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# Hypervalent Organobismuth Complexes: Pathways toward Improved Reactivity, Catalysis, and Applications

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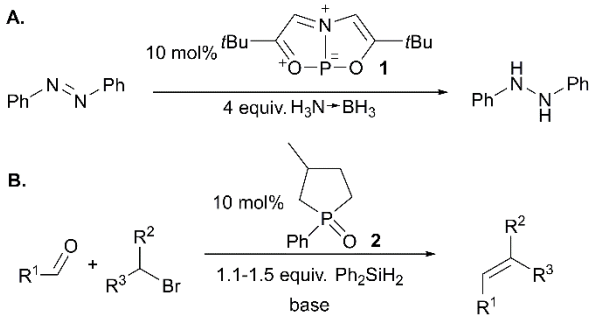
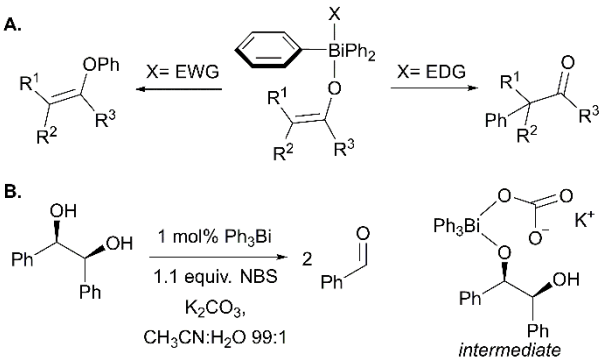
**Hypervalent (three-center, four-electron) bonding in organobismuth complexes has been extensively studied due to its ability to affect molecular geometry, dynamic behavior, or to stabilize the ligand scaffold. This work addresses the effects of this bonding on reactivity, catalytic activity, redox processes, and its potential applications in biosciences, materials science, and small molecule activation.**

The recent interest in Main Group chemistry is driven by the search for unprecedented bonding and reactivity toward small molecules[1, 2], leading to cheaper and more sustainable alternatives to 2nd and 3rd row transition metal catalysts[3]. Transition-metal complexes dominate modern organic synthesis with their effectiveness in bond activation stemming from a small HOMO and LUMO gap and the ability to open up coordination sites, properties usually not associated with Main-Group compounds[3]. In 2012, Radosevich demonstrated hypervalent 10-P-3 platform **1** (Scheme 1A), originally prepared by Arduengo[4, 5], catalyzed transfer hydrogenation between ammonia-borane and azobenzenes via a two electron redox cycle[6]. Another more traditional example of Main-Group catalysis is the Wittig reaction (Scheme 1B), utilizing phosphine oxide **2** as the catalyst in a 2-electron redox manifold using $Ph_2SiH_2$ as a terminal reductant[7]. Many phosphorus-based and other Main-Group redox catalytic systems were recently reviewed by Radosevich[8]. Organobismuthanes emerged as another system capable of redox catalysis[9], reactivity distinctively different from bismuth's traditional role as a potent Lewis acid[10, 11, 12].

Barton pioneered organobismuth chemistry and developed a regioselective arylation using organobismuth(V) complexes (Scheme 2A)[13, 14], and other synthetically relevant transformations[15]. In 1981, Barton presented the first example of organobismuth-based redox catalysis (and perhaps the first example in the Main-Group block), a triphenylbismuth-catalyzed 1,2-diol oxidative cleavage, operating through a Bi(III)/Bi(V) redox pair (Scheme 2B)[16].




**Scheme 1. A.** Hydrogen transfer reaction catalyzed by 10-P-3 complex **1**. **B.** Witting reaction catalyzed by phosphine oxide **2**.




**Scheme 2. A.** Regioselective phenylation using organobismuth(V) reagent. **B.** Oxidative cleavage of 1,2-diols catalyzed by $Ph_3Bi$.

