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Formation of Bismuth(V) Thiolates: Protolysis and Oxidation of Triphenylbismuth(III) with Heterocyclic Thiols**

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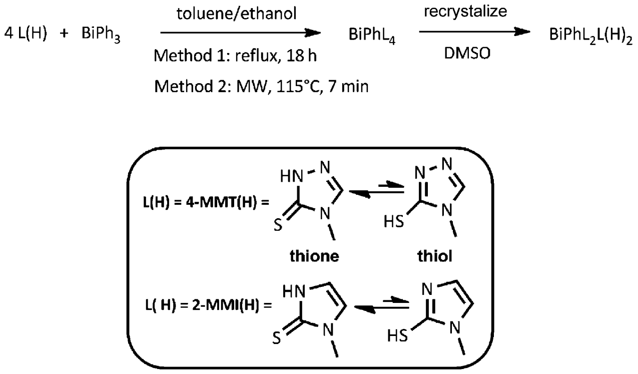
Bismuth(V) compounds are strongly oxidizing[1] and in the absence of stabilizing aryl groups remain extremely scarce. The majority of compounds that show reasonable stability and have been characterized in the solid state are heteroleptic triarylbismuth(V) compounds of the form $[\mathrm{BiAr_3X_2}]$,[2] where X is solely, or a combination of, aryl groups (Ar),[3] halides (except iodide),[4] and anionic oxygen-based ligands; oxido,[5] carboxylates,[6] sulfonates,[7] phenoxides,[8] or nitrate.[9] These are all "hard" ligands, or in the case of aryl groups, are calculated to have high group electronegativities.[10] Thus, the neutral pentaarylbismuth(V) compounds, $[\mathrm{BiAr_5}]$ (Ar = Ph, *p*-Tol, C_6F_5, $C_6H_3F_2$, or C_6H_4F), of which nine have thus far been crystallographically characterized, are stable and often highly colored.[2,3] In contrast, $\mathrm{BiMe_5}$ is unstable and explodes on warming to room temperature.[11] In structural terms, the majority of these compounds adopt a trigonal bipyramidal geometry—$[\mathrm{BiAr_5}]$ compounds being the notable exceptions—in which the more electronegative X ligands occupy the axial positions. The low toxicity of bismuth, the strong oxidizing nature of the complexes, the presence of an electrophilic Bi center, and highly labile ligands, have all contributed to a renewed interest in the role of triarylbismuth(V) complexes in organic synthesis.[12]

Diarylbismuth(V) compounds, $[\mathrm{BiAr_2X_3}]$, are less stable than their triaryl counterparts, and are rare. Known examples are: the oxido-cluster $[\mathrm{Bi_4}(o\text{-Tol})_8\mathrm{O_6}]$,[13] and three complexes supported and stabilized through internal coordination, $[\mathrm{Bi_2}(o\text{-Et_2NCH_2-C_6H_4})_4(\mathrm{CO_3})]$,[14] $[\mathrm{Bi_2}\{(o\text{-Me_2NCH_2})_2\mathrm{C_6H_3}\}_4\mathrm{O_2}]$, and $[\mathrm{Bi}\{(o\text{-Me_2NCH_2})\mathrm{C_6H_3CO_2}\}\{o\text{-Me_2N(O)CH_2C_6H_3}\}]$.[15] There are no reports of stable and/or structurally characterized monoarylbismuth(V) complexes of the form $[\mathrm{BiArX_4}]$.

As is typical for a heavy metal, Bi–S bonds are generally less labile and thermodynamically more stable than Bi–O bonds.[16] Thus, bismuth(III) thiolates are common stable species and have a special relevance in biology and medicine.[17] While both Hoppe and Whitmire[8d] and Sharutin et al.[8a–c] have had some success in synthesizing triarylbismuth(V) phenoxides, there is no corresponding thiolate chemistry. To date, compounds of the type $[\mathrm{BiAr}_{5-n}(\mathrm{SR})_n]$ ($n = 1$–5) are unknown, most likely stemming from the "soft" nature of the thiolate ligands and an inability to stabilize the high charge on the $\mathrm{Bi^V}$ center. In fact, inorganic $\mathrm{Bi^{III}}$ compounds are known to promote disulfide formation from thiols.[18] By studying various methods towards the synthesis of novel biologically active bismuth thiolates, we now describe the formation and characterization of the first monoarylbismuth(V) thiolates, derived from 1-methyl-1*H*-imidazole-2-thiol and 4-methyl-4*H*-1,2,4-triazole-3-thiol, and their subsequent facile transformation into their reduced $\mathrm{Bi^{III}}$ congeners, the crystal structures of which retain the hallmarks of their $\mathrm{Bi^V}$ origin.

