Bismuthinidenes

Introduction:

Bismuthinidenes are mononuclear organometallic compounds and the metal atom is group 15 element bismuth which oxidation state is in +1[1]. Bismuthinidene are extremely rare, and the compounds with dicoordinate bismuth are typical highly reactive[2]. To make bismuthinedenes stable, people utilize sterical bulky groups to protect the bismuth center. Bismuthinidenes was firstly synthesized by Tokitoh and his workmates in 1997, which contains Bi=Bi bond[3]. The central atom is in the oxidation state of +1, so it is highly reactive. Mostly, they can adopt either singlet or triplet electronic ground states. Bismuthindenes can access by stabilization through adduct formation with Lewis bases[4]. In addition, bismuthindenes are regarded as quite strong reducing agents. Bismuthindenes have been suggested to be involved in the electrochemical reduction of carbon dioxide at bismuth electrodes[5]. When embedded in zeolites, they show intriguing photophysical properties such as ultrabroad near-infrared emission[6, 7].
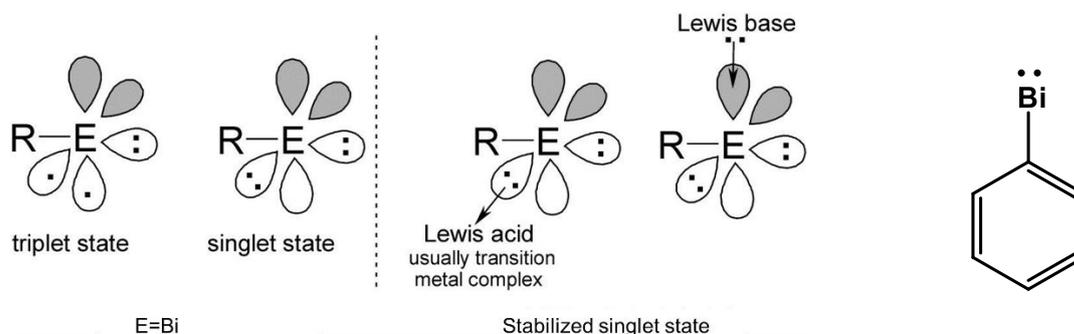
Contents

Synthesis

The earliest succeessful synthesis of bismuthindenes is reported by Tokitoh et al. in 1997, which was prepared by deselenation of triselenatribismane with a phosphine reagent. Dibismuthene has a low solubility and easily separated because of its high symmetry. It is like deep purple single crystals.

$$\text{BiCl}_3 \xrightarrow{\text{TbtLi/THF}} \text{TbtBiCl}_2 \quad \mathbf{3} \xrightarrow{\text{Li}_2\text{Se/THF}} \mathbf{2} \xrightarrow[\substack{- 3(\text{Me}_2\text{N})_3\text{P=Se} \\ \text{tolulene}}]{3(\text{Me}_2\text{N})_3\text{P}} \mathbf{1}$$

Tbt =
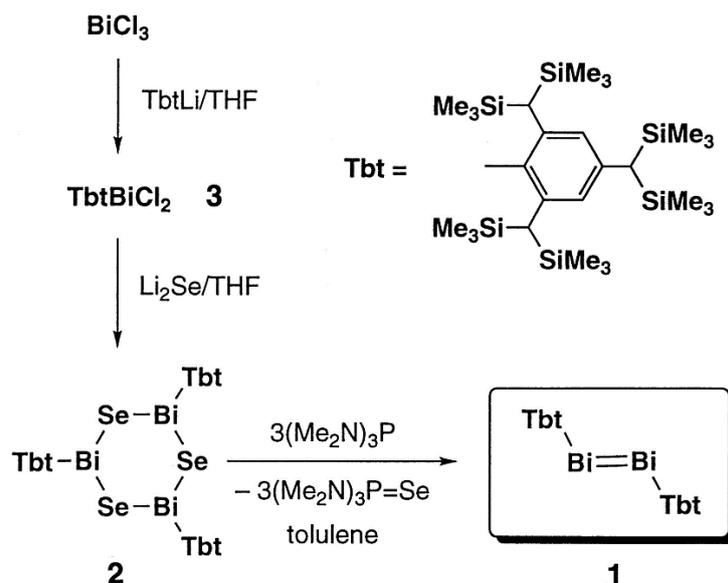
To stablize the bismuth(I) centers, it is evident that it generally leads to the formation of dibismuthenes, adopting a Bi=Bi bond. In 2010, Peter Simon Ing et.al reported the isolation of monomeric bismuthindene [C6H3-2,6-(C(Me)=N-2′,6′-Me2C6H3)2]Bi stabilized by a N,C,N-pincer-type ligand, which is void of any additional intermolecular metal–metal interactions. They applies LMCl2(M=Sb(1) and Bi(2)) from LLi and MCl which are synthesized from Et2O. The key step of the synthesis is using of two equivalents of nBuLi(Et$_2$O, -60℃) for successful lithiation of the ligand[8].