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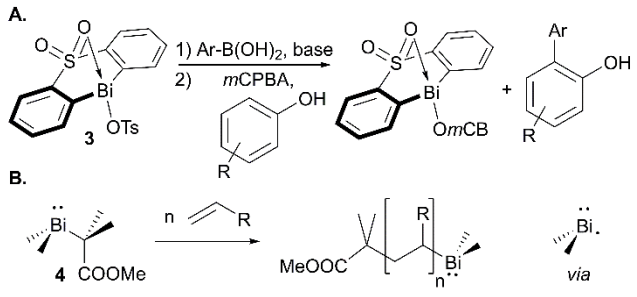
Now, researchers have further advanced this chemistry[17-21], and used bismacycles like **3**, developed by Ball, to facilitate Bi(III)/Bi(V) redox cycle in sequential arylation/oxidation process significantly improving synthesis of biphenyls (Scheme 3A)[22]. Other unprecedented systems were developed such as organobismuth **4** mediated living radical polymerization (BIRP) using Bi(II)/Bi(III) redox couple (Scheme 3B)[23]. Bismuth is also capable of reaching unusual, otherwise fleeting oxidation states I and II when supported with proper ligand scaffolds[24]. For example, Bi(II) **5**, a bismuth centered radical, is supported with bulky tetrakis trimethylsilyl ligand (Figure 1)[25] and notably, Bi(I) **6** (Figure 1), first synthesized by Dostál, is stabilized by a bulky NCN ligand and a three-center, four-electron N-Bi-N bond[26]. Other ligand scaffolds, such as triamide ligand in bismuth complex **7** (Figure 1), enables substrate-dependent shuttling between Bi(I) and Bi(III) oxidation states[27].

Importantly, in the last few years, a number of redox catalytic systems dramatically increased due to the bismuth's ability to cycle between oxidation states including less common oxidation states I and II. For example, Cole's oxidative coupling of $PhSiH_3$ and TEMPO is catalyzed by Bi(II) **8**, a complex structurally analogous to **5**, cycling between Bi(II)/Bi(III) oxidation states (Scheme 4A)[28], and Cornella's transfer hydrogenation catalyzed by Bi (I) **9**, derived from **6**, operating via a Bi(I)/Bi(III) redox manifold (Scheme 4B)[29]. Notably, Cornella also developed numerous systems, greatly expanding bismuth-based redox catalysis, which was recently summarized in an excellent review article[30]. Since then, new contributions to this field have been reported[31-37], and more can be expected. These examples show increasing interest in organobismuth chemistry which possesses a strong synthetic utility and in comparison, with phosphorus analogs, can support larger varieties of oxidation states applicable in redox catalysis.




**Scheme 3. A.** Sequential arylation/oxidation of sulfone bismacycle affording biaryls. **B.** Organobismuth-mediated living radical polymerization (BIRP).

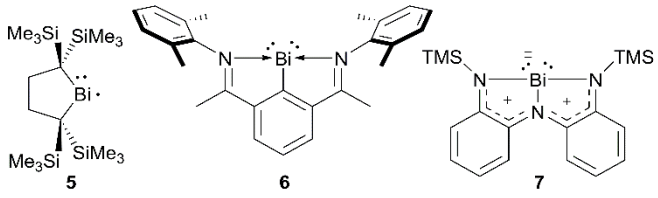
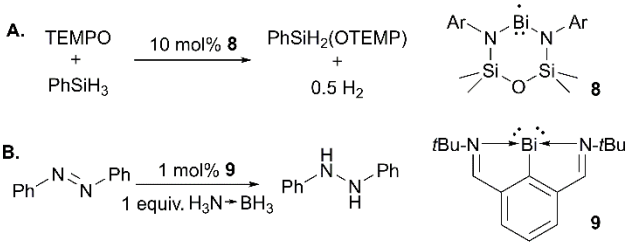



**Figure 1.** Bismuth centered radical **5** stabilized by bulky ligand. Monomolecular Bi(I) complex **6** stabilized by NCN ligand. Triamide bismuth complex **7** with a considerable Bi(I) character.




**Scheme 4. A.** Dehydrocoupling of TEMPO and $PhSiH_3$ catalyzed by bismuth radical **8**. **B.** Transfer hydrogenation catalyzed by Bi(I) complex **9**.

