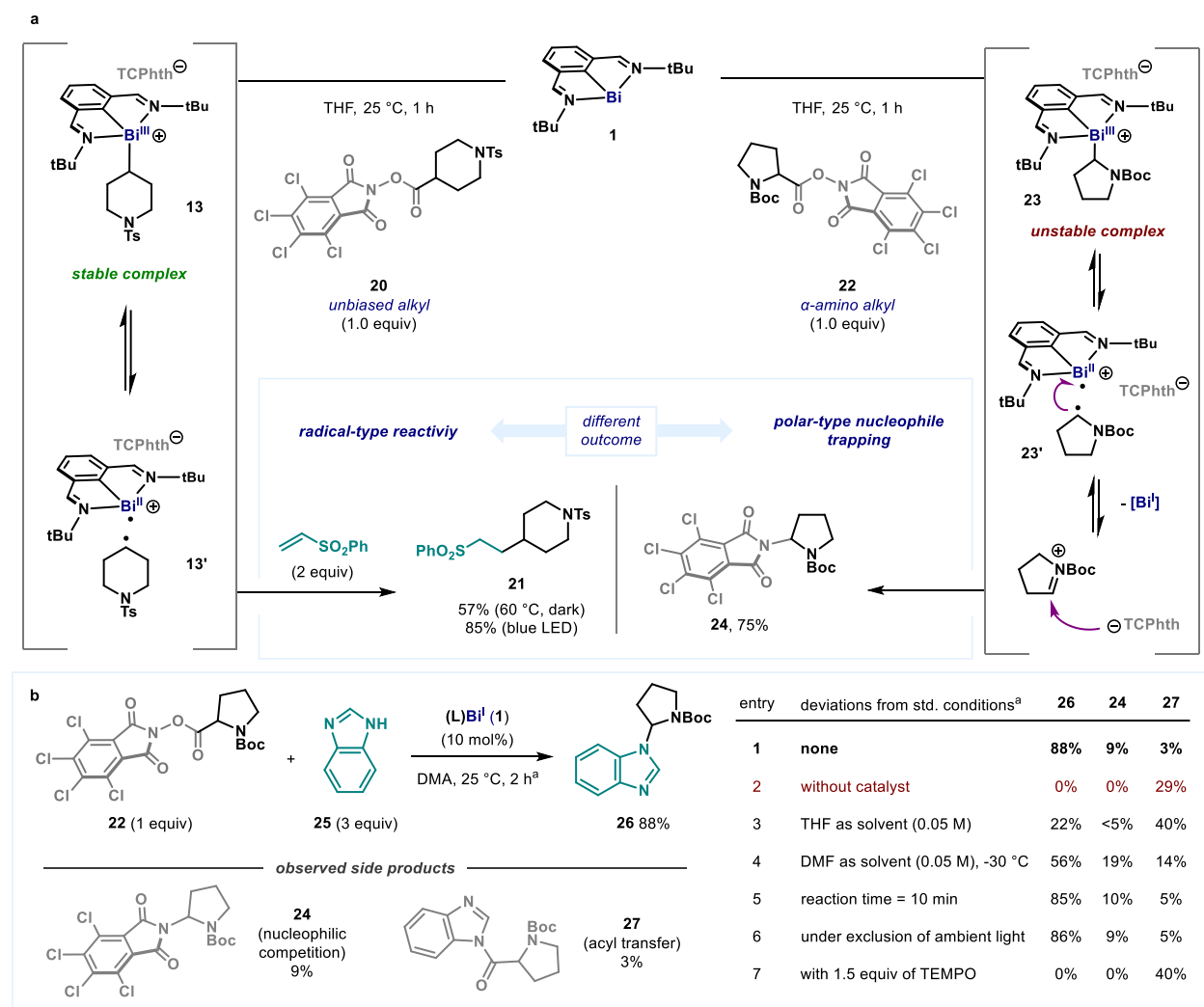
Fig. 3. Divergent reactivity of an unbiased alkyl-bismuth complex and an α-amino alkyl-bismuth complex. a, Stable unbiased alkyl-bismuth(III) intermediates displaying typical alkyl-radical reactivity (left) and unstable α-amino alkyl-bismuth(III) complexes which evolve into iminium ion intermediates upon release of bismuth(I) (right). **b**, Development of a bismuth-catalyzed C–N cross-coupling reaction based on the oxidation of α-amino alkyl radicals. [a] Standard reaction conditions: **22** (1 equiv) and **25** (3 equiv) in the presence of bismuthinidene **1** (10 mol%) in DMA (0.033 M) at 25 °C for 2 h. Yields determined by ^{1}H NMR using diphenylmethane as internal standard. TCPhth = tetrachlorophthalimide.

