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

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Electronic Supporting Information

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• **Materials and methods**

Analytical grade solvents were purchased from Merck. THF and diethyl ether were dried prior to use with M-Braun-SPS-800 solvent purification system and molecular sieves (4Å) were used to store. Standard metathesis reaction was used for the synthesis of triphenyl bismuth by the reaction of bismuth trichloride and phenylmagnesium bromide in dried tetrahydrofuran at 0 °C. Ethanol was used as the solvent for the recrystallisation and small needles like crystals were used. 4-Methyl-4H-1, 2, 4-triazole-3-thiol [4-MTT(H)] and 2-mercapto-1-methylimidazole [2-MMI(H)] were obtained from Sigma Aldrich and used as supplied.

• **Measurements**

Microwave irradiation was carried out in CEM Discoverer Microwave oven. Maximum power 0-300w, model number 9080, maximum current 6.38 A with 50/60 MHz frequency (CEM Matthews. NC). NMR spectra of complexes were recorded on a Brucker 400 spectrometer operating at 400 MHz as solutions in deuterated dimethyl sulfoxide with TMS as internal standard at room temperature. Elemental analyses (C, H, N, S) were performed by the Campbell Microanalytical lab, Department of chemistry, University of Otago, Dunendin, New Zealand. Melting points were determined on a Stuart Scientific SMP3 melting point apparatus.

All voltammetric experiments were carried out at 25 ± 2 °C using a three electrode electrochemical cell configuration and on Potentiostat BAS 100W electrochemical work station. Glassy carbon (GC) disc electrode (d = 1.0 mm) for cyclic voltammetry was polished consecutively with 0.3 µm and 0.05 µm alumina (Buehler, Lake Bluff, IL) on a clean polishing cloth then rinsed with water, sonicated for 20 s and again rinsed with water and dried under nitrogen. For steady state studies, glassy carbon micro electrode (d = 11 µm) was polished with 0.05 µm alumina in the similar way as described above. Indium tin oxide slides (ITO) were used as working electrode during bulk electrolysis of BiV complexes to deposit bismuth metal. ITO was cleaned by sonicating in *iso-
propanol for 15 - 20 mins. A platinum wire was used as the auxiliary electrode and another platinum wire was used as the quasi-reference electrode.

Electrochemical behaviour of a 1.0 mM solution of [PhBi(4-MTT)$_4$] 1 and thiols 4-methyl-4$H$-1, 2, 4-triazole-3-thiol [4-MTT(H)] and 2-mercapto-1-methylimidazole [2-MMI(H)] were studied in DMSO containing 0.1 M tetrabutylammoniumhexafluorophosphate (Bu$_4$NPF$_6$) as the supporting electrolyte. As quasi-reference electrode was used, potentials were calibrated versus Ferrocene by the addition of 1.0 mM Ferrocene. XRD spectra were collected on a Philips PW1140 diffractometer from 2 - 60° (2θ) at 4° min$^{-1}$ with a step size of 0.02° using a Cu K$_{\alpha}$ source ($\lambda = 1.54$ nm). A 1° divergence slit, 1° receiving slit and 0.2° scatter aperture were used. Samples were prepared by bulk electrolysis on Indium tin oxide slides.

• Syntheses

Synthesis of [PhBi(4-MTT)$_4$], 1

Method A: Conventional method

To a hot solution of 4-methyl-4$H$-1,2,4-triazole-3-thiol (0.5 g, 4.0 mmol) in ethanol (7.0 mL) was added triphenyl bismuth (0.59 g, 1.3 mmol) in toluene (15.0 mL) and the reaction mixture heated to reflux for nine hours. The excess of solvent was removed under reduced pressure. The yellow product thus obtained was washed several times with acetone. Yield 0.33 g, 57.0 %.