In contrast to the redox or Lewis acid reactivity, organobismuth complexes also form hypervalent (3c-4e) bonds[38,39, 40] (Figure 2). Although the concept of hypervalency was originally established by Musher in 1969 [38], there is still ongoing debate. Schleyer proposed to replace the term 'hypervalence' with a more accurate term 'hypercoordination', since the number of electron pairs is limited, but the number of surrounding atoms is not [41, 42]. Others revised this qualitative approach with quantitative models [39, 43]. Hypervalent bonding is preferred in chemistry of electropositive heavier elements (3rd row and lower) with electronegative atoms or groups at the apical sites that siphon electron density away from the central atom in usually a linear arrangement and with a formal bond order <1[40]. In this article, most of the hypervalent bonds can be classified as $(LX)^H$ bonds[40] and are provided by internal donor ligands, pendant arms, or by transannular interaction in polycyclic systems with a multidentate ligand . Multidentate ligands offer better stability of complexes[9] due to the weak Bi-C bonds' susceptibility to dismutation, a substituent scrambling process[44]. The hypervalent bonding is responsible for properties unmatched in complexes of lighter congeners. For example, it can be used to stabilize the ligand scaffolds as shown in stabilization of Bi(I) complexes (**6** and **9**, *vide supra*), or lower transition states in edge-inversions or bond switching (bell-clapper) processes [45-49], or to affect the structural features and molecular shapes[50-56].

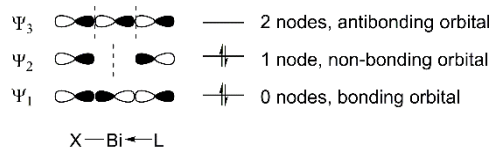
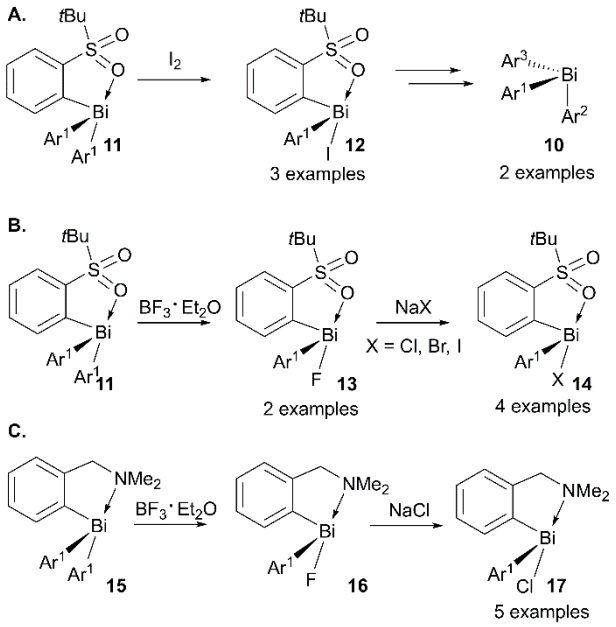



**Figure 2.** Simplified orbital description of $(LX)^H$ bond.

In synthesis, the most elegant use of hypervalent bonding was used in preparation of chiral triarylbismuthanes **10** (Scheme 5A). During the synthesis of **10**, Suzuki argued that sulfonyl intramolecular interaction in **11** led to a selective iododearylation, cleaving only one of the aryl groups forming **12**, whereas the non-hypervalent analogs showed lower selectivity[57]. Analogously, the treatment of **11** with $BF_3{\cdot}Et_2O$ led to selective formation of fluoride **13**, which was derivatized with other halides to **14** (Scheme 5B)[58]. In a similar vein, derivative **15** selectively generated fluoride complex **16** when treated with $BF_3{\cdot}Et_2O$ and corresponding chloride **17** was isolated after washing with brine (Scheme 5C)[59]. The primary benefit of this

methodology is the selective monodearylation without dismutation.