Triphenylbismuth was treated with 4-methyl-4*H*-1,2,4-triazole-3-thiol [4-MTT(H)] or 2-mercapto-1-methylimidazole [2-MMI(H)] in a toluene/ethanol solvent mixture at reflux or by microwave (MW) irradiation, resulting in the formation of a bright yellow solid in both cases (Scheme 1).



Scheme 1. Synthetic routes to the bismuth(V) thiolates [BiPh(4-MTT)$_4$] **1** and [BiPh(2-MMI)$_4$] **2**.

Electrochemical analysis of these solids, supported by NMR spectroscopy, ESI-MS, and FTIR spectroscopy, showed them to be the monophenyl tetrathiolato bismuth complexes [BiPh(4-MTT)$_4$] **1** and [BiPh(2-MMI)$_4$] **2**, in which the bismuth(III) center has undergone oxidation to $\mathrm{Bi^V}$ following protolysis and substitution of two Ph ligands and concomitant addition of two further thiolato ligands. Synthesis under microwave conditions provided slightly higher yields of **1** and **2**, and in a fraction of the time (seven minutes versus nine hours). Full synthetic and analytical details are provided in the Supporting Information.

From integration of the proton signals in the ^{1}H NMR spectrum of both **1** and **2** the L/Ph ratio was calculated as 4:1. There were no residual resonances attributable to NH, which

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are found at $\delta = 13.7$ and 12.0 ppm in MTT(H) and MMI(H), respectively (or to SH because the thiones are stable to tautomerization in DMSO solution at RT). In complex **1**, the signal at $\delta = 8.27$ ppm (8.43 in MTT(H)) can be assigned to the proton on the triazole ring, while the two doublets at $\delta =$ 6.80 and 6.96 ppm in **2** correspond to the protons on the imidazole ring ($\delta = 6.85$ and 7.03 ppm in MMI(H)). The phenyl protons in **1** resonated at 8.36 (*o*), 7.47 (*m*), 7.29 (*p*) ppm, while the corresponding signals in **2** were observed at $\delta = 8.83$ (*o*), 7.49 (*m*), and 7.23 (*p*) ppm.

FTIR spectroscopy of both complexes supports the NMR spectroscopic data. Absorption bands for N–H (observed at 3115 and 3097 cm^{-1} in MTT(H) and MMI(H), respectively), or for S–H bands (not observed in MTT(H) and MMI(H)), were absent in the spectra obtained for complexes **1** and **2**. Further evidence for the formation of the two new hypervalent bismuth(V) complexes came from electrospray mass spectrometry, for which the solid samples were dissolved in DMSO/methanol. Complex **1** showed prominent peaks at *m*/*z* 553.02 (33 %, $[\mathrm{BiPh(O)L_2Na}]^+$), 628.05 (81 %, $[\mathrm{BiPhL_3}]^+$), and 765.05 (46 %, $[\mathrm{BiPhL_4+Na}]^+$), while for **2** peaks were observed at 529.05 (8 %, $[\mathrm{BiPh(O)L_2+H}]^+$), 625.07 (12 %, $[\mathrm{BiPhL_3}]^+$), 839.13 (58 %, $[\mathrm{BiPhL_4(DMSO)+Na}]^+$), 875.11 (70 %, $[\mathrm{BiPhL_4(DMSO)(H_2O)+Na}]^+$), and 911.09 (65 %, $[\mathrm{BiPhL_4(DMSO)(H_2O)_4+Na}]^+$).