Method B: MW assisted synthesis

The mixture 4-methyl-4$H$-1,2,4-triazole-3-thiol (0.1 g, 0.87 mmol) in 2.0 mL of ethanol and triphenylbismuth (0.13 g, 0.29 mmol) in toluene (3.0 mL) was irradiated at 115 °C for seven minutes. The excess of solvent was removed under reduced pressure. The product was then washed with acetone and diethyl ether in order to remove unreacted materials. Yield: 0.08 g, 62.0 %. Mp: 268-270 °C (dec.). Anal Calc for BiC$_{18}$H$_{21}$N$_{12}$S$_4$: C; 29.11, H; 2.85, N; 22.63. Found: C; 29.49, H; 2.92, N; 23.03. $^1$H NMR (400 MHz, d$_6$-DMSO): $\delta$ (ppm) 8.37 (2H, d, o-Ph), 8.36(4H, s, triazole CH), 7.47(2H, t, m-Ph), 7.29 (1H, t, p-Ph), 3.40 (12H, s, triazole CH$_3$). $^{13}$C
NMR (100 MHz, d$_6$-DMSO): δ (ppm) 142.7 (triazole CH), 138.6 (o-Ph), 130.5 (m-Ph), 126.7 (p-Ph), 31.0 (triazole CH$_3$). FT-IR / cm$^{-1}$: 1643 w, 1522 s, 1402, 1205 s, 1155 s, 992 m, 701 m, 650 w.

$m/z$ (ESI$^+$): 553.02 (33 %, [PhBi(O)L$_2$Na$^+$]), 628.05 (81 %, [PhBiL$_3$]$^+$) and 765.05 (46 %, [PhBiL$_4$+Na$^+$]).

**Synthesis of [PhBi(2-MMI)$_4$],** 2

Method A: Conventional method

To a hot solution of 2-mercapto-1-methylimidazole (0.57 g, 5.0 mmol) in ethanol (7.0 mL) was added triphenylbismuth (0.73 g, 1.66 mmol) in toluene (15.0 mL) and the reaction mixture heated to reflux for nine hours. The excess of solvents were removed under reduced pressure. The yellow product thus obtained was washed several times with acetone. Yield 0.39 g, 53 %.

Method B: MW assisted synthesis

The mixture of 2-mercapto-1-methylimidazole (0.1 g, 0.87 mmol) in 2.0 mL of ethanol and triphenylbismuth (0.13 g, 0.29 mmol) in toluene (3.0 mL) was irradiated at 115 °C for seven minutes. The resulting reaction mixture was dried under vacuum and washed with acetone and diethyl ether in order to remove unreacted materials. Yield: 0.08 g, 60 %. Mp: 185-187 °C (dec.). Anal Calc for BiC$_{22}$H$_{25}$N$_8$S$_4$: C; 35.77, H; 3.41, N; 15.17. Found: C; 36.11, H; 3.51, N; 15.61. $^1$H NMR (400 MHz, d$_6$-DMSO): δ (ppm) 8.83 (2H, d, o-Ph), 7.49 (2H, t, m-Ph), 7.23 (1H, t, p-Ph), 6.96 (4H, s, imidazole CH), 6.76 (4H, s, imidazole CH), 3.41(12H, s imidazole CH$_3$). $^{13}$C NMR (100 MHz, d$_6$-DMSO): δ (ppm) 137.8 (o-Ph), 130.9 (m-Ph), 127.3 (p-Ph), 119.7 (imidazole CH), 33.4 (imidazole CH$_3$). FT-IR / cm$^{-1}$: 1631 w, 1512, 1469 s, 1408 s, 1354 s, 1218 s, 1164 s, 869 w, 728m, 691 s. $m/z$ (ESI$^+$): 529.05 (8 %, [PhBi(O)L$_2$+H$^+$]), 625.07 (12 %, [PhBiL$_3$]$^+$), 839.13 (58 %, PhBiL$_4$(DMSO)+Na$^+$), 875.11 (70 %, PhBiL$_4$(DMSO)(H$_2$O)+Na$^+$) and 911.09 (65 %, [PhBiL$_4$(DMSO)(H$_2$O)$_4$+Na$^+$]).