At this point, it was envisaged that this reactivity could be exploited to engage the corresponding iminium with external N-nucleophiles, leading to a formal C–N cross-coupling reaction. After optimization of the conditions, we found that the reaction of RAE **22** with 3 equivalents of benzimidazole (**25**) in the presence of 10 mol% of **1** in DMA at 25 °C afforded the product of C–N cross coupling (**26**) in 88% yield within 2 h (Fig. 3b). Under these conditions, the only observed side products were **24** (nucleophilic competition by TCPhth) and the expected amide bond-formation product **27**, which could be minimized by controlling the stoichiometry and selecting the appropriate solvent (Fig. 3b, entry 1 vs 3), respectively (see Supplementary

Information for optimization details). Control experiments without Bi catalyst led exclusively to acyl-transfer product (entry 2). The high efficiency of the optimized reaction relies on the faster kinetics of the Bi-radical process compared to the background amide formation. For example, the reaction could be carried out at –30 °C in DMF (entry 4), or at room temperature in DMA in only 10 min (entry 5), giving the desired product in 56% and 85% yield, respectively. To exclude completely the requirement of photoexcitation for any of the steps of the transformation to proceed, the reaction was carried out under exclusion of ambient light, giving comparative results (entry 6). Finally, we found that addition of TEMPO completely inhibits the reaction, presumably due to the inertness of the formed bismuth–TEMPO adduct (entry 7).[39]