$$\text{LBr} \xrightarrow{+2n\text{BuLi}} \text{LLi} \xrightarrow[-\text{LiCl}]{+\text{MCl}_3} \text{LMCl}_2 \quad \substack{\text{M = Sb (1)} \\ \text{M = Bi (2)}}$$

+2K[B(iBu)$_3$H]
- 2KCl
- 2B(iBu)$_3$
- H$_2$

LM
M = Sb (3)
M = Bi (4)

Ar = 2,6-Me$_2$C$_6$H$_3$

L =
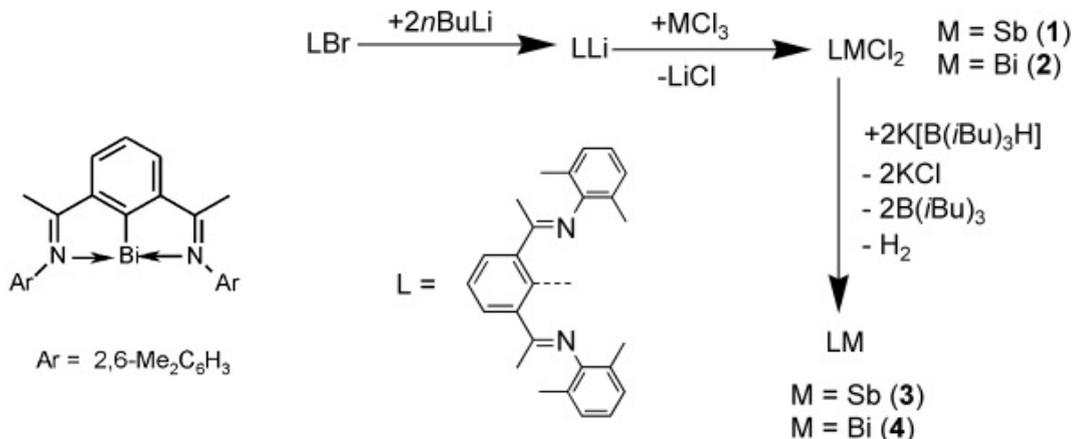
Futhermore, Gilliard et al. synthesized a series of bismuth(III) complexes by using NHCs and CAACs with phenylbismuth dichloride. The CAAC Bi^{III} compounds were obtained in higher yield and were more resistant to isomerization or decomposition compared to the analogous NHC complexes. This is the first time to synthesize compound with CAAC coordination to bismuth. Reduction of (Et2CAAC)Bi(Ph)Cl2 with two equivalents of potassium graphite (KC8) in toluene at −37 °C resulted in a color change from pale yellow to red over one hour (Scheme 1). The solvent was removed, and the residue was extracted with hexane to give a red solution. The UV/Vis spectrum recorded at room temperature of the red solution in hexane showed a new absorption band at λ$_{max}$ 516 nm, which was attributed to the formation of a reduced bismuth species. The red solution rapidly decolorizes, and an insoluble black precipitate was observed. This precipitate was attributed to bismuth metal, obtained through decomposition of the target compound[2].

