Synthesis and Characterization of Heteroleptic Redox Active Bismuth Dithiolene and Dithiolate Complexes

By

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Table of Contents

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List of Figures

List of Schemes

List of Spectra in Appendix

Glossary of Abbreviations and Symbols

NMR	Nuclear Magnetic Resonance
J	Coupling constant
d	doublet
m	multiplet
t	triplet
q	quartet
p	pentet
dd	Doublet-of-doublets
ppm	Parts per million
Me	Methyl
Et	Ethyl
Mes	Mesityl
Mes*	Tritertbutylbenzene
Trip	Triisopropylbenzene
M	Molarity (mol/L)
mL	Millilitre
mmol	Millimole
MeOH	Methanol
THF	Tetrahydrofuran
EtOH	Ethanol
Et_2O	Diethyl ether
Py	Pyridine
tBu	Tert-butyl
iPr	Iso-propyl
mnt	Maleonitriledithiolene
tdt	Toluene-3,4-dithiolene
abt	Amidobenzenethiolate

Abstract

The "twelve principles of Green Chemistry" marked an important transition in the chemical industry's view on waste - moving away from a waste management approach, and towards a waste reduction and prevention approach. The use of catalytic reagents in place of traditional stoichiometric ones is an important aspect of reducing the amount of waste generated during reactions. Transition metal complexes frequently used in redox catalysis, however, feature toxic metal centers which can be harmful to both human health and the environment. Bismuth has recently been the subject of interest as an alternative to toxic transition metal catalysts as redox non-innocent ligands can be used to make the otherwise redox inactive metal, redox active. The current study focuses on the use of dithiolenes and dithiolates as redox non-innocent ligands to impart redox activity on a heteroleptic bismuth complex. Two bismuth complexes, $(Mes_2Bi)_2(tdt)$ and $BiCl(tdt)\text{-}Py_2$, were synthesized and characterized by ^1H and $^{13}C\{^1H\}$ NMR spectroscopy and X-ray crystallography.

1. Introduction

1.1 Green Chemistry

The purpose of Green Chemistry is to invent, develop and apply chemical products and processes that reduce or eliminate the use and generation of substances hazardous to human health and the environment.[1] The field has received significant attention in the last two decades in an effort to reduce the amount of pollution and hazardous effects of chemicals on the environment. The term "Green Chemistry" was originally coined by Paul Anastas and John Warner and the adoption of their "twelve principles of Green Chemistry" marked an important shift in the chemical industry's view on waste - moving away from an end-of-pipe or waste management approach to a waste reduction and prevention approach (Figure 1).[1,2]

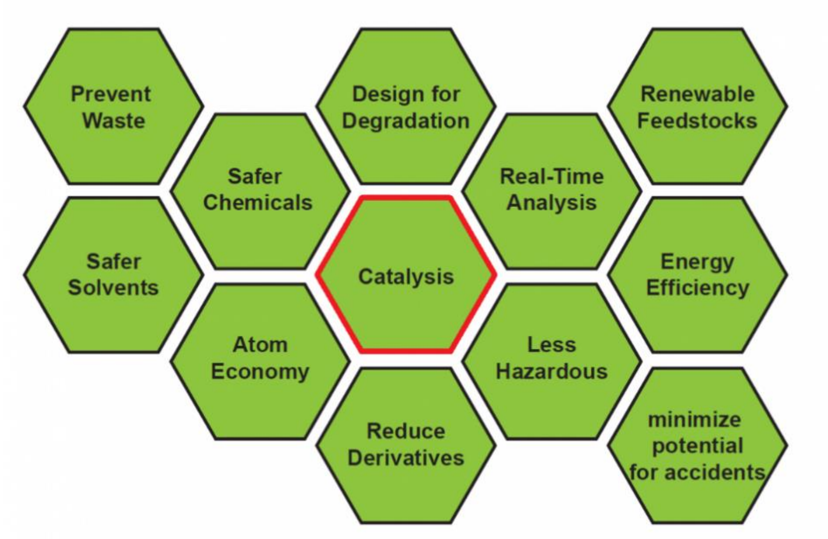


Figure 1 – Twelve principles of "Green Chemistry" as defined by Anastas and Warner[1,2]

The twelve principles became the foundation for chemists to develop and implement more environmentally friendly compounds, syntheses and technological processes.[1] The ninth principle, and that most pertinent to this study, is that catalytic reagents are superior to stoichiometric ones.[1] Catalysis is present in virtually all areas of chemical industry ranging from agriculture, petroleum, polymers and pharmaceutical production and processes.[2] This widespread adoption of catalytic rather than stoichiometric reagents is indicative of large economic and environmental benefits. The pharmaceutical industry, among others, favours catalytic reagents and processes which tend toward the principles of Green Chemistry, including waste reduction and prevention. One of the most commonly used over the counter drugs, ibuprofen, for example, can be synthesized in one of two ways. The first involves six steps, large amounts of solvents, toxic reagents and stoichiometric quantities of reactants, and yields only 40% of the original starting material in the product.[2] The Boots-Hoechst-Celanese (BHC) synthesis in contrast, involves catalytic amounts of reagents, only three reaction steps and uses 80% of the atoms from the starting material in the final product. Evidently, the BHC synthesis is both environmentally friendly while also being economically advantageous.[2] The widespread use of catalyst in both industry and academic has prompted substantial research into new catalysts and novel applications in order to advance the field.

1.2 Metal Toxicity

The use and development of metal catalysts has had a significant impact on the field of organometallic chemistry. Today, more than 90% of industrial process are based on some form of catalysis, largely due to the economic and environmental benefits.[4] The use of catalysts was seen to be superior to stoichiometric reagents as this would reduce the amount of waste produced. The problem with catalysts, however, was the potential for toxicity due to their metal centers. Certain metals, such as tin, can have harmful effects on both the environment and human health, and these concerns have motivated the search for less toxic alternative.

Some of the most frequently used catalyst metal centers are nickel, copper and cobalt. Part of the motivation for using these metals specifically stems from idea that lighter metals are ubiquitously less toxic than heavier metals.[4] Despite the assumption that heavy metals are inherently less toxic, bismuth is markedly less toxic than its neighbours including lead and arsenic.[5] As a result, bismuth is present in commonly used stomach remedies such as Pepto-Bismol (bismuth subsalicylate, BSS), and De-Nol (colloidal bismuth subcitrate, CBS).[5] Due to its low toxicity, bismuth also became an environmentally friendly option for metal centers in catalysts.

1.3 Bismuth and Bismuth Catalyst

Despite being surrounded by notoriously hazardous metals such as arsenic, antimony, lead and tin on the periodic table, bismuth is non-toxic, non-carcinogenic and environmentally friendly.[5] Although these characteristics make bismuth an attractive metal for many purposes, its applications have only grown significantly since the late 1980's when the role of bismuth(III) salts as Lewis acids began to be explored. The electron configuration of bismuth ($[Xe]4f^{14}5d^{10}6s^{2}6p^{3}$) results in weak shielding of the *f* electrons and leads to a lanthanide contraction and Lewis acid behavior of bismuth.[7] These traits garnered bismuth significant attention as an effective alternative to otherwise toxic and expensive metal-based catalysts such as platinum and rhodium.[7] In addition, bismuth complexes capable of oxidative addition, reductive elimination and transmetallation reactions were recently described.[8] These were found to react in a manner similar to those observed during the use of transition metals. These complexes were active in the fluorination of aryl boronic esters and showed bismuth cycling between bismuth(III) and bismuth(V) oxidation states – a cycle which had previously been unachievable with bismuth (Figure 2).[8] Despite its novelty, the cycle is an impractical alternative to traditional fluorination methods as it requires a very rigid and specific structure to obtain the desired reactivity.[8]

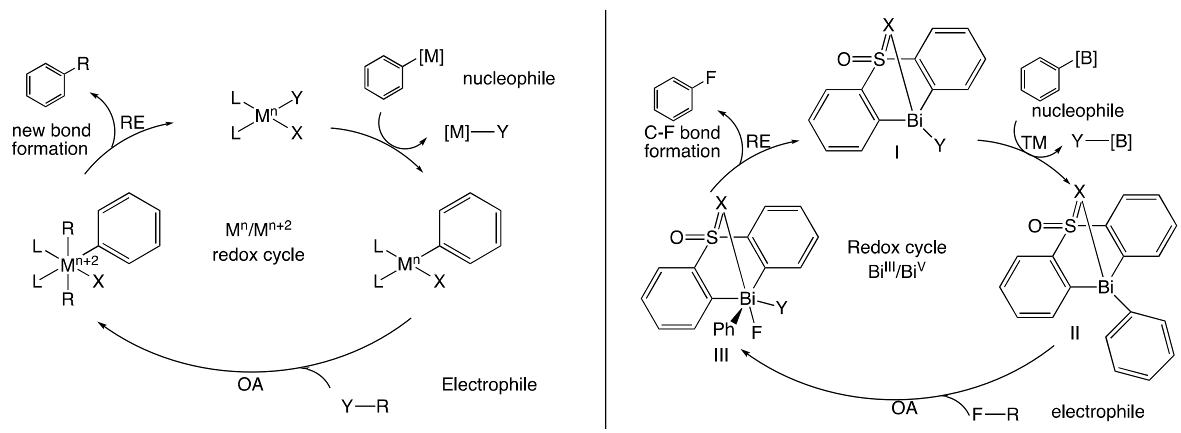


Figure 2 - General catalytic two-electron redox cycle of a transition metal (left). Bi^{III}/Bi^{V} catalytic Bi redox process for electrophilic fluorination of boronic acid derivatives. L, ligand; M, metal; n, oxidation number; R, organic residue; X, halogen atom (A) or non-anionic ligand (B); Y, anionic ligand.

Organobismuth compounds also became attractive for catalytic purposes because other organo-main group compounds, notably organoboron, organotin, organosilicon, organoantimony and organolead compounds, had been successfully applied to organic reactions. The organometallic chemistry of bismuth, however, was challenged by the instability of the bismuth-carbon (Bi-C) bond which slowed progress in the field.[9] In just the last two decades organobismuth compounds have been shown to be effective in C-, N-, and O-arylation reactions, benzoylation reactions and cross coupling reactions.[9] In addition, inorganic bismuth compounds have been shown to be effective in catalyzing the formation of carbon-carbon, carbon-nitrogen, carbon sulfur bonds, oxidation reactions and organic reactions in water.[8] Bismuth salts have been employed as low toxicity Lewis acid catalysts in multiple reactions.[10] The Lewis Acid character of these compounds, however, means they are particularly susceptible to hydrolysis by water, and will react preferentially with water over other substrates making their synthesis challenging.[10] Since Green Chemistry also suggests the use of less harmful solvents, such as water, this creates further concerns. Despite these challenges, previous work has reported water-tolerant (thiolato)bismuth compounds which were found to be capable of behaving as Lewis acid catalysts for esterification and transesterification reactions of fatty acids and fatty acid esters.[10] In addition, sulfur, a soft base, forms a strong bond with bismuth, a soft acid. This bond is further reinforced when sulfur-containing ligands are polydentate as is the case in dithiolene and dithiolate ligands. This metal-sulfur bond is stable against hydrolysis resulting in potentially water-tolerant compounds.