To gain some insight into the structure of both complexes, crystals suitable for X-ray crystallography were obtained from separate DMSO solutions of **1** and **2** after several months. However, the X-ray diffraction data revealed them to be the Bi$^{\mathrm{III}}$ complexes [BiPh(4-MTT)$_2${4-MTT(H)}$_2$] **3** and [BiPh(2-MMI)$_2${2-MMI(H)}$_2$] **4** rather than the anticipated Bi$^{\mathrm{V}}$ complexes, which indicated that protonation of two thiolato ligands had occurred accompanied by reduction of the Bi$^{\mathrm{V}}$ center. Presumably this redox process resulted from the presence of water in the DMSO during crystallization. In dry DMSO under a dry nitrogen atmosphere, no crystallization was observed after two months. Solution ^{1}H NMR studies on the crystals of **3**, which are poorly soluble even in DMSO, showed the NH protons resonating at $\delta = 13.60$ ppm, the triazole CH proton shifted to $\delta = 8.35$ ppm (8.27 ppm in **1**), and the *o*-Ph signal now at 8.27 ppm (8.36 ppm in **1**). These C-H chemical shifts, including those for *m*- and *p*-Ph, are identical to those found in the deliberately prepared Bi$^{\mathrm{III}}$ analogue [PhBi(4-MTT)$_2$] (see below). The NH proton in the spectrum of **4** was found at $\delta = 12.00$ ppm, and the signals for the imidazole CH protons were found at $\delta = 6.81$ and 7.00 ppm (compared with 6.80 and 6.93 ppm in **2**), shown in Figure 1.

In the realm of bismuth(III) thiolate chemistry, complexes **3** and **4** (Figure 2 and Figure 3 respectively) are rare examples of crystallographically characterized homometallic complexes containing a triazole-thiolate or imidazole-thiolate ligand system. The only other related examples are based on substituted imidazole-thione ligands which are bound datively to the Bi$^{\mathrm{III}}$ center.[19–22] This indicates that when deprotonated, the stable thione form converts to the more stable thiolate anion upon bonding with bismuth, providing a thermodynamically stable and non-labile Bi–S bond.

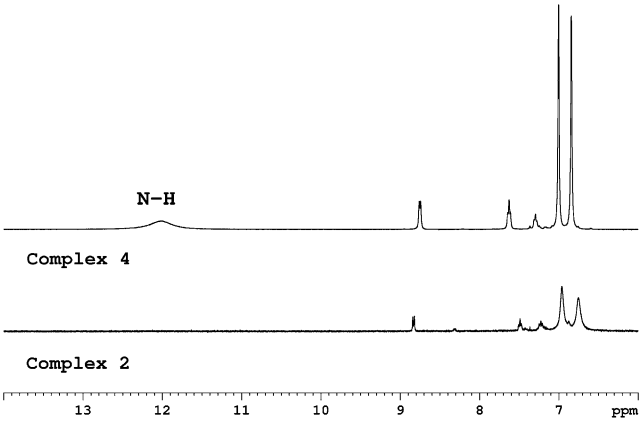


Figure 1. ^{1}H NMR spectral comparison of [BiPh(2-MMI)$_4$] **2** and [BiPh(2-MMI)$_2${2-MMI(H)}$_2$] **4**.

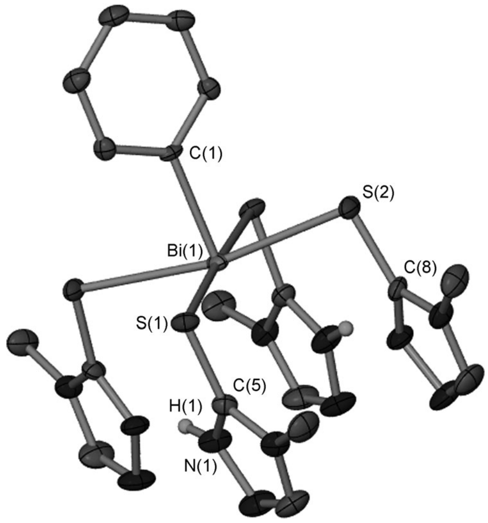


Figure 2. Molecular structure of [BiPh(4-MTT)$_2${4-MTT(H)}$_2$] **3**. Only one of two independent molecules is shown; thermal ellipsoids at 50 % probability. Hydrogen atoms (except N-H ones) have been omitted for clarity. Selected bond lengths (Å) and angles (°): Bi(1)-S(1) 2.8236(11), Bi(1)-S(2) 2.8055(11), Bi(1)-C(1) 2.204(5), S(1)-C(5) 1.725(4), S(2)-C(8) 1.715(4), N(1)-H(1) 0.880, H(1)-N(4)′ 1.861, Bi(1)-S(1)-C(5) 90.05(15), Bi(1)-S(2)-C(8) 96.68(15), C(1)-Bi(1)-S(1) 91.42(2), C(1)-Bi(1)-S(2) 84.32(2), S(1)-Bi(1)-S(2) 88.20(4), S(1)-Bi(1)-S(1)′ 177.17(4), S(2)-Bi(1)-S(2)′ 168.64(5), S(1)-Bi(1)-S(2)′ 92.08(4).