Proposed structure

Isolated Yield: 0%
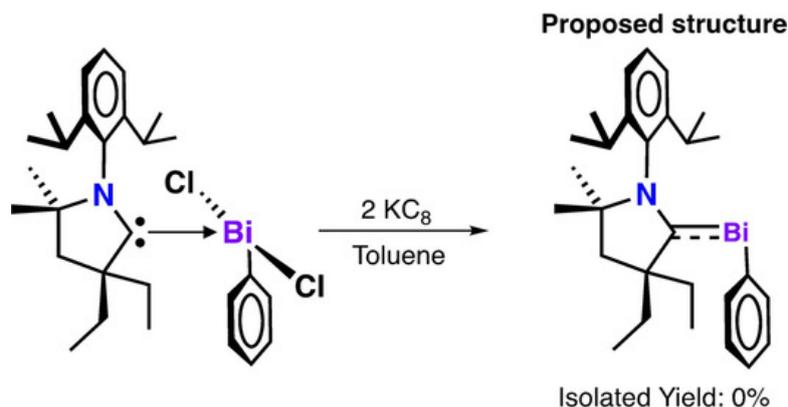
Functionalization:

In the Bi system, the highly reactive tetrahedral complex could easily convert to the halo-substituted compound $[ClBi(Cr(CO)_5)_3]^{2-}$ and $[BrBi(Cr(CO)_5)_3]^{2-}$ upon the reaction with CH_2Cl_2 or $CH\equiv CCH_2Br$. Moreover, when reacted with alkyl halides RI (R = Me, Et), the alkyl-substituted bismuth complexes $[RBi(Cr(CO)_5)_3]^{2-}$ (R = Me,Et) were formed. This reaction type was parallel to that of the structurally similar bismuth complex $[Bi(Fe(CO)_4)_4]^{3-}$ with alkyl halides as abovementioned[9]. The functionalization of was very sensitive to the reactivity of these halogen derivatives because of the ease of the formation of halo-substituted bismuth complexes.
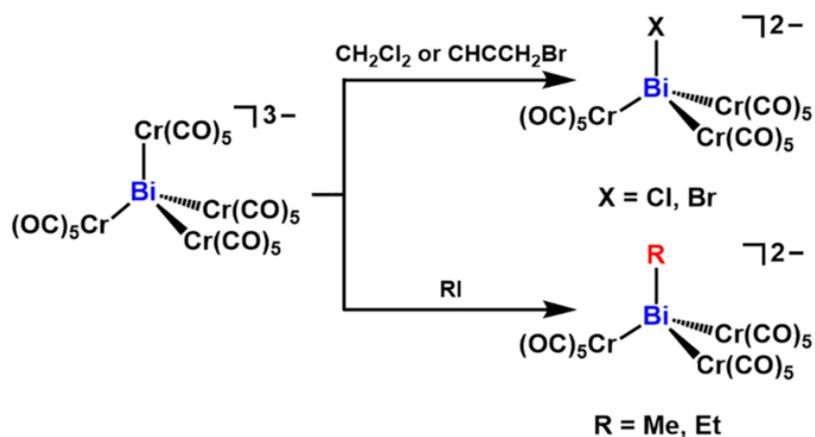
Reactivity and catalytic ability

Redox reaction

The presence of the bismuth(I) center is a mark for their inherent interesting redox activity. A transfer-hydrogenation of azo-compounds by amino-borane complex that is catalyzed by the bismuthinidene[10]. The catalytic cycle relies on the Bi(I)/Bi(III) redox-pair is involving oxidative addition/reductive elimination couple[11].
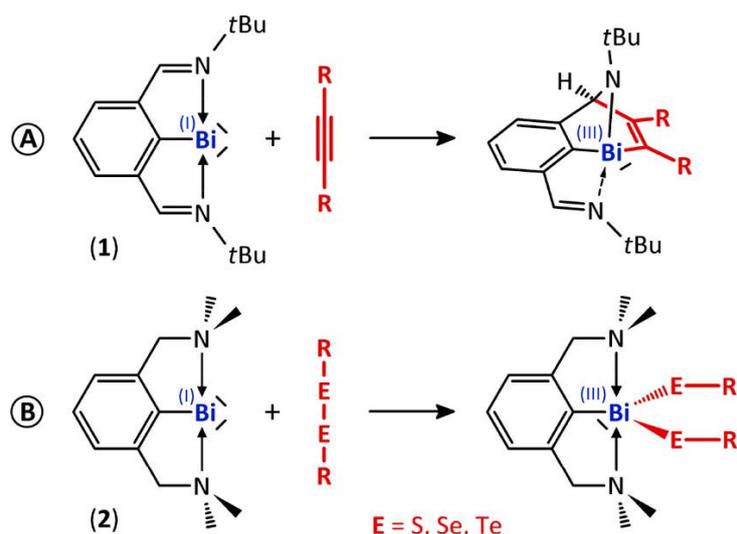
N₂O reaction