1.4 Redox Active Ligands

The use of catalysts in redox reactions has been widely studied and applied in both chemical research and industry. Two-electron transfer reactions (multi-electron, $2e^-$) processes have been dominated primarily by precious metals such as rhodium and palladium (Figure 3), which prompted concerns surrounding environmental, health and financial issues associated with these precious metals.[11] Cheaper alternatives that use base metals however, often tend to undergo primarily one-electron redox processes.[12] Redox non-innocent ligands, as a result, became an area of research interests as they may permit for the use of base metals for two-electron transfers.

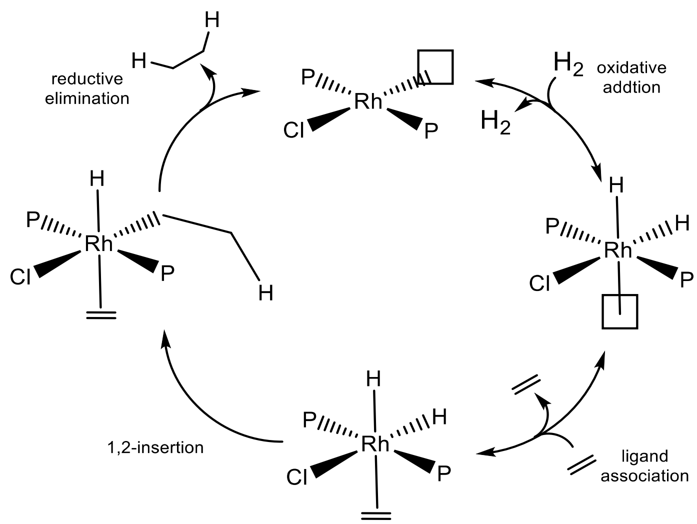


Figure 3 – Wilkinson's Catalyst mediated hydrogenation of alkenes

New approaches to this type of catalysis make use of the ligand in a more active role in the reaction process. This can occur most generally, in one of two ways – spectator ligands or actor ligands. Spectator ligands act as electron donors or acceptors for the catalytic cycle whereas actor ligands are actively involved in making or breaking chemical bonds on the substrate.[12] In both roles, the ligand can enable the complex to catalyze new types of reactions by controlling the loss or gain of protons and electrons.[12] This also allows the catalyst to adopt a different electronic structure allowing for new reactivity. This is commonly observed in nature where many multi-electron processes are performed using base metals with redox active ligands to enable such reactions. Metallo-enzymes, such as galactose oxidase, hydrogenases and cytochrome p450 for example, use systems in which the ligands are active participants in the redox process[12]. Many complexes have thus been developed which use similar techniques to access new reactivities.

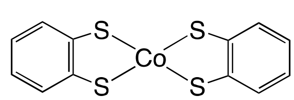


Figure 4 – Cobalt catalyst with two redox active benzene dithiolate (bdt) ligands

Similarly, $[Co(bdt)_2]^-$ (Figure 4) makes use of redox-active benzene dithiolate ligands to catalyse the light-driven reduction of protons from water.[13]

1.5 Dithiolene Ligands

Dithiolene ligands are described as ligands with bidentate sulfur-donor ligands connected via an unsaturated carbon-carbon bond (Figure 5).[14] The term dithiolene was initially introduced by McCleverty in 1968 to describe the delocalized electronic structure and redox non-innocence.[15] This definition was suitable to describe several different ligands with the same basic structure. In the years since its initial description, experimental evidence to support its redox non-innocence has accumulated and the catalogue of complexes which make use of dithiolenes has grown significantly.[15]

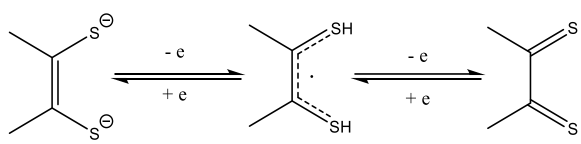


Figure 5 – Two-electron redox activity of dithiolene ligand

Dithiolene ligands were first described by Schrauzer and Mayweg upon synthesis of a nickel dithiolene complex (Figure 6)[16]. The nickel center of the complex was assigned an oxidation state of 2^+ in order to agree with the square planar structure.[16] This assignment led to the conclusion that the dithiolene ligands were each one electron reduced, demonstrating the non-innocence of these ligands.

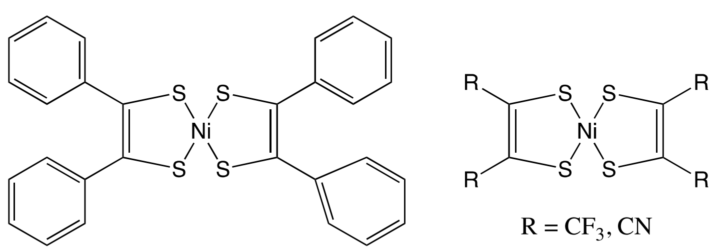


Figure 6 – Bis(dithibenzil)nickel complex prepared by Schrauzer and Mayweg[16] (left) and CF_3 and CN derivatives (right)

Similarly, structures in which the phenyl were substituted for CN or CF_3 groups (Figure 6) were also shown to have characteristics associated with one-electron redox reactions accompanied by low reorganization energies for electron transfer.[17] These conclusions further supported the belief that these ligands were potentially redox active.

Since the development of procedures to synthesize these ligands were developed in the 1960s, the number of dithiolene coordinated compounds has increased. Some of the first ligands were maleonitriledithiolate $(mnt)^{2-}$ and toluene-3,4-dithiolate $(tdt)^{2-}$, which were coordinated to metals such as nickel, palladium, platinum, cobalt and copper.[17] Homoleptic bis(dithiolene) complexes have been studied extensively and their applications have ranged from material science, precursors for molecular conductors, semiconductors for field effect transistors, as NIR dyes for lasers, liquid crystal devices (NLO), and probable olefin purification systems.[15]

1.6 Dithiolate and Amidothiolate Ligands

Dithiolate and amidothiolate ligands possess the same non-innocent character as dithiolene ligands making them useful in the formation of redox active metal catalysts. Unlike dithiolenes, however, these ligands primarily undergo one-electron redox activities (Figure 6). Dithiolenes have much

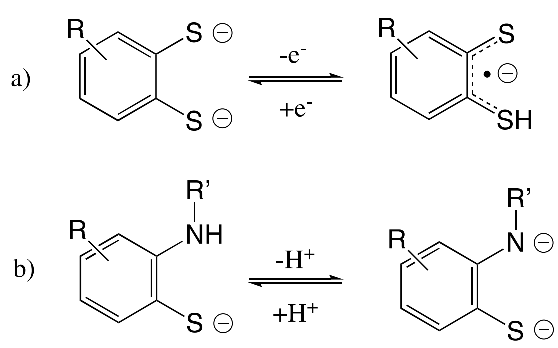


Figure 7 – Redox activity of dithiolate (a) and amidothiolate (b)

of the same character exhibited by dithiolenes. Conversely, amidothiolates have an increased layer of versatility resulting from the nitrogen atom which can adopt a singly or doubly protonated state as well as alkyl chains (R' in Figure 6b). This added versatility has resulted in several novel structures containing amidothiolate ligands and in turn, several potential applications and reactivities. Although dithiolates lack the same diversity, several dithiolates have been described and used as redox active ligands in metal complexes (Figure 7).[15]

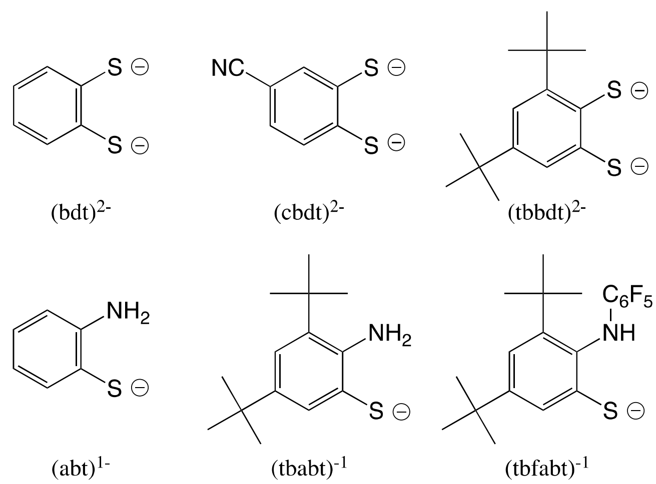
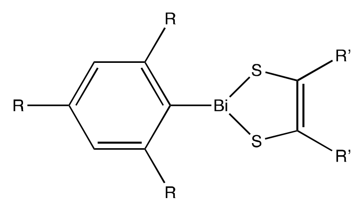


Figure 8 – benzene-1,2-dithiolato $(bdt)^{2-}$, 4-cyanobenzene-1,2-dithiolato $(cbdt)^{2-}$, 3,5-di-tert-butylbenzene-1,2-dithiolato $(tbbdt)^{2-}$, aminobenzenthiolato $(abt)^{1-}$, 4,6-di-tert-butyl-2-aminobenzenthiolato $(tbabt)^{1-}$, 4,6-di-tert-butyl-2-[(pentafluorophenyl)amino] benzenethiolato $(tbfadt)^{1-}$ [15]

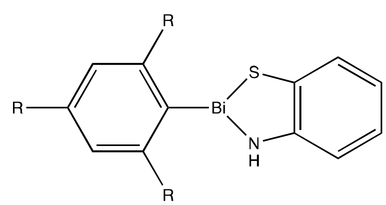
1.7 Current Study

The purpose of this study is to synthesize and characterize novel, heteroleptic bismuth dithiolene and dithiolate complexes for use as catalysts in redox processes. Target compounds will be composed of a redox active ligand and an aryl group whose steric bulk will be varied to determine the effect of different substituents on reactivity and solubility (Figure 8 & 9). Four aryl groups (phenyl, mesityl, 2,4,6-triisopropylphenyl and 2,4,6-tritertbutylphenyl) will be tested alongside three dithiolene ligands, a dithiolate and an amidothiolate ligand. Bismuth complexes will be characterized using ^{1}H NMR, $^{13}C\{^{1}H\}$ NMR, FT-IR, Raman, melting point and X-ray crystallography. Upon successful syntheses of the compounds, their redox properties will be tested using cyclic voltammetry.