Complexes **3** and **4** contain a C$_2$ axis along C(4), C(1), Bi(1) and C(12), C(9) and Bi(1), respectively, and adopt a distorted square-pyramidal geometry. The centrally located Bi$^{\mathrm{III}}$ atom is coordinated to one phenyl, two 4-MMT and two MTT(H) ligands (**3**), or two 2-MMI and two 2-MMI(H) ligands (**4**), giving each Bi$^{\mathrm{III}}$ center a total coordination number of five. The two hydrogen atoms H(1) and H(2N) located on the neutral 4-MTT(H) and 2-MMI(H) ligands in **3** and **4**, respectively, were located by residual density in the electron difference maps and placed in the calculated positions. Interestingly, with an overall C_{4v} symmetry the two complexes resemble the unusual structural motif only observed with [BiAr$_5$] complexes, which provides insight into their Bi$^{\mathrm{V}}$ origin.

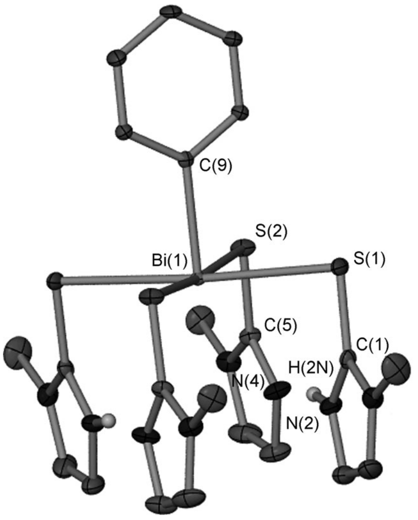


Figure 3. Molecular structure of [BiPh(2-MMI)$_2${2-MMI(H)}$_2$] **4** showing thermal ellipsoids at 30% probability. Hydrogen atoms (except N-H ones) have been omitted for clarity. Selected bond lengths (Å) and angles (°): Bi(1)-S(1) 2.8112(10), Bi(1)-S(2) 2.8132(14), Bi(1)-C(9) 2.235(5), S(1)-C(1) 1.717(4), S(2)-C(5) 1.719(4), N(2)-H(2N) 0.880, H(2N)···N(4) 1.848, Bi(1)-S(1)-C(1) 91.04(12), B(1)-S(2)-C(5) 95.92(12), C(9)-Bi(1)-S(1) 88.303(19), C(9)-Bi(1)-S(2) 87.67(2), S(1)-Bi(1)-S(2) 91.84(4), S(1)-Bi(1)-S(1)′ 176.61(4), S(2)-Bi(1)-S(2)′ 175.33(4), S(1)-Bi(1)-S(2)′ 88.03(4).

The Bi–S bond lengths in complexes **3** and **4** are essentially identical ranging from 2.8055(11)–2.8236(11) Å, showing little variation for the covalent versus dative (coordinative) bonding modes. Thus, they constitute an average between typical covalent Bi–S (approximately 2.6 Å),[23] and coordinate dative $Bi\leftarrow S$ (approximately 3.0 Å) bonds.[23d] This most likely arises from an averaging of the four bonds throughout the crystal owing to the possibility of the two calculated NH protons on the neutral ligands being located on any two of the heterocyclic ligands at any one time.

In complex **3**, bismuth and three of the sulphur atoms are co-planar to within ±0.03 Å with the S(2) atom lying out of this plane by 0.624(3) Å. In contrast the BiS_4 equatorial grouping in complex **4** is essentially co-planar (±0.04 Å). Perpendicular to this BiS_4 basal plane, the triazole-thione ligand in **3** and the imidazole-thione ligand in **4** make a hydrogen-bond contact to their symmetry-generated acceptors (1.861 Å, **3** and 1.848 Å, **4**) which lie almost co-planar, twisted by 7.76(22)° in **3** and 8.67(22)° in **4**. The Bi-S-C angles in both complexes **3** (Bi(1)-S(1)-C(5) 90.05(15)°, Bi(1)-S(2)-C(8), 96.98(15)°) and **4** (Bi(1)-S(1)-C(1), 91.04(12)°, Bi(1)-S(2)-C(5), 95.92(12)°) are obtuse in nature and far removed from the expected bond angle of around 109° seen in other similar Bi-S-C bonded complexes.[24]

