

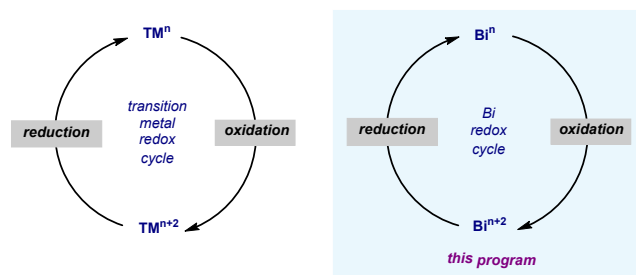
2.7.2 Bismuth Redox Catalysis

Sustainable Catalysis for Organic Synthesis by Josep Cornella

ABSTRACT: Our laboratory focuses in the development of efficient strategies for organic synthesis. Specifically, interests can be divided in four major research lines, namely (i) the catalytic decoration of heterocycles; (ii) the activation of C-N bonds *via* newly designed pyrylium reagents; (iii) the exploration of new reactivity modes for low-valent Ni complexes, and (iv) bismuth redox catalysis. Herein, we summarize our results in the latter program, since the ability of bismuth to maneuver between different oxidation states in a catalytic redox cycle, is an elusive and unprecedented approach in the field of homogeneous catalysis. The main goal of this research program is to translate the unique properties, traditionally associated to transition metals, to bismuth; an earth abundant, non-toxic and inexpensive main group element. In this report, we provide an overview on our efforts to unlock the elusive two-electron redox cycles $\text{Bi(III)} \rightleftharpoons \text{Bi(V)}$ and $\text{Bi(I)} \rightleftharpoons \text{Bi(III)}$ in the context of different organic transformations.

Introduction. The great success of transition metals in homogeneous catalysis is mainly owing to their orchestrated maneuvering between different oxidation states, operating in synchrony for productive catalysis. These features placed transition metals in a privileged situation to serve as workhorse catalysts in a plethora of relevant chemical processes.

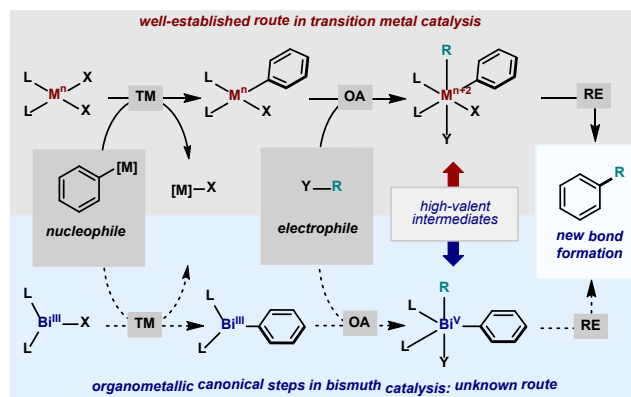
Figure 1. Schematic representation of catalytic redox cycles: transition metals *versus* bismuth.



However in recent years, chemists have questioned the possibility of conferring transition-metal like properties to elements beyond the *d*-block.¹ Indeed, strategies based on FLP (Frustrated Lewis Pairs), alkali, alkaline, and group 13-17 elements are recently emerging as competent alternatives in certain domains of catalysis.² However, the quest for developing methodologies based on the *redox properties of a main-group element* that surpass the reactivity of transition metals still remains a challenge in organometallic. Herein we describe our recent findings on the catalytic redox properties of bismuth (Bi); an Earth-abundant, non-toxic and inexpensive main-group element, whose redox properties have been largely underexplored (Figure 1).

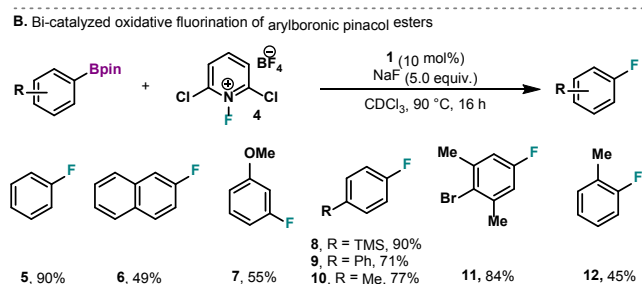
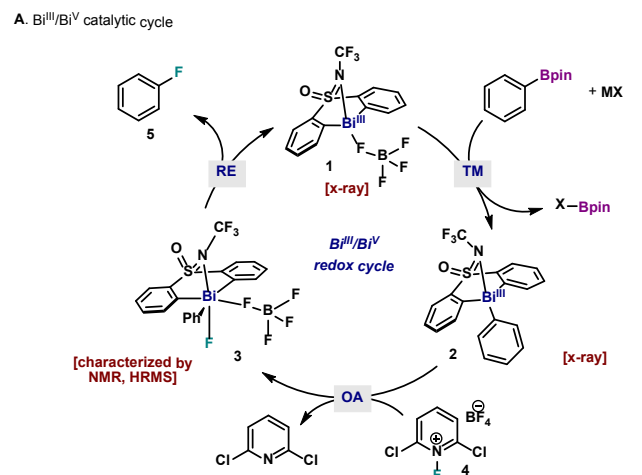
Bi(III) \rightleftharpoons Bi(V) Catalysis. We hypothesized that the provocative idea of exploiting the redox properties of Bi(III) compounds could successfully be realized if a suitable complex was capable of mimicking the canonical fundamental steps in a transition-metal catalytic cycle: transmetalation (TM), oxidative addition (OA) and reductive elimination (RE) (Scheme 1). To explore this hy-

pothesis, we focused on the transition-metal-mediated oxidative fluorination of aromatic boronic acids, a transformation currently restricted to the use of stoichiometric amounts of transition metals (Cu, Pd and Ag).³



Scheme 1. Organometallic steps in a catalytic redox cycle: transition metal (M) and bismuth (Bi).