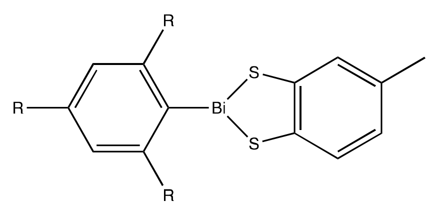


R = H, Me, iPr, tBu
R' = CN, Me, Ph

Figure 9 – Target bismuth dithiolene complexes with varying aryl groups and dithiolene ligands



R = H, Me, iPr, tBu



R = H, Me, iPr, tBu

Figure 10 – Target bismuth amidothiolate (top) and dithiolate (bottom) complexes with varying aryl groups

2. Experimental

2.1 Instrumentation

An Innovative Technology glove box and standard Schlenk line techniques with a dinitrogen atmosphere were used for all reactions unless otherwise stated. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR were obtained on a Varian

Mercury 200 MHz+ Spectrometer. Melting Points were recorded on an Electrothermal MEL-TEMP and are uncorrected.

2.2 Reagents

Bismuth (III) chloride ($\geq$ 98%), bismuth (III) bromide anhydrous powder (99.999%), 2-mesitylmagnesium bromide (1.0 M in THF), n-butyllithium (1.6 M in hexanes), 1-bromo-2,4,6-tritertbutylbenzene (95%), 1-bromo-2,4,6-triisopropylbenzene (95%), phosphorus pentasulfide (99%), benzoin (98%), methanol and dioxane were used as received from Sigma Aldrich. Toluene-3,4-dithiol (97%) was used as received from Fisher Scientific. Tetrahydrofuran (anhydrous, $\geq$99%, inhibitor-free), hexanes anhydrous (95%), diethyl ether anhydrous ($\geq$99%), dichloromethane anhydrous ($\geq$99.8%), pyridine anhydrous (99.8%) were dried with molecular sieves and sodium metal prior to use.

2.3 Synthesis of Lithium Reagents

2.3.1 Synthesis of (Trip)Li[17]

n-BuLi (13.28 mL, 1.6 M, 21.248 mmol) was added dropwise to a solution of 1-bromo-2,4,5-triisopropyl benzene (4.00 g, 14.1 mmol) in hexane (40 mL). The resulting solution was heated to 50°C and stirred for 24 h. The solution was filtered, concentrated to ~2 mL and placed at -15°C for 16 h. Resulting white product was collected and dried under vacuum. Yield: 2.581 g, 12.274 mmol, 87%; ^{1}H NMR (C_6D_6, ppm): 1.25 (d, $^{3}J_{HH}$ = 13 Hz, 18H), 2.69 (m, 3H), 6.96 (s, 2H).

2.3.2 Synthesis of (Mes)Li*[17]

1-bromo-2,4,6-tritertbutylbenzene (5.00 g, 15.4 mmol) was added to THF (7.5 mL) and Et_2O (31 mL). The solution was cooled to -78°C and n-BuLi (9.6 mL, 1.6 M, 15 mmol) was added dropwise. The reaction was allowed to warm to room temperature and stir for 2.5 h. The solvent was removed under vacuum and the product washed with Et_2O (15 mL) and dried under vacuum. Yield: 1.456 g, 10.624 mmol, 38 %; ^1H NMR ($CDCl_3$, ppm): 1.31 (s, 27H), 7.236 (s, 2H).

2.3.3 Synthesis of Li_2-(abt)[17]

n-BuLi (18.24 mL, 1.6M, 29.18 mmol) was added dropwise to a solution of 2-aminothiophenol (1.8268 g, 14.592 mmol) in hexane (35 mL). The reaction mixture was stirred for 2 hrs at room temperature. The solvent was removed under vacuum from the resulting yellow solution under vacuum, affording a yellow powder. Yield: 1.782 g, 13.00 mmol, 89%.

2.3.4 Synthesis of Li_2-(tdt)[17]

Toluene-3,4-dithiol (0.9294 g, 5.948 mmol) was dissolved in hexane (8 mL) and cooled to 0°C in an ice bath. n-BuLi (7.43 mL, 1.6 M, 11.9 mmol) was added dropwise and the solution was warmed to room temperature and stirred for 1 hr. Solvent was removed under vacuum to give a fine white powder. Yield: 2.332 g, 13.87 mmol, 88%.

2.4 Synthesis of Organobismuth Reagents

2.4.1 Synthesis of Mes_3Bi[18]

$BiCl_3$ (2.84 g, 9.00mmol) was dissolved in THF (10 mL) and the solution cooled to 0°C. 2-mesitylmagnesium bromide (30.00 mL, 1M, 30.00 mmol) in THF was cooled on ice and added dropwise. The solution was heated to 55°C for 4 hrs. The resulting grey solution was filtered and the solvent removed under vacuum. The resulting yellow powder was dissolved in hexanes (50 mL), gravity filtered and placed at -15°C overnight. Yellow product was collected and dried. Yield: 1.82 g, 3.21 mmol, 36%; ^1H NMR ($CDCl_3$, ppm): 6.94 (s, 6H), 2.28 (s, 18H), 2.24 (s, 9H)

2.4.2 Attempted Synthesis of $MesBiCl_2$[19]

Mes_3Bi (0.6618 g, 1.169 mmol) in diethyl ether (3 mL) was added dropwise to a solution of $BiCl_3$ (0.7370 g, 2.337 mmol) in diethyl ether (4 mL) and stirred for 18 hrs. The reaction vessel was wrapped in aluminum foil to prevent light decomposition. The solvent was removed under vacuum and the resulting yellow powder was stored. After 48 hrs the product was found to have decomposed.

2.4.3 Synthesis of $PhBiCl_2$[16]

Ph_3Bi (1.2299g, 2.7934mmol) and $BiCl_3$ (1.7617 g, 5.5868 mmol) were dissolved in diethyl ether (50 mL) and stirred for 1 hr. The solvent was removed under vacuum producing a pale-yellow powder. Yield: 0.3786 g, 1.064 mmol, 77%.

2.5 Ligand synthesis

2.5.1 Attempted Synthesis of $((C_6H_5)_2C_2S_2)P(S)(SCH_3)$[20]

P_2S_5 (4.89 g, 11.00 mmol), NH_4Cl (0.59 g, 11.00 mmol) and benzoin (5.00 g, 11.00 mmol) were dissolved in dioxane (60 mL) and heated at 90°C for 2 h. The reaction was cooled to room temperature and filtered. The solution was then cooled to 0°C and MeI (6.17 g, 44.0 mmol) was added dropwise. The resulting mixture was heated to 50°C for 4 hrs. The reaction mixture was allowed to sit overnight, or until a dark red solid had precipitated. The clear dark red solution was decanted and the solvent removed by rotary evaporation. The resulting residue was extracted with 3 x 50 mL 1:4 Et_2O:hexane. The cloudy yellow solution was concentrated to an oily residue, redissolved in minimal amounts of Et_2O and purified using a silica gel column eluted with 1:4 Et_2O:Hexane. Pale yellow needles readily crystalized from the eluent.

2.6 Attempted Synthesis of Bismuth Dithiolene Complexes

2.6.1 Attempted Synthesis of PhBi(mnt)

Na_2(mnt) was dissolved in THF (2 mL) and added to a stirred solution of $PhBiCl_2$ in THF (4 mL) cooled to -50°C. The reaction was warmed to -10°C and stirred for 1.5 h. The resulting solution was filtered, concentrated to ~1.5 mL and placed at -15°C overnight. After 24 h, a precipitate had formed. The solvent was removed under vacuum and the resulting product characterized by ^1H NMR, which showed the absence of the Ph group.

2.6.2 Synthesis of BrBi(mnt)[24]

$BiBr_3$ (0.6035 g, 1.345 mmol) was added to a solution of Na_2(mnt) in THF (25 mL). After stirring at room temperature for 1 h, the red-brown reaction mixture was filtered, and the clear solution was dried under vacuum. The resulting brick-red residue was washed with dichloromethane and dried again under vacuum to afford a purple powder.

2.6.3 Attempted Synthesis of MesBi(mnt)

<u>Method 1.</u> Mes_3Bi (0.226g, 0.399 mmol) and $BiCl_3$ (0.2520 g, 0.7990 mmol) were dissolved in diethyl ether (10 mL) and stirred for 18 h in the dark. The resulting pale yellow solution was dried and the yellow power product ($MesBiCl_2$) was immediately redissolved in THF (10 mL) and cooled to -50°C. Na_2(mnt) was dissolved in THF (10 mL) and added dropwise to the cooled $MesBiCl_2$ solution. The reaction mixture was stirred at 0°C for 3 h. The resulting solution was filtered and the clear orange-brown solution was placed at -15°C overnight. After 24 h a precipitate had formed. ^1H NMR data of the precipitate showed the absence of the Mes group.

<u>Method 2.</u> BrBi(mnt) (0.5971 g, 1.388 mmol) was dissolved in THF (10 mL) and cooled to 0°C in an ice bath. MesMgBr (1.4 mL, 1 M in THF, 1.4 mmol) was added dropwise. The resulting dark red reaction mixture was allowed to stir at 0°C for 3 h, filtered, concentrated to ~2 mL and placed at -15°C overnight. The solution was layered with diethyl ether and a black oil formed overnight.

*2.6.4 Attempted Synthesis of Mes*Bi(mnt)*

(Mes*)Li (0.2397g, 0.9500 mmol) and $BiCl_3$ (0.5992g, 1.900 mmol) were each dissolved in 5 mL THF. The $BiCl_3$ solution was cooled to 0°C in an ice bath and the (Mes*)Li was added dropwise. The resulting mixture was stirred for 2 h. The solvent was removed under vacuum and resulting product immediately redisolved in THF (5 mL) and cooled in an ethyl acetate bath (-83°C). [Na_2(mnt)] was dissolved in THF anhydrous ethanol (10 mL) and added dropwise to the Mes*$BiCl_2$ solution. The resulting mixture was stirred for 3 h. The brown solution was filtered, concentrated to 5 mL and filtered a second time through a syringe filter. The solution was concentrated to 2 mL and placed at -15°C. After 24 h a precipitate had formed. ^1H NMR data of the precipitate showed the absence of the Mes* group.

2.7 Attempted Synthesis of Bismuth Dithiolate Complexes

2.7.1 Attempted Synthesis of PhBi(tdt)

$PhBiCl_2$ (0.0524 g, 0.1473 mmol) was dissolved in THF (3 mL). Li_2-(tbt) (0.0247 g, 0.1473 mmol) in THF (3 mL) was added dropwise and the solution was stirred at room temperature for 3 h. The resulting bright red reaction mixture was filtered, and to 1 mL and left at room temperature. Powder precipitated overnight. ^{1}H NMR data showed the absence of the Ph group.