**Scheme 5. A.** Iodoarylation of *tert*-butylsulfonyl triarylbismuthane, intermediate to chiral triarylbismuthane. **B.** Fluorodearylation of *tert*-butylsulfonyl triarylbismuthane with $BF_3{\cdot}Et_2O$ followed by a halide exchange. **C.** Fluorodearylation of dimethylaminomethyl triarylbismuthane followed by a chloride exchange.

The hypervalent cationic organobismacycle **18** (Figure 3) with a weakly coordinated $B(C_6F_5)_4^-$ anion is an excellent Lewis acid, capable of coordinating to various substrates, including weak donors such as dichloromethane[60]. Hypervalent complexes **19**-**22** in Figure 3 demonstrated efficiency in Lewis-acid catalyzed reactions. Complexes **19** and **20** catalyzed the Mannich reaction[61, 62], while complex **21** catalyzed cross aldol condensation with high *E* selectivity[63], and complex **22** catalyzed aldehyde allylation with tetraallyltin[64]. All these hypervalent complexes are air-stable, and the tested reactions were run in water or aqueous methanol, showing good recyclability and often improved activities and selectivities in comparison with traditional bismuth-based Lewis acids such as $Bi(OTf)_3$. Complex **23** was even used for aerobic oxidation of thiophenol to diphenyldisulfide[65]. However, the advantage of the hypervalent bond in these complexes toward the Lewis

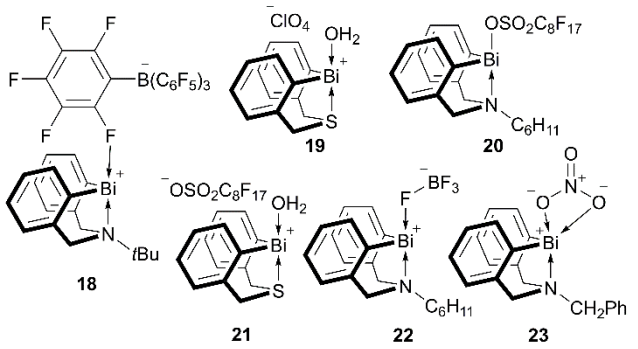
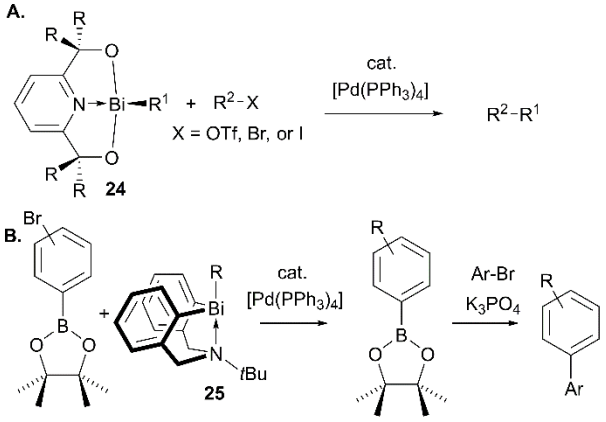



**Figure 3.** Hypervalent cationic organobismacycles used as Lewis-acids.

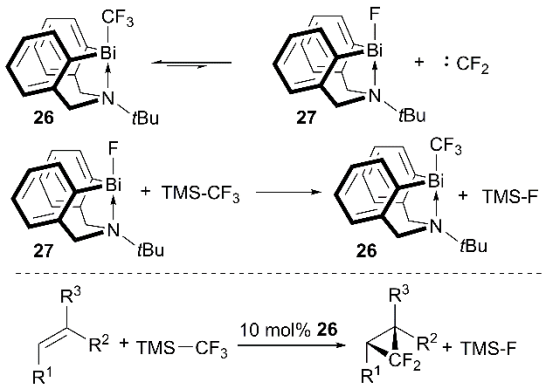
acidity has not been explained. Perhaps the extra donor would be expected to mitigate Lewis acidity at the bismuth atom, but bismuth cations lacking hypervalent bonding from an intramolecular donor were potent Lewis acids as well[66]. It is likely that the observed stability of complexes **19**-**23** can be attributed to the extra bond from the internal donor forming a stable tridentate ligand.