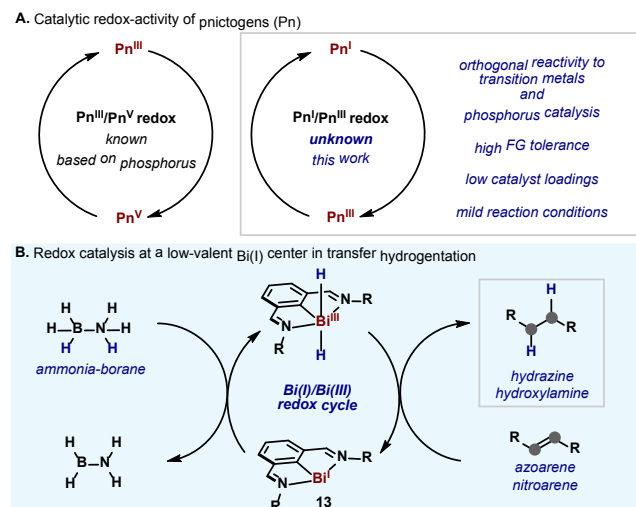
To this end, we designed a bismine complex (**1**) featuring a bis-aryl tethered ligand bearing a sulfonimine, and a BF_4 moiety as a weakly coordinating anion (Scheme 2A).⁴ The presence of the sulfonimine ligand permits hypervalent coordination of the N atom to the Bi center which proved crucial in the three 'organometallic' steps. The rational design of the ligand permitted a catalytic cycle for the fluorination of arylboronic esters with a fluoropyridinium salt (**4**). A detailed investigation of each individual step resulted in the characterization of the intermediates from a putative mechanism shown in Scheme 2A, where the Bi circulates between oxidation states (III) and (V). A summary of the scope and the substitution patterns in the aryl group is shown in Scheme 2B.



Scheme 2. (A) Mechanism of the Bi-catalyzed fluorination of arylboronic esters; (B) Scope of the fluorination reaction.

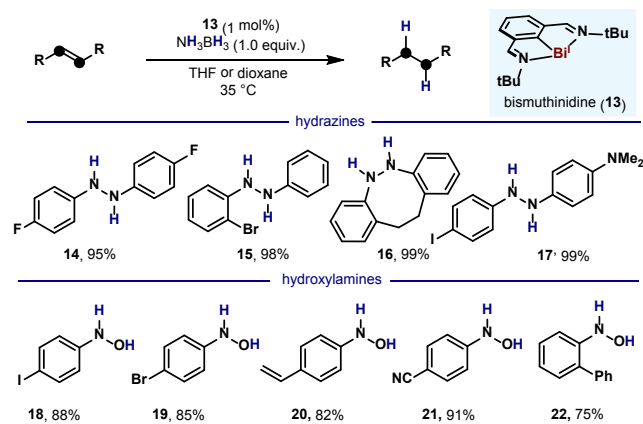
Bi(I)⇌Bi(III) Catalysis. While Bi(III) and Bi(V) compounds are largely known in the literature, the low-valent Bi(I) counterparts are really rare, mainly due to the instability and sensitivity towards oxidation of the $6p^2$ orbital.

Figure 2. (A) Pnictogens in redox-catalysis. (B) Bi-catalyzed transfer hydrogenation.



Although P(III)/P(V) catalysis has been demonstrated in the context of transfer hydrogenation,⁵ redox catalysis of pnicogens at the Pn(I) oxidation state was still elusive (Scheme 3A). To this end, we capitalized on Dostál's bismuthinidine **13**⁶ featuring a NCN pincer ligand and demonstrated its catalytic activity in a transfer hydrogenation reaction (Scheme 3B).⁷ Capitalizing on the

high reactivity of Bi hydrides, we speculated that the transfer of the hydrogen atoms to an acceptor would be within reach. Indeed, when **13** was utilized as catalyst in the reduction of azoarenes and nitroarenes with ammonia-borane, excellent yields of the reduced products were obtained under mild conditions. Kinetic analysis of the reaction indicated that **13** is the resting state and the formation of Bi(III) hydrides is rate-determining. Although the nature of the intermediates still remains elusive, high-resolution mass-spectrometry identified putative Bi(III)-H intermediates during catalysis.



Scheme 4. Bi(I)-catalyzed transfer hydrogenation.

Conclusions. We have established the feasibility of performing redox transformations based on bismuth catalysis. Initially, we developed a fluorination of boronic acids proceeding via an unprecedented Bi(III)/Bi(V) redox cycle. Exploring complexes in lower oxidation states, enabled the disclosure of the catalytic activity of Bi(I) compounds in transfer hydrogenation reactions. These suggest that Bi holds great potential in the discovery of new reactivity.

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