2.7.2 Attempted Synthesis of MesBi(tdt)

Mes_3Bi (0.1654 g, 0.2921 mmol) and $BiCl_3$ (0.1842g, 0.5842mmol) were dissolved in THF (3 mL) and stirred overnight at room temperature in the dark. Li_2-(tbt) (0.1473 g, 0.1473 mmol) in THF (3 mL) was added dropwise and the solution was stirred at room temperature for 3 h. The resulting bright red reaction mixture was filtered, and the solution was concentrated to ∼1 mL and left at room temperature. Powder precipitated overnight. ^{1}H NMR data showed the absence of the Mes group.

2.7.3 Synthesis of TripBi(tdt)

$BiCl_3$ (0.2248g, 0.713 mmol) was dissolved in THF (2 mL) and cooled to 0°C in an ice bath. (Trip)Li (0.150 g, 0.713 mmol) in THF (2 mL) was added dropwise and the resulting mixture was stirred at room temperature for 3 h. The bright red solution was filtered, concentrated to ∼2 mL and placed at -15°C overnight. The solvent was removed under vacuum. ^{1}H NMR data for the resulting powder showed the absence of the Trip group.

2.8 Synthesis of Bismuth Dithiolate Complexes

2.8.1 Synthesis of BiCl(tdt) [23]

Under dinitrogen, toluene-3,4-dithiol (0.7854 g, 5.026 mmol) in MeOH (20 mL) was added dropwise to a solution of $BiCl_3$ (1.5849 g, 5.0259 mmol) in MeOH (10 mL). The reaction mixture was stirred at room temperature for 2 h. The red solution turned dark purple and purple precipitate had formed within 1 h. The product was collected by suction filtration, washed with cold MeOH and dried under vacuum. Purple product was dissolved in THF (20 mL) and dried under vacuum to remove residual MeOH. (1.483 g, 3.720 mmol, 75%). ^1H NMR (DMSO-d_6, ppm): 2.22 (s, 3H), 6.485 (dd, $^3J_{HH}$ = 8, 1.2 Hz, 1H), 6.91 (s, 1H), 6.98 (d, $^3J_{HH}$ = 7.8 Hz, 1H).

2.8.2 Synthesis of BiCl(tdt)-(py)$_2$[23] (**2**)

BiCl(tdt) (1.48 g, 3.72 mmol) was dissolved in a ∼20 mL of hot pyridine. The resulting orange solution was allowed to cool to room temperature before being placed at -15°C overnight. The mixture was filtered, and the yellow crystalline product was dried under vacuum and collected. Yield: 0.6539 g, 1.643 mmol, 27%. ^1H NMR (DMSO-d_6, ppm): 2.23 (s, 2H), 6.49 (dd, $^3J_{HH}$ = 8, 1.2 Hz, 1H), 6.92 (s, 1H), 6.99 (d, $^3J_{HH}$ = 8.2 Hz, 1h), 7.39 (m, 2H), 7.70 (m, 1H), 6.61 (m, 2H).

*2.8.3 Synthesis of $(Mes_2Bi)_2$(tdt) (**1**)*

<u>Method 1.</u> BiCl(tdt) (0.6539 g, 1.643 mmol) was dissolved in THF (10 mL) and cooled to 0°C. MesMgBr (1.64 mmol, 1 M, 1.64 mL) in THF was added dropwise and the reaction mixture was allowed to stir at 0°C for 3 h. The reaction mixture was filtered, concentrated to ∼2 mL and placed in the freezer for 48 h after which pale yellow crystals had precipitated. ^1H NMR data showed a mixture of two products. ^1H NMR (DMSO-d_6, ppm): 2.09 (s, 10H), 2.13 (s, 8H), 2.19 (d, 16H), 6.28 (dd, 3H), 6.38 (dd, 1H), 6.74 (s, 5H),

6.77 (s, 4H), 6.81 (s, 1H), 8.85 (d, 1H), 7.06 (d, 5H). X-ray crystallography showed one of the products to be **1**.

Method 2. BiCl(tdt) (0.5701 g, 1.430 mmol) was dissolved in THF (13 mL) and cooled to 0°C. MesMgBr (2.86 mL, 1 M, 2.86 mmol) in THF was added dropwise to the cooled solution. The resulting bright yellow solution was allowed to stir for 3 h. The solution was filtered and concentrated until precipitate began to form. The solution was allowed to sit at room temperature. After 48 h, large orange-yellow needle crystals had formed. The product was confirmed to be (**1**) by X-ray crystallography.

2.8.4 Attempted Synthesis of PhBi(tdt)

BiCl(tdt) (0.6783 g, 1.704 mmol) was dissolved in THF (5 mL) and cooled to 0°C. PhMgBr (1.70 mL, 1 M, 1.70 mmol) in THF was added dropwise and the reaction mixture was allowed to stir at 0°C for 3 h. The red reaction mixture was filtered, and the solution concentrated and stored at -15°C overnight. Removal of the solvent under vacuum resulted in an insoluble oil.

2.8.5 Attempted Synthesis of MesBi(tdt)-(py)$_2$

BiCl(tdt)-(py)$_2$ (0.6520 g, 1.171 mmol) in THF (4 mL) was cooled to 0°C. MesMgBr (1.17 mL, 1 M, 1.171 mmol) in THF was added dropwise and the reaction mixture was allowed to stir for 3 h. The reaction mixture was filtered, and the solution concentrated until precipitate began to form. The solution was filtered again and allowed to sit at room temperature. Small orange crystal had formed after 48 h. The crystals were found to be $MgCl_2$-(Py)$_2$ by X-ray crystallography.

2.9 Attempted Synthesis of Bismuth Amidothiolate Complexes

2.9.1 Attempted Synthesis of PhBi(abt)

$PhBiCl_2$ (0.3479 g, 0.9773 mmol) was dissolved in THF (4 mL) and cooled to -78°C. Li_2-(abt) (0.1339 g, 0.9773 mmol) dissolved in THF (3 mL) was added dropwise to the cooled solution. The reaction mixture was allowed to stir at room temperature for 3 h, filtered and concentrated to 2 mL and placed at -15°C overnight. After 24 h, a powder product had precipitated and was collected by filtration. ^1H NMR data for the resulting powder suggested the absence of the Ph group.

2.9.2 Attempted Synthesis of MesBi(abt)

Mes_3Bi (0.1673g, 0.2954 mmol) and $BiCl_3$ (0.1863 g, 0.5908 mmol) were dissolved in THF (3 mL) and stirred overnight in the dark. The resulting solution of $MesBiCl_2$ was cooled to -78°C Li_2-(abt) (0.0404 g, 0.2954 mmol) in THF (2 mL) was added dropwise. The reaction mixture was stirred at room temperature for 3 h, filtered, concentrated to 2 mL and placed at -15°C overnight. After 24 h, a powder product had precipitated and was collected by filtration. ^1H NMR data for the resulting powder suggested the absence of the Mes group.

2.9.3 Attempted Synthesis of TripBi(abt)

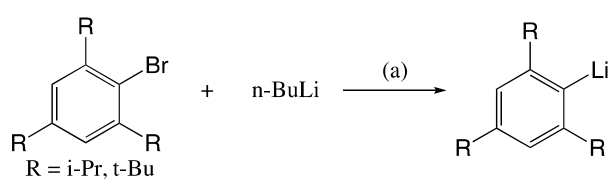
$BiCl_3$ (1.4267 g, 0.4498 mmol) was dissolved in THF (2 mL) and cooled to 0°C. (Trip)Li (0.1051 g, 0.4998 mmol) in THF (2 mL) was added dropwise. The reaction mixture was stirred at room temperature for 2 h then cooled to -78°C. Li_2-(abt) (0.0616g, 0.4498 mmol) in THF (2 mL) was added dropwise. This solution was stirred at room temperature for 3 hours, filtered and concentrated to ∼2 mL. After 24 h, a powder product had precipitated and was collected by filtration. ^1H NMR data for the resulting powder suggested the absence of the Trip group.

3. Results and Discussion

3.1 Synthesis of Lithium Reagents

3.1.1 Synthesis of (Trip)Li and (Mes)Li*

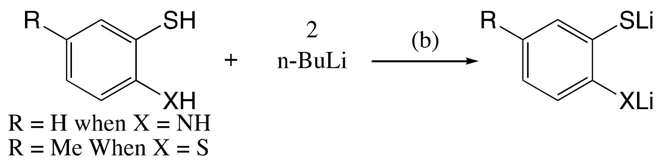
The synthesis of 1-lithium-2,4,6-triisopropylbenzene [(Trip)Li]] and 1-lithium-2,4,6-tritertbutylbenzene [(Mes*)Li] were performed by addition of n-BuLi to 1-bromo-2,4,6-triisopropylbenzene or 1-bromo-2,4,6-triisopropylbenzene, respectively (Scheme 1). The synthesis of (Trip)Li was initially attempted in THF according to previously published literature procedures.[25] When performed in THF, however, the solvent appears to complex to the lithium and the desired product cannot be fully dried. To avoid this problem, the reaction was performed in hexane and heated at 50°C for 2 hours.[26] The resulting white product was dried and characterized by ^1H NMR spectroscopy. The synthesis of (Mes*)Li was performed in a 1:3 THF:Et_2O mixture and the addition was performed at -78°C using a cold ethanol bath. The 1:3 THF:Et_2O prevented the complexing of THF to the lithium. The solution was dried, and product washed with diethyl ether a second time before being dried under vacuum and collected in order to remove any residual THF. The unexpected low yield of this reaction (19%) was likely the consequence of a low concentration of n-BuLi or, loss of product by sublimation while the solvent was being removed. Addition of a second cold trap during removal of the solvent greatly improved yields (98%).



Scheme 1 – Synthesis of (Trip)Li (a) Hexane, 50°C, 2hrs, N_2; (Mes*)Li (a) THF:Et_2O, -78°C, 2.5 hrs, N_2

3.1.2 Synthesis of Li_2-(tdt) and Li_2-(abt)

The synthesis of dilithium toluene-3,4-dithiolate [*Li_2-(tdt)*] and dilithiumamidobenzenethiolate [Li_2-(abt)] were both performed in hexane through the addition of n-BuLi to the dithiol or aminothiol (Scheme 2). Similarly, to the synthesis of (Trip)Li and (Mes*)Li, yields were significantly improved by the addition of a second cold trap during solvent removal to prevent the product subliming into the vacuum line.