**Synthesis of [BiPh(4-MTT)$_2$(4-MTT(H))$_2$],** 3

Complex 1 was dissolved in hot DMSO and deep yellow coloured crystals of 3 suitable for single crystal X-ray diffraction studies were obtained over a period of
eight weeks. Anal Calc for BiC\textsubscript{18}H\textsubscript{23}N\textsubscript{12}S\textsubscript{4}: C; 29.03, H; 3.11, N; 22.57. Found: C; 29.38, H; 3.52, N; 22.80. \textsuperscript{1}H NMR (400 MHz, d\textsubscript{6}-DMSO): \(\delta\) (ppm) 13.6 (2H, s, triazole NH), 8.35 (4H, s, triazole CH), 8.27 (2H, d, \textit{o}-Ph), 7.55 (2H, t, \textit{m}-Ph), 7.33 (1H, t, \textit{p}-Ph), 3.42 (12H, s, triazole CH\textsubscript{3}). \textsuperscript{13}C NMR (100 MHz, d\textsubscript{6}-DMSO): \(\delta\) (ppm) 144.0 (triazole CH), 139.4 (\textit{o}-Ph), 132.2 (\textit{m}-Ph), 127.3 (\textit{p}-Ph), 31.1 (triazole CH\textsubscript{3}). \textit{FT-IR} / cm\textsuperscript{-1}: 3092 m, 2940m, 1653 w, 1524, 1472 s, 1410 s, 1361 s, 1280 s, 1164 s, 869 w, 728 m, 691 s, 639 m.

**Synthesis of [BiPh(2-MMI)\textsubscript{2}(2-MMI(H))\textsubscript{2}], 4**

Complex 2 was dissolved in hot DMSO and orange coloured crystals of 4 suitable for single crystal X-ray diffraction studies were obtained over a period of eight weeks. Anal Calc for BiC\textsubscript{22}H\textsubscript{27}N\textsubscript{8}S\textsubscript{4}: C; 35.67, H; 3.67, N; 15.13. Found: C; 35.81, H; 3.71, N; 15.20. \textsuperscript{1}H NMR (400 MHz, d\textsubscript{6}-DMSO): \(\delta\) (ppm) 12.03 (2H, s, imidazole NH), 8.75 (2H, d, \textit{o}-Ph), 7.63 (2H, t, \textit{m}-Ph), 7.29 (1H, t, \textit{p}-Ph), 7.00 (4H, s, imidazole CH\textsubscript{3}), 6.84 (4H, s, H\textsubscript{2}), 3.42 (12H, s, imidazole CH\textsubscript{3}). \textsuperscript{13}C NMR (100 MHz, d\textsubscript{6}-DMSO): \(\delta\) (ppm) 160.1 (imidazole CS), 138.9 (\textit{o}-Ph), 131.8 (\textit{m}-Ph), 127.1 (\textit{p}-Ph), 119.7 (imidazole CH), 115.1 (imidazole CH\textsubscript{3}), 33.4 (imidazole CH\textsubscript{3}). \textit{FT-IR} / cm\textsuperscript{-1}: 3107 s, 2898 w, 1659 w, 1576 w, 1357 s, 1279 s, 933 w, 731 m, 689 s.

- **Synthesis of 1 from [BiPh(4-MTT)\textsubscript{2}] and the disulfide (4-MTT)\textsubscript{2}**