The scope of the transformation is presented in Fig. 4a. RAEs of readily available natural and non-natural α-amino acids were interrogated (either fully protected, or with free N–H bonds) as electrophilic partners. C–N coupling products derived from proline (**26**), phenylalanine (**28**), valine (**29**) or pipecolic acid (**30**, **32**) were successfully obtained in good to excellent yields. In order to compete favorably with TCPhth, synthetically relevant N-heterocycles bearing free N–H bonds were evaluated. Using proline-derived RAE **22**, the corresponding C–N coupling products with a variety of benzimidazoles (**26**, **40**), imidazoles (**33**, **39**, **41**), and pyrazoles (**31**, **32**, **35**–**38**) were obtained. Non-symmetrical heterocycles such as benzotriazole (**34**) could also be accommodated, providing the product in a 5:1 N1/N2 ratio of regioisomers. A range of functional groups with different electronic properties were also tolerated (**38**, **41**, **45**). Since the radical process is orthogonal to classical transition metal-catalyzed cross-coupling reactions, different heteroaryl halides (**35**–**37**) and heteroaryl boronic esters (**31**, **32**) could be well tolerated.
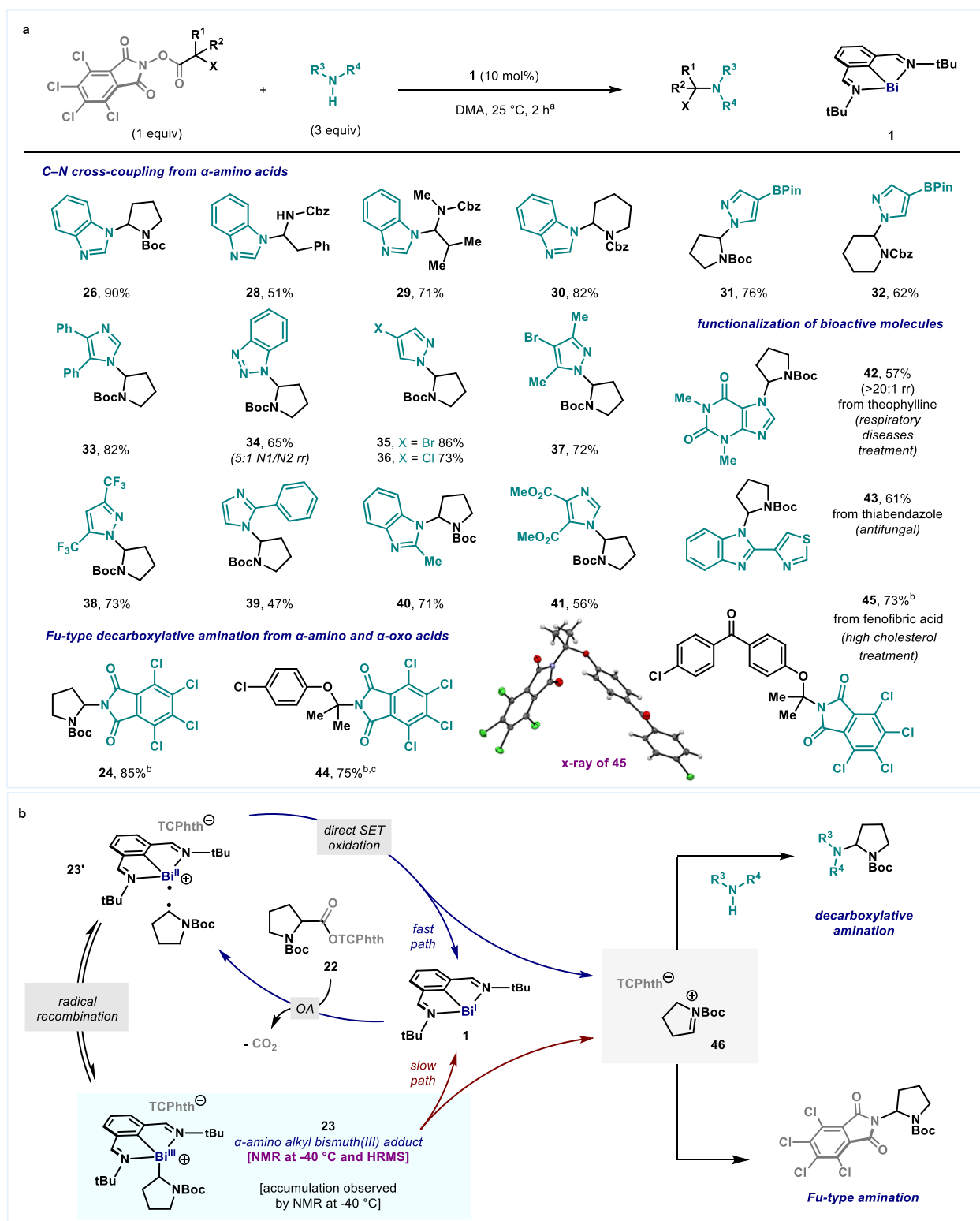
Fig. 4. C–N cross-coupling reaction of α-amino and α-oxo acids via bismuth(I)-catalyzed SET. a, Scope of the coupling reaction. **b**, Proposed mechanistic rationale. [a] Reaction conditions: RAE (1 equiv, usually 0.2 mmol) and N-nucleophile (3 equiv) in the presence of bismuthinidene **1** (10 mol%) in DMA (0.033 M) at 25 °C for 2 h. [b] In the absence of external N-nucleophile. [c] DMA/MeCN 1:1 (0.05 M) as solvent. rr = ratio of regioisomers.