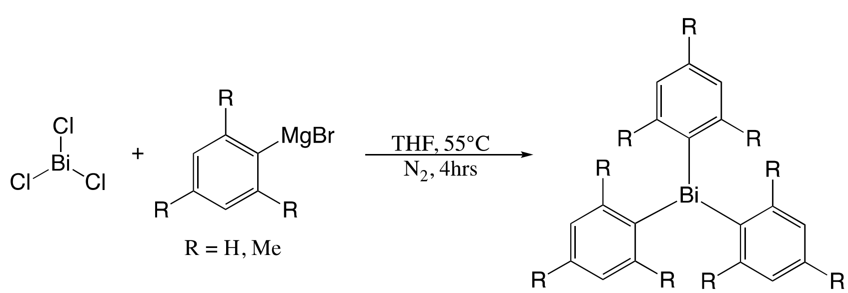


Scheme 2 – Synthesis of Li_2-(tdt) and Li_2-(abt)

3.2 Synthesis of Bismuth Reagents

3.2.1 Synthesis of Mes_3Bi[18]

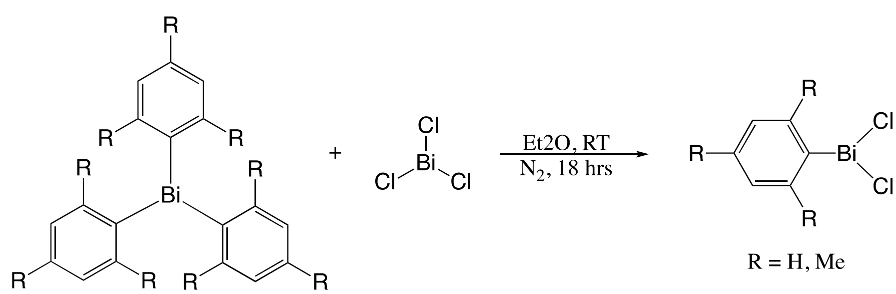
Mes_3Bi was prepared by reaction of MesMgBr and $BiCl_3$ (Scheme 3). Initial attempts produced a thick black solution and low yields. Subsequent attempts at this reaction involved cooling the Grignard prior to addition and resulted in a grey slurry. The slurry was filtered, and the clear solution was dried under vacuum. The resulting yellow powder was redissolved in hexane and gravity filtered. The filtrate was concentrated and placed at -15°C. After 24 h sufficient product had precipitated and was collected and dried. Attempts which avoided the use of water were found to be preferred as they avoided the need to use anhydrous drying agents and resulted in improved yields.



Scheme 3 – Synthesis of Mes_3Bi

3.2.2 Attempted Synthesis of $MesBiCl_2$ and $PhBiCl_2$

$MesBiCl_2$ was prepared by the 1:2 reaction of Mes_3Bi to $BiCl_3$ at room temperature (Scheme 4). The reaction vessel wrapped in aluminum foil to prevent decomposition from light. Although the product was dried and isolated, it was found to have decomposed after 48 h. Subsequent reactions used an *in-situ* generation of $MesBiCl_2$ to avoid decomposition. Based on the instability of $MesBiCl_2$, $TripBiCl_2$ and Mes^*BiCl_2 were synthesized *in situ* as it was predicted that they would also be unstable. $PhBiCl_2$ was prepared by 1:2 reaction of $BiCl_3$ and $BiPh_3$ in THF (Scheme 4). After stirring for 2 h the solution had become pale yellow.[20] $PhBiCl_2$ was found to be stable at room temperature in an inert atmosphere, and was found to be the only stable $ArylBiCl_2$ among those synthesized ($PhBiCl_2$, $MesBiCl_2$, $TripBiCl_2$, Mes^*BiCl_2)

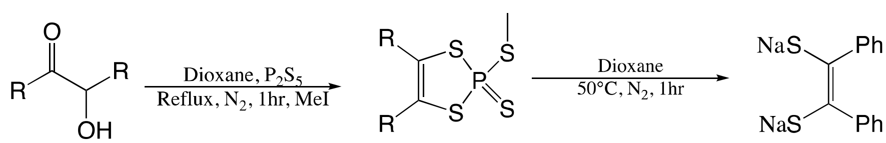


Scheme 4 – Synthesis of $MesBiCl_2$ and $PhBiCl_2$

3.3 Attempted Synthesis of Dithiolene Ligands

3.3.1 Attempted Synthesis of Methyl Protected Thioester Sodium Salt[20]

In attempt to synthesize isolable dithiolene ligands, a methyl protecting group was added to the sulfur atom of an in situ generated dithiolene phosphate ester, as reported previously.[20] The method involved addition of P_2S_5 to α-hydroxy ketone (benzoin) followed by addition of MeI. (Scheme 5). The resulting product was purified using column chromatography. Yellow crystals readily precipitated from the eluent as reported in the literature. However, the shape, melting point, ^{1}H NMR data did not support the synthesis of the desired compound. The procedure was found to be tedious and unsuccessful and was abandoned. The unsuccessful synthesis of the diphenyl dithiolene led to the use of the maleonitrile disodium salt [Na_2(mnt)], which had already been successfully synthesized in the group, according to previously reported literature procedures.[21]

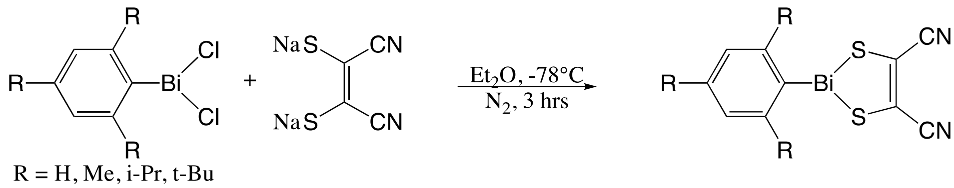


Scheme 5 – Synthesis of methyl-protected thioester sodium salt

3.4 Attempted Synthesis of Maleonitrile Dithiolene Bismuth Complexes

3.4.1. Attempted synthesis of ArylBi(mnt) (Aryl = Mes, Ph, Trip, Mes)*

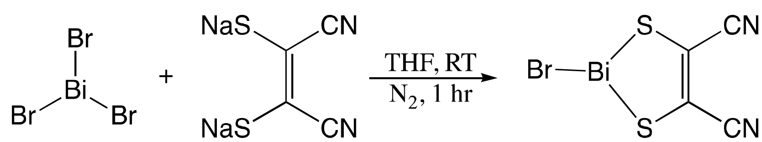
Initial attempts to synthesize PhBi(mnt), MesBi(mnt), TripBi(mnt) and Mes*Bi(mnt) were carried out at room temperature using $ArBiCl_2$ and [Na_2(mnt)] (Scheme 6). NMR data however suggested that the aryl group was being removed by the $(mnt)^{2-}$ ligand during the reaction, resulting in the formation of $[Bi(mnt)_2]^-$. These reactions were repeated at -78°C and shorter stir time was used in order to prevent the loss of the aryl group. ^{1}H NMR data again suggested loss of the aryl group and the approach was abandoned.



Scheme 6 – Synthesis of maleonitrile dithiolene bismuth complexes

3.4.2 Synthesis of BiBr(mnt)

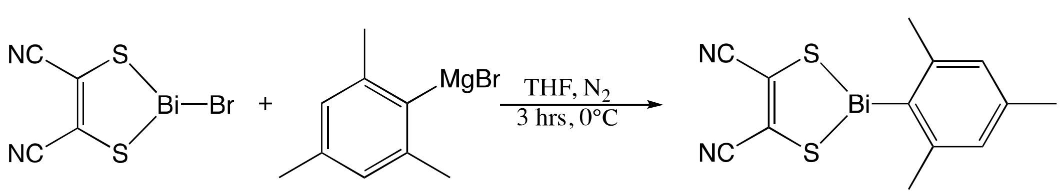
Synthesis of a BiX(mnt) (X = halogen) was initially attempted via the reaction of $BiCl_3$ and $[Na_2(mnt)]$ in order to isolate BiCl(mnt). This produced an insoluble grey-brown powder and an oil like solution. A similar procedure was then attempted[24] using $BiBr_3$ to afford BiBr(mnt) (Scheme 7). This resulted in a purple powder consistent with the desired compound described in the literature[24]. Attempts to recrystallize the product from pyridine following a similar procedure to that used for BiCl(tdt)-$(py)_2$ did not produce any product.



Scheme 7 – Synthesis of BiBr(mnt)

3.4.3 Attempted synthesis of MesBi(mnt)

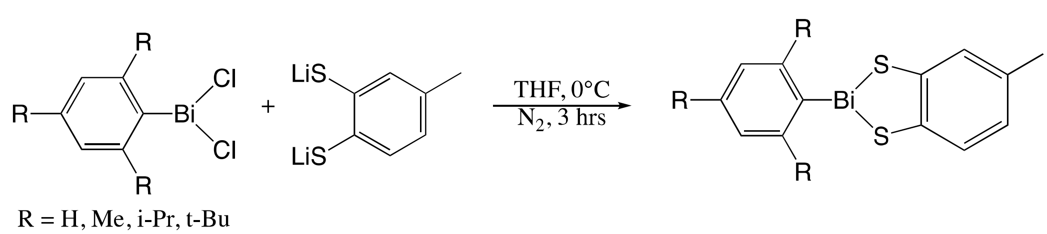
The attempted synthesis of MesBi(mnt) from the reaction of BrBi(mnt) and Grignard reagent produced a dark brown solution (Scheme 8). No precipitate formed after 48 h, at -15°C. The solution was layered with diethyl ether which resulted in the formation of an oil.



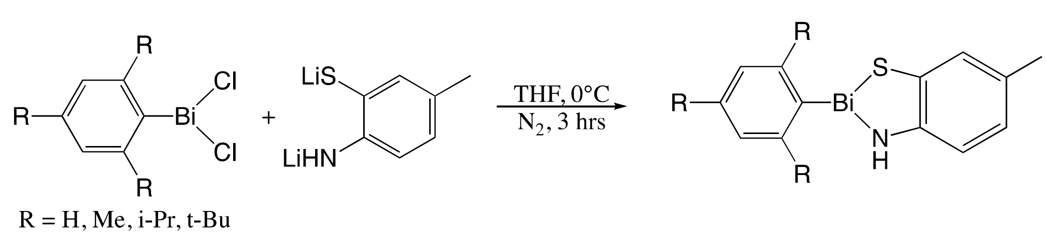
Scheme 8 – Synthesis of MesBi(mnt)

3.5 Attempted Synthesis of Bismuth Dithiolate and Amidobenzenethiolate Complexes

Synthesis of PhBi(tdt), PhBi(abt), MesBi(tdt), PhBi(abt), TripBi(abt) and TripBi(tdt) were carried out under dinitrogen. Initial attempts to synthesize these products were carried out at room temperature using *in-situ* generated $ArBiCl_2$ and Li_2-(tdt) or Li_2-(abt) (Schemes 9 & 10). ^1H NMR data of the products suggested loss of the aryl group during the reaction. In order to prevent this, the reactions were repeated at -78°C. Initially, reaction solutions were concentrated and placed in the freezer overnight. This did not result in any crystalline product and gave an impure oil-like solution. Layering with Et_2O was also ineffective in crystalizing the product when the solution was placed in the freezer. The reactions were repeated, and reaction solutions were allowed to sit at room temperature under dinitrogen overnight, producing a powder. Finally, two equivalents. of DMSO were added to the concentrated reaction solution in attempt to produce the corresponding DMSO adduct. This produced an insoluble oil. The same procedure was attempted with pyridine and DMF, both of which produced oils as well.