In principle, voltammetric techniques can be used to distinguish the redox level of inorganic compounds. Typically, a Bi^{V} compound is expected to be reduced to the elemental Bi^{0} state in two steps, when the potential is scanned in the negative direction. That is, Bi^{V} is reduced to Bi^{III} in a two-electron step followed by a further three-electron step in which Bi^{III} is reduced to elemental Bi^{0}. Subsequently, elemental Bi^{0} deposited on the electron surface can be stripped from the surface to give Bi^{III}, by scanning the potential in the positive direction. Figure 4a shows a steady state voltammogram at a microelectrode for the reduction of the presumed Bi^{V} compound in dry DMSO under a N_2 atmosphere. The initial reduction step (process A) is well defined. Upon scanning more negative potentials, a second more drawn out reduction process is detected (process B). The ratio of the limiting current for processes A and B is 2:3. Thus, processes A and B are assigned to the reactions in Equations (1) and (2), respectively.

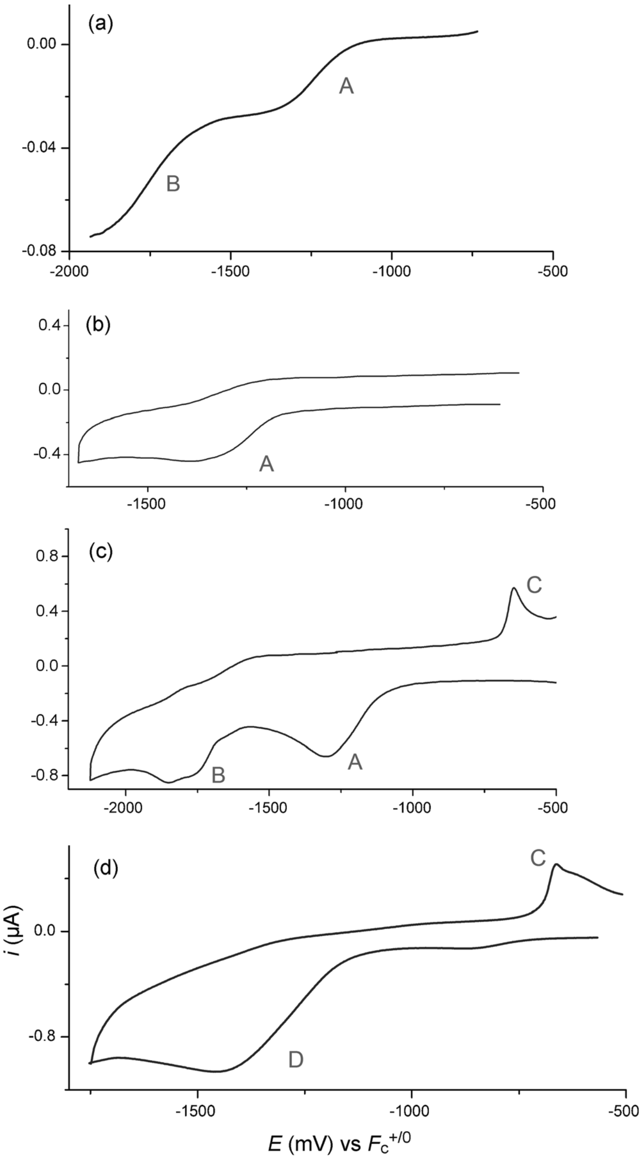


Figure 4. a) Two-step reduction of Bi^{V} in [BiPh(4-MTT)$_4$] **1** to Bi^{0} under conditions of steady-state voltammetry at a carbon microelectrode; b–d) cyclic voltammetry at a glassy carbon electrode; b) potential switched after process A for complex **1**; c) potential switched after process B for complex **1**; d) potential switched after process D giving rise to reduction of Bi^{III} in [BiPh(4-MTT)$_2${4-MTT(H)}$_2$] **3** to Bi^{0}.