BiI⇌BiIII redox cycling can be applied that N,C,N-chelated bismuthinidenes are able to catalyze N_2O deoxygenation in the presence of pinacolborane (HBpin). When it was exposed to a N_2O atmosphere at room temperature, the color slowly changed from dark purple to pale yellow and evolution of N_2 was observed. 1H NMR analysis at −50°C confirmed the full consumption after 40 min and indicated the formation of a single species with an asymmetric N,C,N-pincer backbone. Examples of mono-organobismuth(III) oxides are rare. (22,23,29) Due to the high polarity of the Bi–O bond and the large difference in orbital size between Bi and O, these oxides readily undergo dimerization or polymerization[3, 12-15].
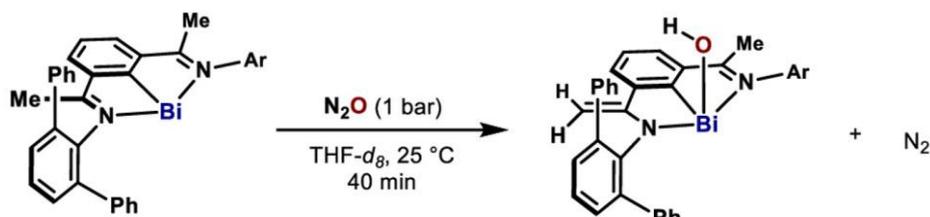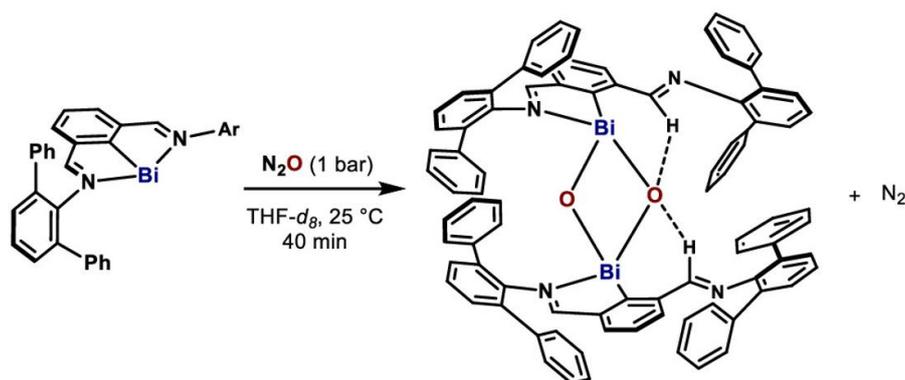
Hydrodefluorination