On the other hand, hypervalent organobismuthanes, but not their non-hypervalent analogs[67], are excellent transmetalation agents in Pd-catalyzed cross-couplings. Shimada and Tanaka developed complex **24**[68], which was utilized in Pd-catalyzed cross couplings with aryl and vinyl triflates[69], and aryl bromides and iodides[70] (Scheme 6A). Although these complexes showed much improved reactivity in comparison to triarylbismuthanes, their moisture sensitivity has limited their use. The same authors reported that complex **25** displays an excellent selectivity allowing a sequential cross-coupling with boronic esters performed in one pot (Scheme 6B)[71].




**Scheme 6. A.** Pyridinedimethoxide monoorganobismuth in palladium catalyzed cross-coupling. **B.** A sequential palladium-catalyzed cross-coupling with organobismuth and boronic esters.

Inspired by Shimada and Tanaka's work, our research group explored the reactivity of trifluoromethyl derivative **26** (Scheme 7), discovering a novel, non-redox catalytic process operating solely through hypervalent bond activation[72]. In this reaction, complex **26**, through a concerted reversible mechanism, forms fluoride **27** and free difluorocarbene, which reacts with an alkene forming the corresponding 1,1-difluorocyclopropane moiety. In the next step, transmetalation between fluoride **27** and TMS-$CF_3$ (Ruppert-Prakash reagent), cycled back trifluoromethyl complex **26** and released TMS-F as a side product. The mechanistic investigation revealed that the presence of a highly endergonic equilibrium in $CF_2$ release is responsible for excellent reaction control and high reagent selectivity suppressing $CF_2$ dimerization. However, attempts toward an enantioselective variant of this reaction was unsuccessful[73]. Although a non-redox catalytic cycle was reported[74], to the best of our knowledge, this is the only example of an organobismuth non-redox catalytic process requiring a hypervalent bond for activation. Non-hypervalent analogs of **26**, complexes **A** and **B** (Figure 4) were inactive, and




**Scheme 7.** Olefin difluorocyclopropanation catalyzed by trifluoromethyl complex **26**.

DFT calculations predicted significantly higher activation barrier for $CF_2$ release. Interestingly, the DFT calculations revealed that

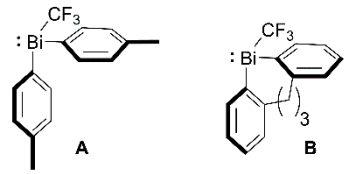
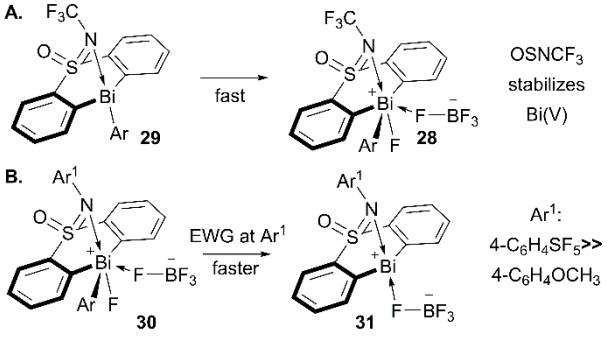



**Figure 4.** Non-hypervalent complexes ditolyl(trifluoromethyl)bismuthane **A** and 12-(trifluoromethyl)-5,6,7,12-tetrahydrodibenzo[*b*,*g*]bismocine **B**

the Bi-C bond activation does not necessarily mean weakening a bond.