Scheme 9 – Synthesis of toluene-3,4-dithiolate bismuth complexes

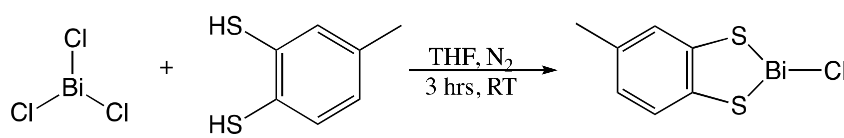


Scheme 10 – Synthesis of amidobenzene thiolate bismuth complexes

3.6 Synthesis of Bismuth Dithiolate Complexes

3.6.1 Synthesis of BiCl(tdt)

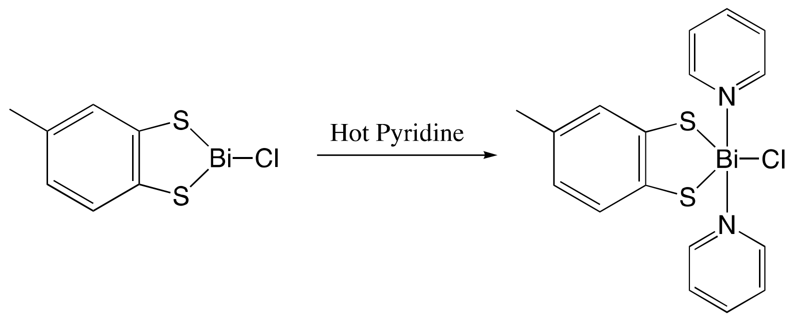
BiCl(tdt) was synthesized by addition of (tdt) to $BiCl_3$ in MeOH (Scheme 11).[18] The initially clear solution of $BiCl_3$ in MeOH becomes red immediately upon addition of the dithiol. Within 20 min, the brick-red solution turns dark purple. The reaction was allowed to proceed for 2 h in order to ensure the reaction had gone to completion. The reaction was carried out under a flow of dinitrogen although literature procedures suggest that the reaction can be successfully carried out in air. When attempted under air, yields were found to decrease by ~10%.



Scheme 11 – Synthesis of BiCl(tdt)

3.6.2 Synthesis of BiCl(tdt)-Py_2

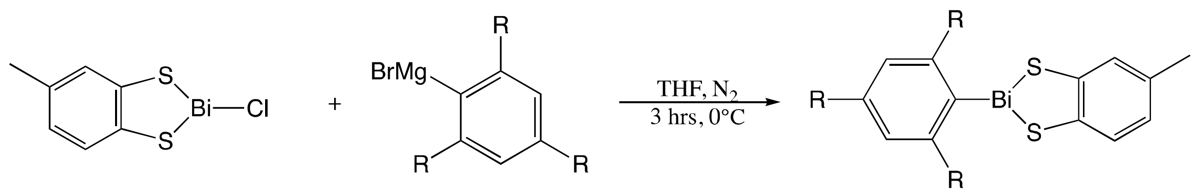
The pyridine adduct, BiCl(tdt)-$(py)_2$, was obtained by recrystallizing BiCl(tdt) from hot pyridine (Scheme 12). Crystals of the product precipitated when the solution was placed in the freezer overnight. The crystals were collected, and the process repeated. All product was assumed to have been collected when the solution turned pale yellow with crystals at the bottom of the vessel.



Scheme 12 – Synthesis of BiCl(tdt)-Py_2

*3.6.3 Synthesis of $(Mes_2Bi)_2$(tdt) (**2**)*

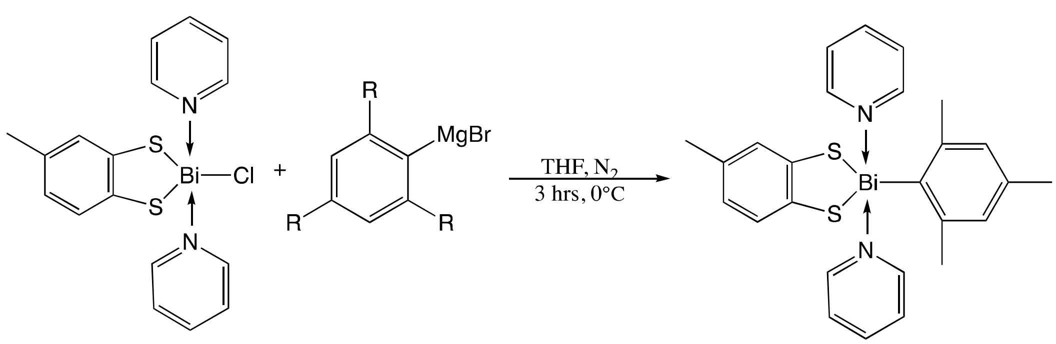
The synthesis of MesBi(tdt) was attempted by addition of MesMgBr to a solution of BiCl(tdt) in THF (Scheme 13). The initially cloudy solution became clear within one minute of the addition. The reaction mixture was filtered and concentrated to afford a dark red solution. The solution was placed in the freezer for 48 h after which time small pale-yellow crystals were found to have precipitated. These crystals were found to be too small for X-ray crystallography. The solution was then decanted and allowed to sit at room temperature. After 24 h larger crystals had formed. X-ray crystallography revealed that rather than the expected MesBi(tdt) product, $(Mes_2Bi)_2$(tdt) was isolated. In addition, the ^{1}H NMR data suggested a mixture of products, however, only (**2**) was identified by x-ray crystallography. This may have been due to inaccurate measurements of the Grignard reagent or changes in concentration of the Grignard. Additional attempts to produce $(Mes_2Bi)_2$(tdt) using the same procedure were unsuccessful. Attempts to reproduce the product using a 2:1 ratio of MesMgBr to BiCl(tdt) resulted in orange needle shaped crystals. X-ray crystallography revealed that the product was $(Mes_2Bi)_2$(tdt). This product may be more thermodynamically stable and therefore was the only product obtained. These crystals were found to have significantly different appearances. Those obtained from the 1:1 reaction were small plates while those obtained from the 1:2 reaction were needles.



Scheme 13 - Synthesis of MesBi(tdt)

3.6.4 Attempted synthesis of MesBi(tdt)-(py)$_2$

The attempted synthesis of MesBi(tdt)-(py)$_2$ by reaction of BiCl(tdt)-(py)$_2$ and Grignard reagent (Scheme 14) resulted in the isolation of crystals which were found to $MgCl_2$-(py)$_2$, as determined by X-ray crystallography. This suggested that the magnesium chloride was precipitating rather than the bismuth product. This occurred in all procedures where isolation of a pyridine adduct was attempted. As a result, this procedure was abandoned.



Scheme 14 – Synthesis of MesBi(tdt)-Py$_2$

3.7 X-Ray Crystal Structures

Crystals suitable of X-ray crystallography were isolated from the recrystallization of BiCl(tdt) in pyridine, and from reaction mixtures in synthesis of (Mes$_2$Bi)$_2$(tdt) as described above. Crystallographic data are given in Table 1.

Table 1 – Crystallographic data for (**1**) and (**2**).

	$BiCl(tdt)\text{-}py_2$ (**1**)	$(Mes_2Bi_2)_2(tdt)$ (**2**)
Empirical Formula	$C_{17}H_{16}BiClN_2S_2$	$C_{43}H_{50}Bi_2S_2$
fw	556.87	1048.91
Crystal System	Monoclinic	Monoclinic
Space Group	P 121/c 1	P 1 21/n 1
a (Å)	10.4142(4)	11.7817(5)
b (Å)	8.4392(3)	22.5166(10)
c (Å)	21.0827(9)	14.7158
α (deg)	90	90
b (deg)	98.017(2)	97.5200(10)
γ (deg)	90	90
V ($Å^3$)	183.80(12)	3870.3(3)
Z	4	4
F(000)	1056	2024
ρ_{calcd}, $Mg\ m^{-3}$	2.016	1.800
μ, mm^{-1}	9.982	9.218
T, K	100.0	125.0
λ, $Å$	0.71073	0.71073
R_1	0.0220	0.0340
wR_2	0.0452	0.0713

*3.7.1 Structure of BiCl(tdt)-(py)₂ (**1**)*

The X-ray crystal structure of $BiCl(tdt)\text{-}(py)_2$ (Figure 11) shows bismuth bonded to two pyridine nitrogen atoms, two sulfur atoms of a chelating 1,2-toluenedithiolate ligand, and two chlorine atoms. The geometry at bismuth is distorted octahedral, with the pyridine nitrogen atoms in *trans* positions and the chlorine atoms and sulfur atoms of the 1,2-toluenedithiolate ligand in *cis* positions. Both chlorine atoms are weakly bonded to the bismuth centre [Bi1-Cl1 = 3.0317(7) Å and Bi1-Cl1* = 3.0352(8) Å] and bridge neighbouring bismuth atoms to afford a polymeric structure.

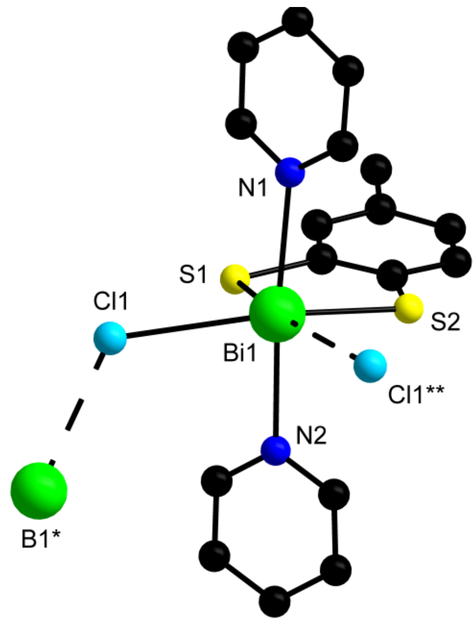


Figure 11 – X-ray crystal structure for BiCl(tdt)-py$_2$. – Selected bond distances (Å) and bond angles (°): Bi1-Cl1 = (3.0317(7)), Bi1-Cl1* = (3.0352(8)), Bi1-S1 = (2.5424(8)), Bi1-S2 = (2.5424(7)), Bi1-N1 = (2.565(3)), Bi1-N2 = (2.529(3)); Cl1-Bi1-Cl1* = (113.894(10)), S1-Bi1-Cl1 = (81.23(2)), S1-Bi1-Cl1* = (163.07(2)), S1-Bi1-S2 = (84.55(3)), S1-Bi1-N1 = (86.74(7)), N1-Bi1-Cl1* = (96.90(6)), N2-Bi1-N1 = (172.35(8))

*3.7.2 Crystal Structure of (Mes$_2$Bi)$_2$(tdt) (**2**)*

The X-ray crystal structure of (Mes$_2$Bi)$_2$(tdt) (Figure 12) shows two crystallographically unique bismuth centres bridged by a 1,2-toluenedithiolate ligand. Each bismuth centre is also bonded to two Mes groups, giving a trigonal pyramidal geometry at each metal atom.