A hydrodefluorination reaction of polyfluoroarenes is catalyzed by bismuthinidenes, Phebox-Bi(I) and OMe-Phebox-Bi(I).A Bi(I)/Bi(III) redox cycle is applied that comprises C(sp2)–F oxidative addition, F/H ligand metathesis, and C(sp2)–H reductive elimination. Isolation and characterization of a cationic Phebox-Bi(III)(4-tetrafluoropyridyl) triflate manifests the feasible oxidative addition of Phebox-Bi(I) into the C(sp2)–F bond. The formation of a transient Phebox-Bi(III)(4-tetrafluoropyridyl) hydride takes place during catalysis, which decomposes at low temperature to afford the corresponding C(sp2)–H bond while regenerating the propagating Phebox-Bi(I)[16].
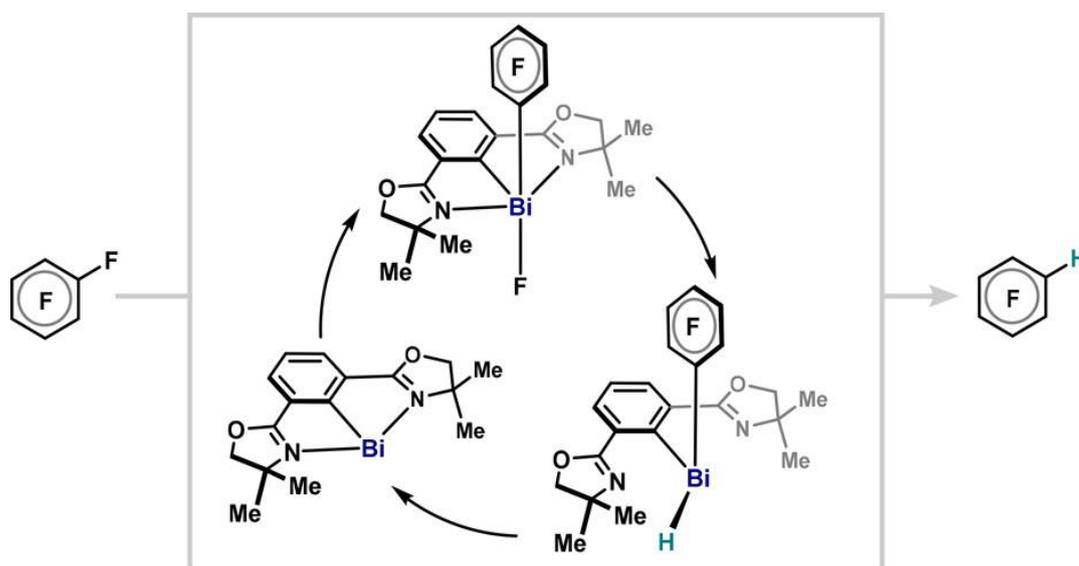
Properties

Photophysical properties

Bismuthinidenes combines with zeolites which will lead to strong, air-stable, long-lived, ultrabroadband and tunable NIR photoluminescence[17-20]. As is well-known, zeolites usually contain more than 20 wt % water molecules owing to their porous structures. Thus, the efficiency of optical emitters becomes problematic in the near-infrared (NIR) spectral region due to the fast relaxation of the excitation energy through nonradiative vibrational deactivation. Results suggested that bismuth-related active centers contribute to the observed emissions, and these centers are sealed in a low-vibrational environment by nonactive bismuth agglomerates.

Electrocatalytic properties

Feng Wang et al. has developed a catalytic transfer-hydrogenation utilizing a well-defined Bi(I) complex as catalyst and ammonia-borane as transfer agent[10]. This transformation represents a unique example of low-valent pnictogen catalysis cycling between oxidation states I and III, and proved useful for the hydrogenation of azoarenes and the partial reduction of nitroarenes. The bismuthinidene catalyst performs well in the presence of low-valent transition-metal sensitive functional groups and presents orthogonal reactivity compared to analogous phosphorus-based catalysis. Mechanistic investigations suggest the intermediacy of an elusive bismuthine species, which is proposed to be responsible for the hydrogenation and the formation of hydrogen.

Bi[I]/Bi[III] redox catalysis
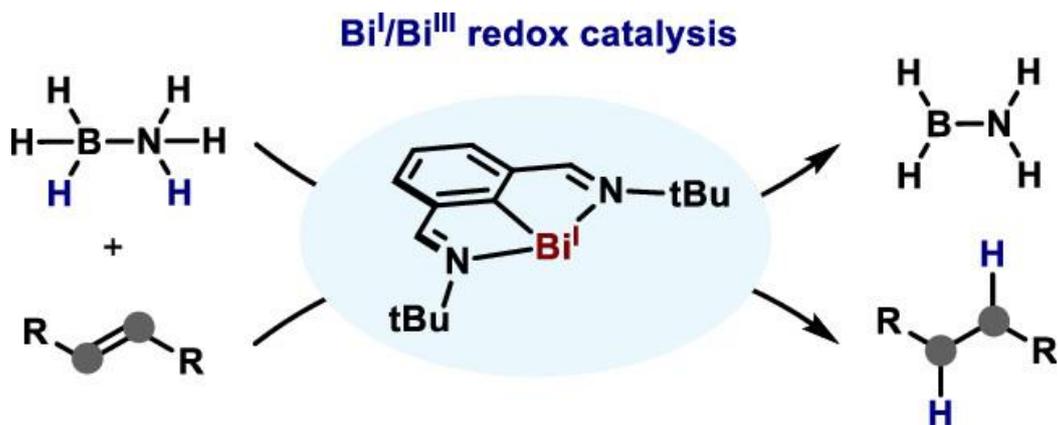
The BiI/BiIII couple recently have discrete redox events in this manifold been explored. Of particular note is the seminal work of Dostál, who has demonstrated that Lewis base-stabilized aryl-Bi(III) dihydrides undergo facile release of H2 to generate the corresponding aryl-Bi(I) compounds[8, 21], which are then amenable to oxidative addition to deliver Bi(III) species[22-24]. Bismuth(III) alkoxides also undergo Bi–O homolysis in certain cases[25, 26], a potentially relevant step in the SOHIO ammoxidation process for the synthesis of acrylonitrile from propylene[27-29].