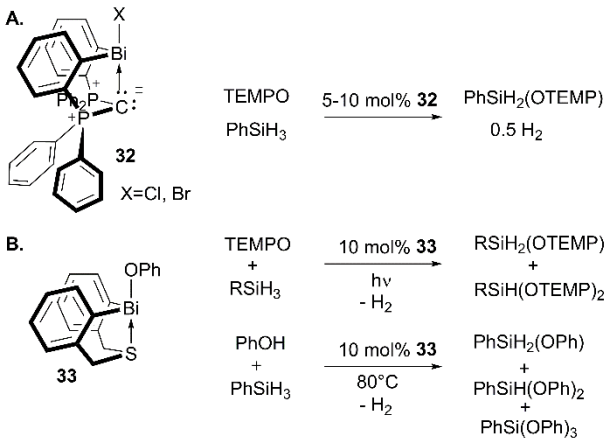
As in **26**, it was calculated that the Bi-$CF_3$ bond is much stronger than in non-hypervalent derivatives **A** and **B**. However, the Bi-F bond in **27** is even more stabilized through hypervalent bonding as F is more inductively withdrawing than the $CF_3$ group. The stabilization of Bi-F bond lowers the energy of **27** and thus it lowers the energy of TS of $\alpha$-$CF_2$ elimination step in agreement to the Hammond postulate. In short, in this case, the ease of $CF_2$ generation can be attributed to the selective Bi-F bond stabilization rather than Bi-$CF_3$ bond destabilization. Based on this analysis, the effect of hypervalent bonding on halogendearylations (Scheme 5) and transmetalations in palladium-catalyzed cross-couplings (Scheme 6) could be explained in a similar manner. The driving force in these transformations is expected to stem from the stability of formed hypervalent Bi-Halogen bonds in comparison to the hypervalent Bi-C bonds in the starting complexes. Notably, this is highlighted by a superior reactivity of the complex **25** with a linear hypervalent bond in comparison to **24** where the accepting orbital is perpendicular to the donor.

One could envision that two-electron redox reactivity and hypervalent bond activation could act in synergy, instead of being viewed as separate reaction pathways. The presence of the internal donor group forming a hypervalent bond would increase the electron density at the central atom[39] promoting oxidative addition, as reported in a recent theoretical study of bismuth mediated fluorination of arylboronic acids[75]. The study predicted that formation of the highly electrophilic Bi(V) complex **28** from **29** was stabilized by weak coordination from the -$OSNCF_3$ group providing the extra electron density (Scheme 8A). However, the increase of electron density through an internal donor is disadvantageous for reductive elimination, such as from **30** to **31**, preferring rather decreased electron density and a weaker donor atom if any, as supported by theoretical and experimental study (Scheme 8B)[76]. Hence, the overall effect on the catalytic cycle would depend on which elemental step would be the rate limiting.




**Scheme 8. A.** Oxidative addition is accelerated by internal donor ligand -$OSNCF_3$. **B.** Reductive elimination is retarded by an internal donor ligand.

The effects of hypervalent bonding on 1-electron redox reactivity can also be expected. Gilliard reported complex **32** (Scheme 9A) with carbodiphosphorane donor group with a strong *trans*-effect, catalyzing dehydrocoupling of TEMPO and $PhSiH_3$ under thermal conditions through a Bi(II)/(III) redox manifold[77]. It was proposed that the strong donor destabilizes the radical Bi(II) species and thus increases its reactivity. This could be envisioned in the way that **32** possess a good accepting orbital due to a Bi-Halide bond and distributing the electron density to the non-bonding orbital (Figure 2), while the Bi(II) radical does have this ability and thus its reactivity would increase more than in the non-hypervalent derivative. Another example of radical catalysis, reported by Lichtenberg, was demonstrated on the same type of dehydrocoupling, promoted by complex **33** (Scheme 9B) under thermal and photochemical conditions operating via different mechanisms[78].




**Scheme 9. A.** Dehydrocoupling of TEMPO and $PhSiH_3$ catalyzed by **32** under thermal conditions. **B.** Dehydrocoupling catalyzed by **33** under thermal and photochemical conditions.