**Synthesis of [BiPh(4-MTT)\textsubscript{2}]**

In a Schlenk flask under a dry N\textsubscript{2} atmosphere 2-mercapto-1-methylimidazole (0.23 g, 2.00 mmol) was lowly added to a dry methanol solution (10.0 mL) of NaOH pellets (0.08 g, 2.00 mmol). The resultant colourless solution was cooled below 0 °C and phenylbismuth dichloride (0.36 g, 1.00 mmol) added as a solid. The reaction mixture was stirred for overnight and resultant precipitate collected by filtration and washed with methanol and ethanol. Yield: 0.35 g (69.0 %). Mp: 281 °C (dec.). \textsuperscript{1}H NMR (400 MHz, d\textsubscript{6}-DMSO): \(\delta\) (ppm) 8.32(1H, s, triazole CH), 8.28 (2H, d, \textit{o}-Ph), 7.55 (2H, t, \textit{m}-Ph), 7.33 (1H, t, \textit{p}-ph), 3.42 (6H, s, triazole CH\textsubscript{3}). Anal Calc for BiC\textsubscript{12}H\textsubscript{13}N\textsubscript{6}S\textsubscript{2}: C; 28.01, H; 2.55, N; 16.34. Found: C; 28.24, H; 2.83, N; 16.39.
To a hot solution of [BiPh(4-MTT)$_2$] (0.26 g, 0.50 mmol) in toluene (25.0 mL) was added the pre-prepared disulfide (4-MTT)$_2$[27] (0.12 g, 0.50 mmol) and the reaction mixture heated to reflux for 12 h. The yellow product thus obtained was washed several times with acetone. Yield 0.25 g (63.0 %). All analysis was consistent with the formation of [BiPh(4-MTT)$_4$], 1.

• **Crystallographic data:**

Crystallographic data of compound 4 was collected at the MX1 beamline at the Australian Synchrotron, Melbourne, Victoria, Australia with silicon monochromated MoKa radiation (λ = 0.71070 Å). All data was collected at 100 K, maintained using an open flow of nitrogen. The software used for data collection and reduction of the data were BluIce and XDS. Crystallographic data for compound 3 was obtained on an OXFORD Gemini Ultra equipped with an OXFORD Cryosystems 700 Cryostream and cooled to 123(1) K. Data was collected with monochromatic (graphite) Mo Ka radiation (λ = 0.71073 Å) and processed using the CrysAlisProv 1.171.34.36 software; Lorentz, polarization and absorption corrections (multi-scan) were applied. Compounds 3 and 4 were solved and refined with SHELX-97. All non-hydrogen atoms were refined with anisotropic thermal parameters unless otherwise indicated and hydrogen atoms were placed in calculated positions using a riding model with C-H = 0.95-0.98 Å and \( U_{iso}(H)=xU_{iso}(C) \), x = 1.2 or 1.5. Data has been deposited with the Cambridge Crystallographic Database and have the numbers: CCDC 922418 for 3 and 922417 for 4.


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Figure S1: $^1$H NMR spectrum of complex 1 in d$_6$-DMSO

Figure S2: $^{13}$C NMR spectrum of complex 1 in d$_6$-DMSO
**Figure S3**: $^1$H NMR spectrum of complex 2 in d$_6$-DMSO

**Figure S4**: $^{13}$C NMR spectrum of complex 2 in d$_6$-DMSO
Figure S5: $^1$H NMR spectrum of complex 3 in d$_6$-DMSO

Figure S6: $^{13}$C NMR spectrum of complex 3 in d$_6$-DMSO
Figure S7: $^1$H NMR spectrum of complex 4 in d$_6$-DMSO

Figure S8: $^{13}$C NMR spectrum of complex 4 in d$_6$-DMSO
**Figure S9**: XRD pattern for electrodeposited bismuth metal (red) of complex 1 and 2. Background scan is shown in black.

**Figure S10**: Steady state voltammogram at a GC electrode for the reduction of 1.0 mM complex 2 in DMSO solution (0.1 M Bu4NPF6), scan rate (100 mV/s).
**Figure S11:** Cyclic voltammogram in DMSO solution (0.1 M Bu₄NPF₆) at a GC electrode using a scan rate of 100 mV/s for 1.0 mM complex 2 when potential is switched after process E.

**Figure S12:** Cyclic voltammogram in DMSO solution (0.1 M Bu₄NPF₆) at a GC electrode using a scan rate of 100 mV/s for 1.0 mM complex 2 when potential is switched after process F.
**Figure S13:** Cyclic voltammogram in DMSO solution (0.1 M Bu₄NPF₆) at a GC electrode using a scan rate of 100 mV/s for 1.0 mM complex 4 when potential is switched after process E.