The strategy was successfully applied in the modification of bioactive molecules, such as theophylline (**42**, 57%, single regioisomer). The successful coupling using thiabendazole (**43**, 61%) provides another illustrative example of the orthogonal reactivity to transition metals, as the Lewis-basic sites on both starting material and product could inhibit catalysis by binding to a metal center. In the absence of external nucleophiles, the product of decarboxylative amination via formal CO_2 extrusion was obtained. For this process, both α-amino RAEs and α-oxo RAEs reacted, giving hemiaminal-type structures such as **44** and **45** in good yields. Overall, this strategy is complementary to the photochemical protocol reported by Fu and co-workers, allowing the use of α-heteroatom RAEs, instead of unbiased alkyl substrates.[29]

To shed light into the mechanism, we monitored the catalytic reaction of α-amino RAE **22** by NMR with 10 mol% of bismuthinidene **1** at –40 °C using DMF-d_7 as solvent. In this scenario, the pair of rotamers of α-amino alkyl-bismuth(III) intermediate **23** accumulated upon consumption of the RAE, coexisting with bismuthinidene **1**. It is important to mention that complex **23** was characterized by reaction of **1** with **22** in a separate stoichiometric experiment (see Supplementary Information for details). The accumulated **23** decays into **1** after 1 h at –20 °C (Fig. 4b, slow Bi(I/II/III) pathway). However, we observed that the consumption of RAE **22** to give decarboxylative-amination product **24** occurs at a faster rate than the former process (for details on kinetic analysis, see Supplementary Information). Thus, an alternative pathway should be considered in which in-cage radical pair **23'** reacts through SET, leading to iminium cation **46** upon regeneration of Bi(I) (Fig. 4b, fast Bi(I/II) pathway).[43] Competing radical recombination of **23'** leads to some accumulation of **23**, which eventually collapses into the reaction product (**24**) and **1**. Overall, the radical oxidative addition appears to be the rate-limiting step of the dominant pathway, as suggested by the continuous presence of **1** throughout the entire course of the reaction.

Conclusions

In summary, we have developed a radical oxidative addition of redox-active carbon electrophiles to low-valent bismuth, based on the SET from a well-defined Bi(I) complex to alkyl RAEs and KS. This process led to a family of alkyl-bismuth(III) complexes, which were found to be in equilibrium with the

corresponding in-cage radical pair formed by bismuth(II) and a free alkyl radical. Unbiased alkyl-bismuth(III) complexes are stable and can be characterized both in solution and in solid state. On the other hand, α-amino alkyl-bismuth(III) intermediates collapse back to bismuth(I) upon releasing iminium cations, which can be trapped by external N-nucleophiles. This led to the development of a bismuth-catalyzed C–N cross-coupling reaction, using complex N-heterocyclic compounds. This new type of radical catalysis is promoted by bismuth in an autonomous manner, through a radical Bi(I/II) or Bi(I/II/III) redox cycle, without the need of a photoredox system, a chemical oxidant, an external base, or an electrochemical set-up. Overall, these findings open up a field of radical couplings by a main-group element and pave the way for the rational design of synthetically relevant transformations based on Bi radical catalysis.

Data availability

The Supplementary Information contains all experimental procedures and analytical data (^{1}H, ^{19}F, ^{13}C NMR, HRMS and crystallographic data) for all new compounds. Electrochemical, EPR and kinetic data are also included, together with details on the optimization and mechanistic investigations. Crystallographic data for compounds **9** (CCDC-2178464), **12** (CCDC-2178465) and **45** (CCDC-2178503) can be downloaded free of charge from the Cambridge Crystallographic Data Center www.ccdc.cam.ac.uk.

Author Contributions

M.M. and D.S. developed the radical oxidative additions and studied the properties and reactivity of the resulting alkyl-bismuth adducts. M.M. developed the C–N cross-coupling reaction and prepared the Supplementary Information. M.L. conducted the kinetic studies and helped with the characterization of compounds using NMR spectroscopy. H.W.M. conducted electrochemical analysis. E.R. conducted EPR-spectroscopy analysis. J.C. and M.M. conceived the idea and prepared the manuscript. J.C. directed the project.

Competing interests

No conflict to declare.

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