$$Bi^{V} + 2\,e^{-} \rightarrow Bi^{III} \qquad (1)$$

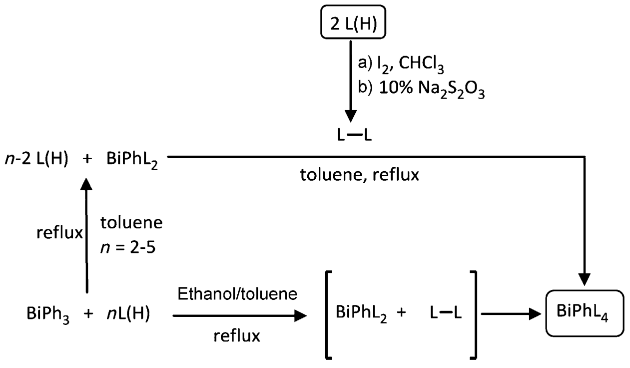
$$\mathrm{Bi^{III}} + 3\,e^- \rightarrow \mathrm{Bi^0} \qquad (2)$$

Under transient conditions of cyclic voltammetry, process A is still well defined [Figure 4b]. However, no bismuth metal (here $\mathrm{Bi^0}$) is produced, as evidenced by the lack of a bismuth stripping ($\mathrm{Bi^0} \rightarrow \mathrm{Bi^{III}}$) process at positive potentials on the reverse positive potential direction scan. In contrast, if the potential is switched at a value more negative than process B [Figure 4c], upon reversing the potential scan direction, the characteristic bismuth-stripping peak is now detected (process C). Furthermore, upon holding the potential at values between the first and second reduction process for ten minutes, no elemental $\mathrm{Bi^0}$ was detected. However, if the potential is held at a value slightly more negative than process B, then upon removal of the working electrode from the solution, a deposit can be visually detected on the glassy carbon electrode. The XRD spectrum, provided in the Supporting Information, confirmed that elemental bismuth was deposited onto the electrode surface.

Voltammetry of the compound tentatively assigned as a $\mathrm{Bi^{III}}$ material was significantly different to that described above for the nominally $\mathrm{Bi^V}$ compound [Figure 4c]. In this case, the initial process D is more drawn out than process A but leads directly to detection of elemental bismuth (process C) when the potential is reversed, as shown in Figure 4d. Thus, process D can be assigned to the reaction $\mathrm{Bi^{III}} + 3\,e^- \rightarrow \mathrm{Bi^0}$. Other processes detected for the $\mathrm{Bi^V}$ and $\mathrm{Bi^{III}}$ compounds at very negative and positive potentials (data not shown) were attributed to ligand reduction and oxidation, respectively. The voltammetric data therefore lend support to the redox level assignments given to the Bi compounds on the basis of NMR and other data.

The voltammetric features of complexes **2** and **4** mimic those of complexes **1** and **3**. Thus, Bi metal is produced after two steps with steady-state limiting currents in the ratio of 2:3 (Supporting Information, Figure S10) for complex **2**, whereas Bi metal is produced from the first step for complex **4** (Figure S13).

Having established definitively that the $\mathrm{Bi^V}$ complexes were formed in the reaction of $\mathrm{BiPh_3}$ with the *N*-heterocyclic thiols the question remained as to how this oxidation of the $\mathrm{Bi^{III}}$ species occurs. A recent paper by John and co-workers suggests a possible mechanism,[25] illustrated for our systems in Scheme 2. Here the thiol converts to the disulfide under reflux conditions in ethanol. Thermally induced homolytic decomposition of the disulfide into two radical species[26] would then allow formation of the $\mathrm{Bi^V}$ complex through Bi–S bond formation, using the two available electrons on the $\mathrm{Bi^{III}}$ center, nominally the lone-pair electrons. To probe the validity of this mechanism, $\mathrm{BiPhL_2}$ (L = 4-MTT(H)) was synthesized by treating $\mathrm{BiPhCl_2}$ with two equivalents of [4-MMI Na]. The yellow solid product was washed with water and ethanol and the composition confirmed through NMR spectroscopy and elemental analysis (see Supporting Information). The disulphide, 1,2-bis(4-methyl-4*H*-1,2,4-triazol-3-yl)disulfane (L-L), derived from 4-MTT(H) was also prepared.[27] Finally, $\mathrm{BiPhL_2}$ and L-L were dissolved in toluene in a 1:1 ratio and heated under refluxing conditions for six hours under a nitrogen atmosphere. The yellow product obtained was washed with diethyl ether and shown to be complex **1**, [BiPh(4-MTT)$_4$]. The radical nature of this oxidation process is being probed further as we seek to determine the generality of this reaction in forming novel $\mathrm{Bi^V}$ thiolato species.



Scheme 2. Mechanistic reaction pathway where L = 4-MTT or 2-MMI.

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