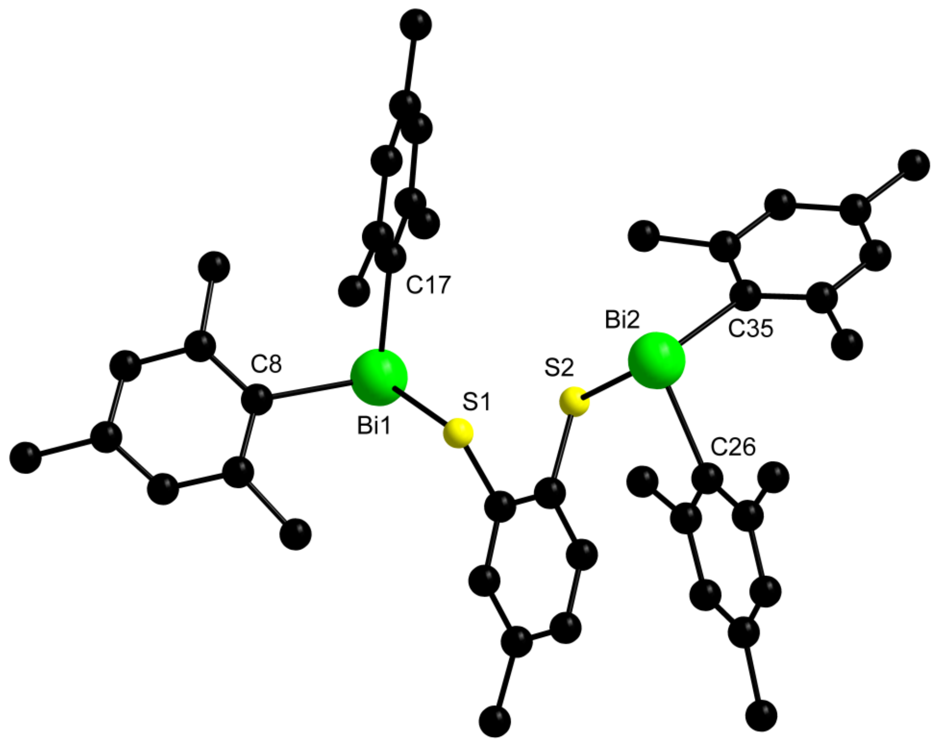


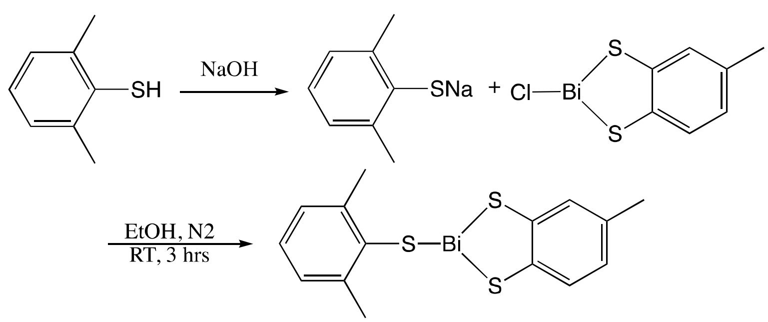
Figure 12 – X-ray crystal structures for $(Mes_2Bi)_2(tdt)$. Selected bond distances (Å) and bond angles (°): Bi1-C8 = 2.299(4), Bi1-C17 = 2.275(5), Bi1-S1 = 2.574(1), Bi(2)-S(2) = 2.5866(14), Bi(2)-C(26), Bi(2)-C(35); C8-Bi1-S1 = 103.09(12), C17-Bi1-S1 = 92.90(1), C1-S1-Bi1 = 96.13(17)

4. Conclusions

The purpose of this study was to synthesize and characterize novel heteroleptic redox active bismuth dithiolene and dithiolate catalysts as environmentally friendly alternative to otherwise toxic transition metal catalysts. Initial attempts to synthesize (Ar)Bi(mnt) by reacting $ArBiCl_2$ with Na_2(mnt) resulted in formation of the bis(dithiolene) product $[(mnt)_2Bi]^-$ and the loss of the aryl group. Similar results were observed with the use of the dithiolate and amidothiolate ligands $(tdt)^{2-}$ and $(abt)^{2-}$, respectively. Attempts to synthesize these products by reacting a bismuth dithiolene or dithiolate (XBi(L), X = Cl, Br; L = mnt, tbt, abt) with aryl Grignard (ArMgBr, Ar = Ph, Mes) proved more promising. The crystal structure of the reactant BiCl(tdt)-$(py)_2$ (**1**) was obtained. $(Mes_2Bi)_2(tdt)$ (**2**) was isolated as a crystalline product from both the 1:1 and 1:2 reactions of BiCl(tdt) and MesMgBr, although attempts to consistently isolate this product have been unsuccessful thus far.

5. Future Work

Future work in the synthesis of target bismuth dithiolate and dithiolene complexes involves attempting to reproduce the synthesis of $(Mes_2Bi)_2$(tdt)and characterize the product using cyclic voltammetry, FT-IR and Raman spectroscopy. Variations of the aryl group (Ph, Trip and Mes*) should also be attempted using the procedure which successfully produced the $(Mes_2Bi)_2$(tdt) product. Variations of the aryl group will provide access to molecules which feature variable steric bulk and solubility. In addition, complexes featuring benzenethiolate groups instead of aryl group (Scheme 16) may provide alternative routes to the synthesis of heteroleptic bismuth catalysts. By substituting the bismuth-carbon bond with a strong bismuth-sulfur bond the obstacles resulting from loss of the aryl group may be avoided.



Scheme 15 – Synthesis of 2-dimethylbenzene bismuth dithiolate

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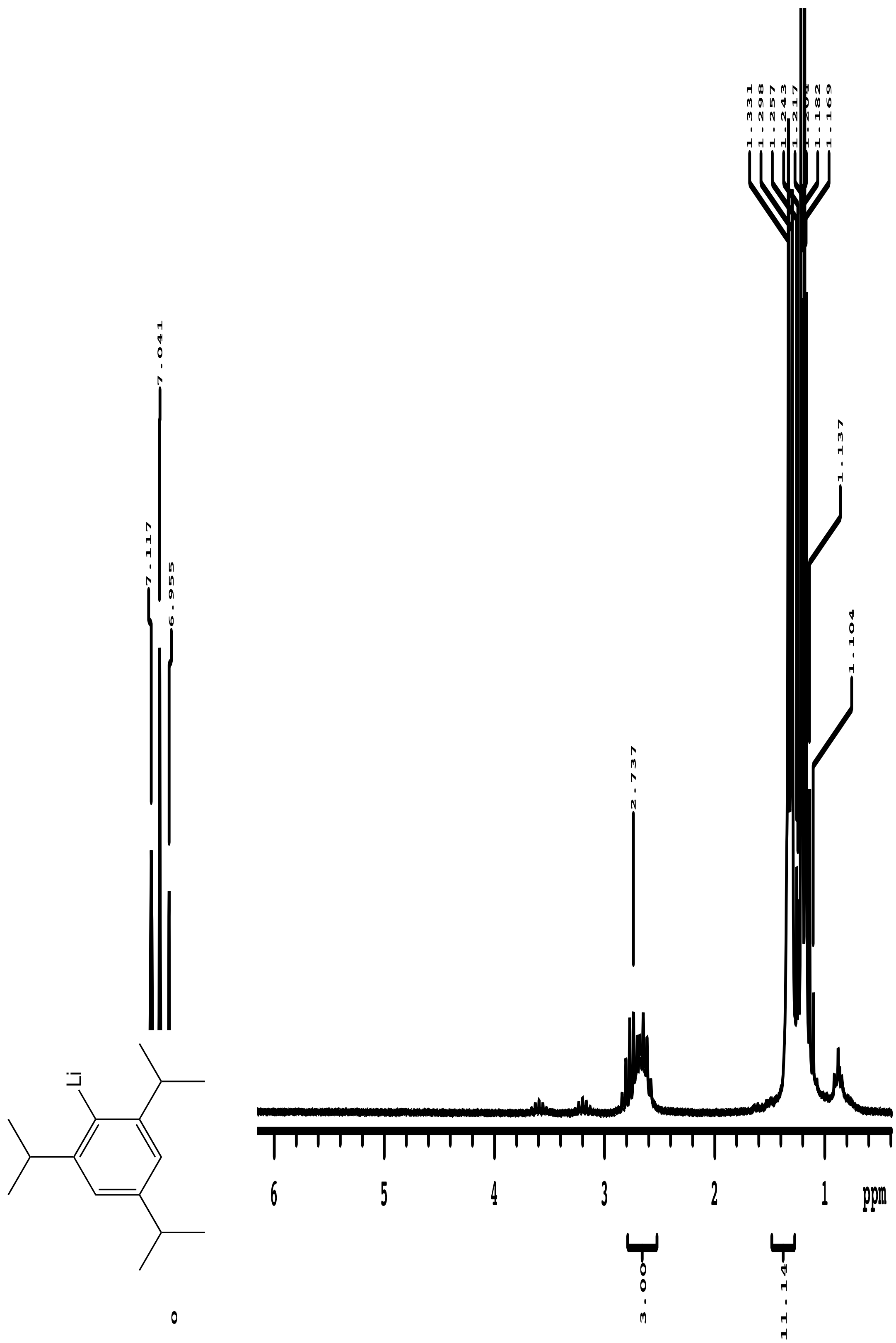
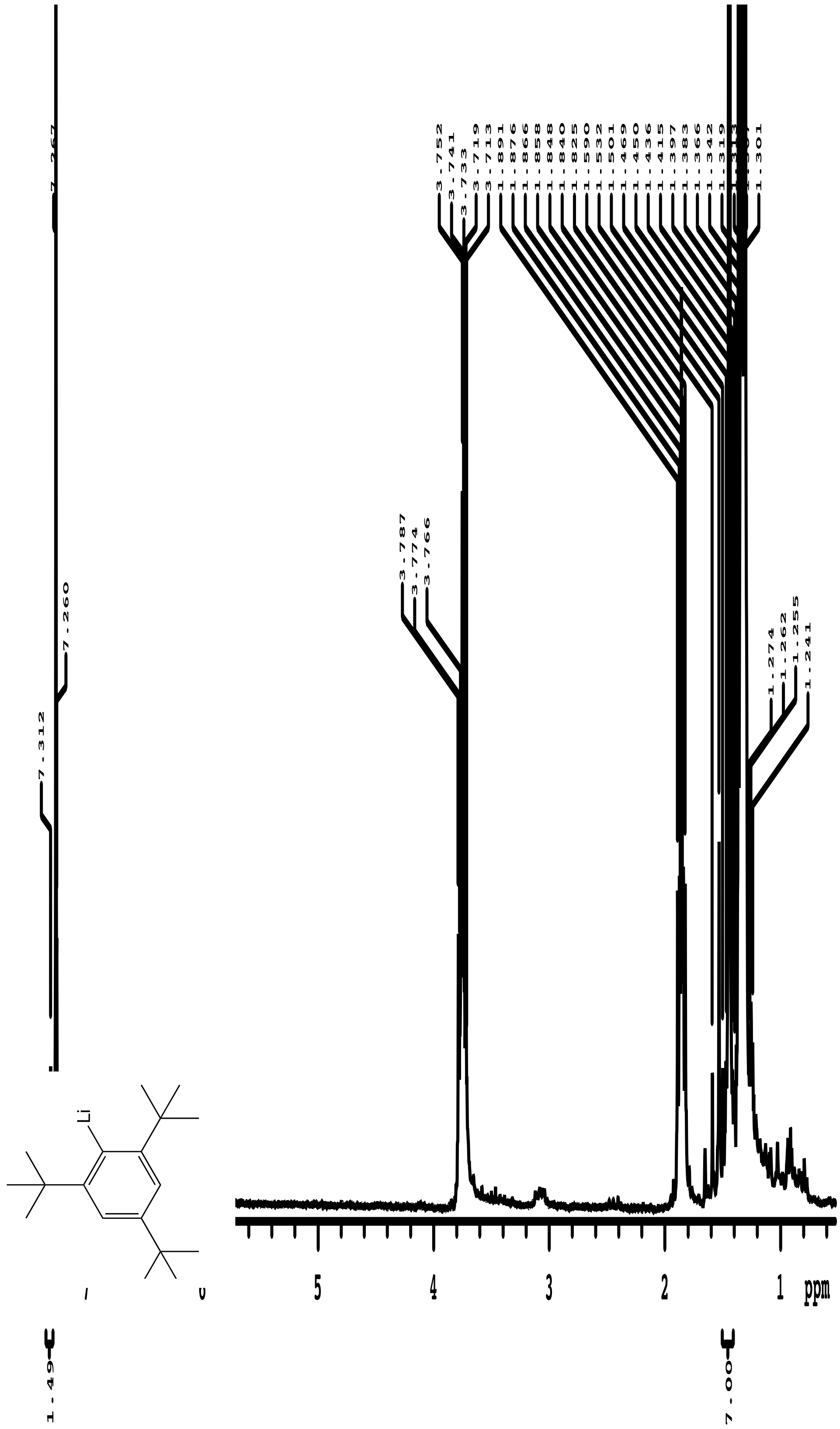
Appendix 1 ^{1}H NMR spectrum of Mes_3Bi