Besides catalysis, the organobismuth complexes are explored for various applications in biosciences, materials science, and small molecule activation. For example, hypervalent organobismacycles **34** and **35** (Figure 5) showed good activity against gram-positive bacteria; the activity against gram-negative bacteria was low due to inability to permeate the outer membranes[79]. Recently, Chen tested antimicrobial activities with organobismuthanes bearing bidentate ligands and compounds **36** and **37** were also active against gram positive bacteria. It was suggested that hypervalent bonding is advantageous for increasing pharmacological activity due to improved stability for successful transport to the target, since they contain otherwise labile Bi-X bonds[80]. However, non-hypervalent triarylbismuthanes showed similar activities[81]. Hypervalent bismacycles **38** showed good antifungal[82, 83] and compound **35** antileukemic[84] activities. In materials research, hypervalent bismuth complex **39** was explored for molecular sensing benefiting from electron-donating and electron-accepting abilities of the hypervalent bismuth[85]. Complex **40** showed better optoelectronic properties due to the hypervalent bonding perturbing 6s electrons and thus enabling photoluminescence through MLCT[86]. The hypervalent organobismuth complexes were also proficient in small molecules activation. For example, complexes **41** and **42** showed reactivity toward the $CO_2$ fixation, and in the former case, it was suggested that the hypervalent bonding contributes to the higher stability of the formed bismuth carbonate[87, 88]. Complex **43** demonstrated reactivity toward CO, which was attributed to the ring strain release[89].

## Conclusions

Organobismuth complexes recently attracted significant interest due to their ability to catalyze organic transformations via redox processes. This success is due to the bismuth's ability to cycle between common oxidation states III and V, and less common oxidation states I and II. This redox catalysis is decidedly different from its traditional role as a Lewis acid. In addition, bismuth as a heavy Main Group element is also capable of forming hypervalent three-center, four-electron

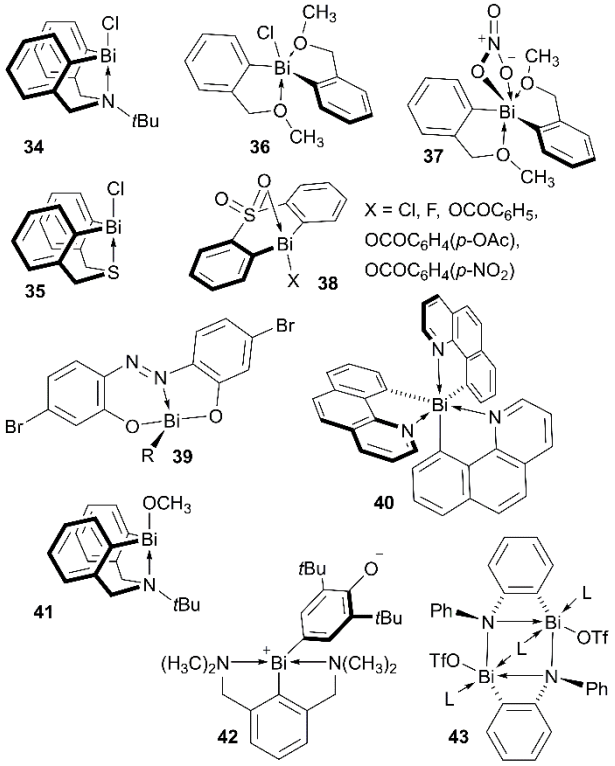



**Figure 5.** Complexes with potential applications in bioscience, materials science and small molecule activation.

bonds, a type of bonding much explored in inorganic chemistry, due to its ability to affect the molecular geometry, dynamic behavior, or support a ligand scaffold of bismuth complexes in less stable oxidation states. Here, the hypervalent bonding demonstrated its usefulness, *e.g.*, in selective dearylation reactions, stabilizing organobismuth cations, increasing its ability to transmetalate to Pd(II), or in activating trifluoromethyl group for a controlled $CF_2$ release. The hypervalent bonding can also play a significant role in the organometallic-type redox processes, such as oxidative addition and reductive elimination, or it can affect the stability of bismuth centered radicals. Lastly, the hypervalent complexes shown relevance in biosciences, materials science, and small molecule activation. In the future, more work in the area of the organobismuth catalysis can be expected as it offers unprecedented reactivity, and better sustainability in comparison with traditional transition-metal catalysts.

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## Conflicts of interest

There are no conflicts to declare.

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