Cornella et al. explored the BiI/BiIII couple for catalysis in the context of transfer hydrogenation of azoarenes and nitroarenes[10]. Using an NCN-chelated bismuthinidene (Bi5) first described by Dostál[8, 21], an unstable Bi(III)-dihydride (Bi5a) is putatively formed by reaction with ammonia borane, in reverse analogy to the loss of H2 from a Bi(III)-dihydride (Bi5a) originally described by Dostál. In this catalytic reaction, the putative Bi(III)-dihydride (Bi5a) intermediate delivers H2 across either N–N or N–O π-bonds, accomplishing a transfer hydrogenation with good functional group tolerance. Mechanistic studies support the intermediacy of the Bi(III)-dihydride (Bi5a), as its protonated cation (Bi5b) can be detected by HRMS in both stoichiometric and catalytic reactions. Here, the BiI/BiIII cycle is exploited to first receive an equivalent of H2 from ammonia borane and then deliver it to an activated π substrate.
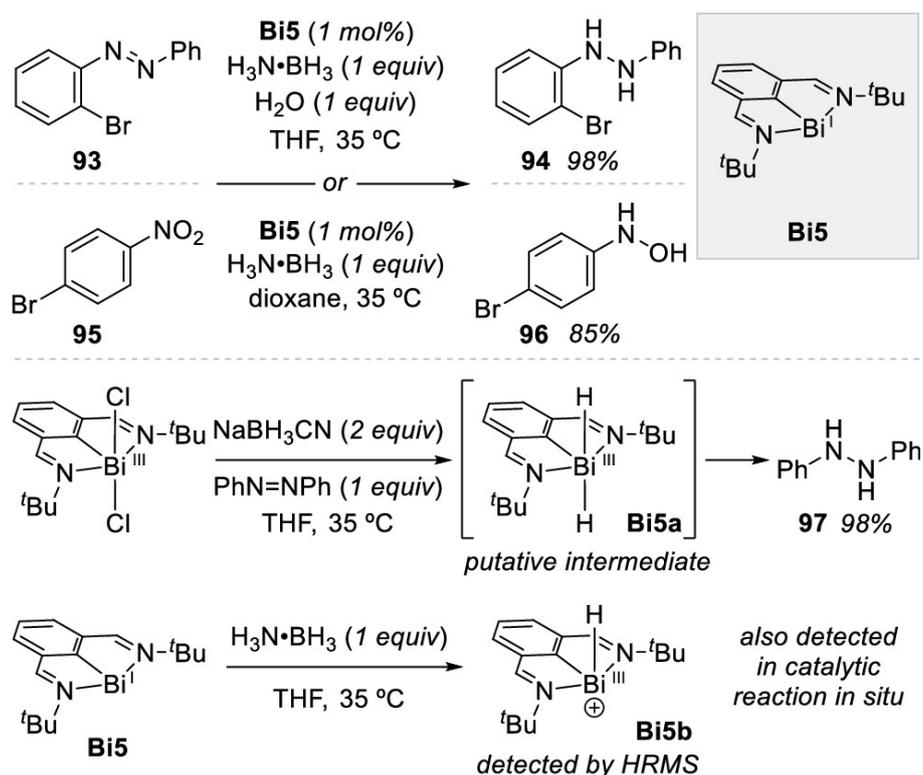
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