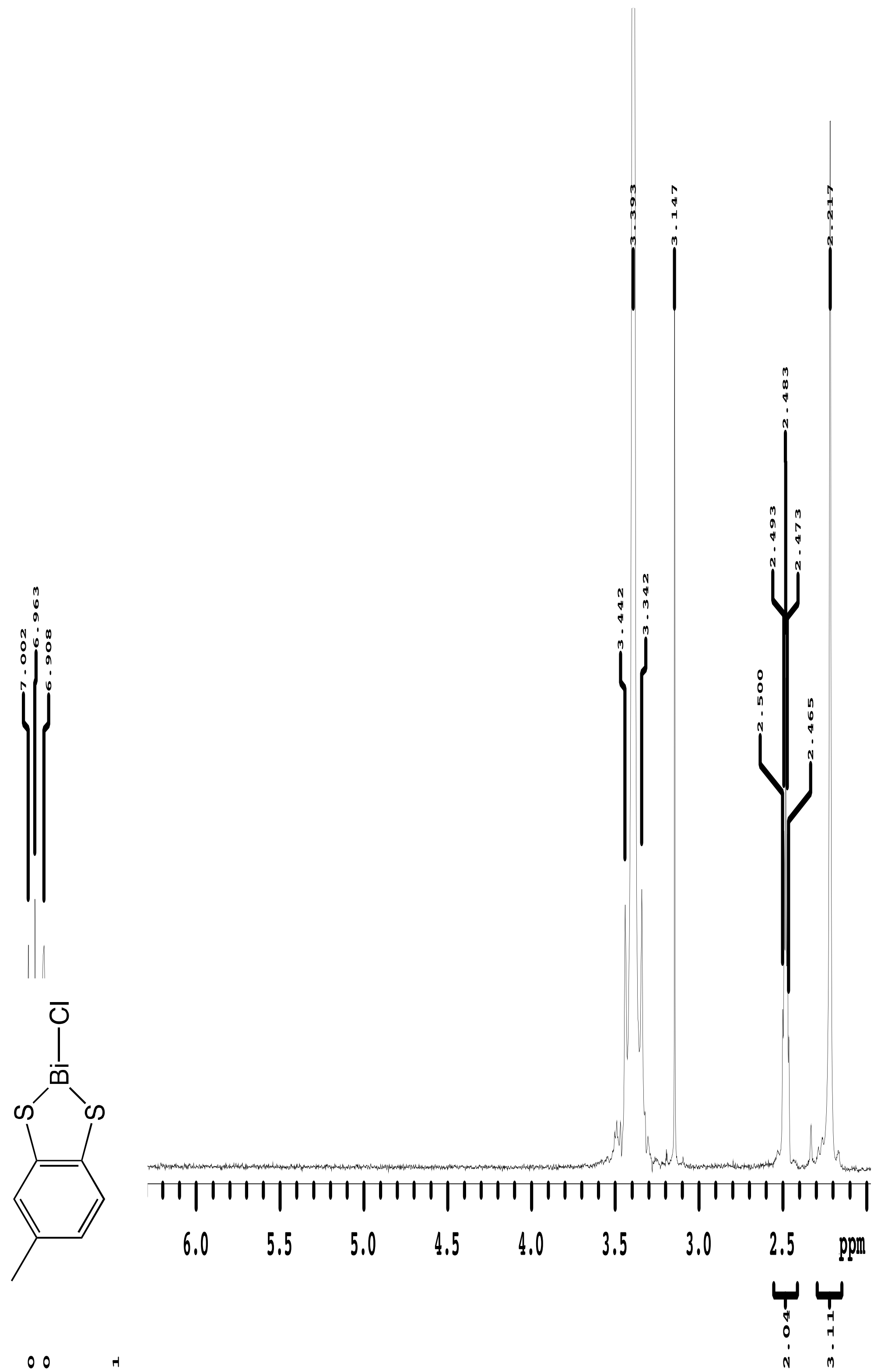
Appendix 2 ^{1}H NMR spectrum of (Trip)Li



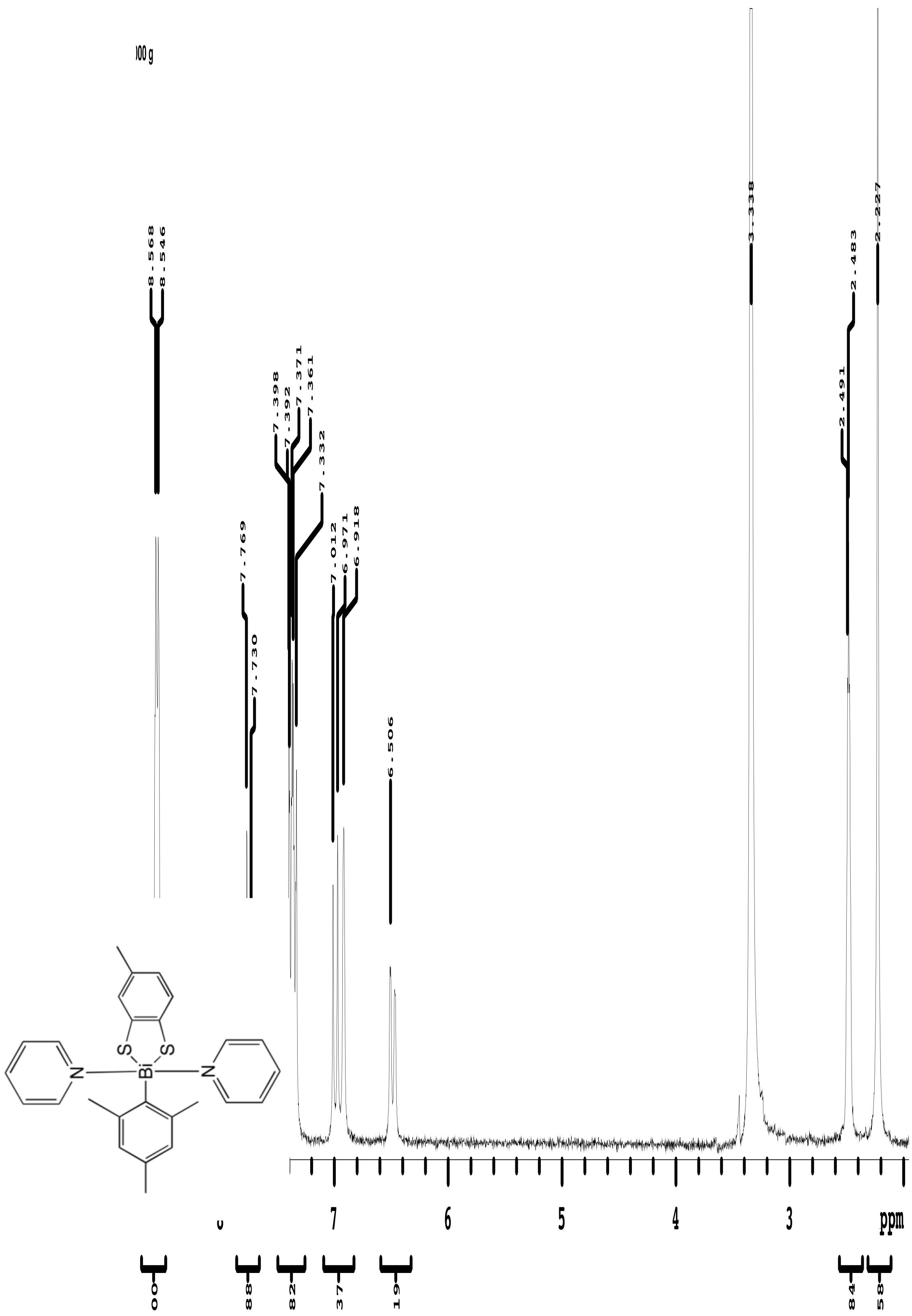
Appendix 3 ^{1}H NMR spectrum of (Mes*)Li



Appendix 4 ^{1}H NMR spectrum of BiCl(tdt)



Appendix 5 ^{1}H NMR spectrum of BiCl(tdt)-(py)$_2$ (**1**)



Appendix 6 ^{1}H NMR spectrum of $(Mes_2Bi)_2(tdt)$ (**2**)