

OPTICALLY ACTIVE BISMUTH HETEROBIMETALLIC COMPLEXES CONTAINING ALKALI METAL-CAPPED BINAPHTHOXIDE LIGATION

LUKE E. TURNER¹, MATTHEW G. DAVIDSON², AMANDA J. CHMURA²,
MATTHEW D. JONES²

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Abstract. *The reaction of monometallated (Li, Na, K) (R)-2,2'-dihydroxy-1,1'-binaphthyl (BINOL) with [Bi(OBu^t)₃] affords optically pure bismuth tris(binaphthoxides) with three capping Group I counterions. The stable monomeric complexes have been characterised in solution and the solid state and exhibit structural features similar to previously reported lanthanide analogues. The solution and solid state analysis are reported as well as the catalytic application of the complexes to an asymmetric Michael addition reaction. NMR analysis suggests the octahedral structure is maintained in solution, and the moderate stability of the complexes in the solid state allows for handling under ambient conditions without significant decomposition. The title complexes effectively catalyze the Michael addition of dimethyl malonate to cyclohexenone, albeit with minimal chiral induction.*

Keywords: *bismuth aryloxides, heterobimetallic complexes, trischelate octahedral complexes, asymmetric Michael addition.*

1. INTRODUCTION

Since the initial reports of an effective, asymmetric mixed alkali/rare-earth metal catalyst by Shibasaki [1-6], a multitude of literature concerning heterobimetallic complexes has appeared [7, 8]. The enantioselectivity of these “chemzymes” toward a range of organic transformations is attributed to the synergism of the proximal Bronsted basic and Lewis acidic sites, analogous to an enzymatic structure [9]. Research of heterobimetallic complexes has spanned a wide range of metals including main group and transition metals [10]. Heterobimetallic complexes containing alkali and p-block metals, as well as alkali-lanthanides, have proven to be among the most selective and well-studied catalysts. Given the efficacy of heterobimetallic complexes toward a variety of synthetic applications and our interest in the bismuth aryloxides as viable Lewis acid catalysts, we have endeavored to explore routes toward mixed alkali metal-bismuth complexes. The use of bismuth halides, triflates, and triflamides as Lewis acid catalysts has been reported in Diels-Alder [11-13] and other transformations [14-24], and these complexes represent a significant class of green metal catalysts. However, the application of well-defined, monomeric bismuth aryloxides

¹ The Meadows School, 8601 Scholar Lane, Las Vegas, NV 89128, United States.

E-mail: moleoffun@gmail.com.

² University of Bath, Department of Chemistry, Claverton Down, Bath BA2 7AY, United Kingdom.

E-mail: m.g.davidson@bath.ac.uk.

[25-35] as Lewis acid catalysts remains unexplored, with no reports of structurally characterized chiral aryloxide complexes listed in the Cambridge Structural Database (CSD) [36, 37]. Herein, we report the synthesis and characterization of optically pure bismuth-alkali metal complexes supported by binaphthoxide ligands. Details of the solution and solid state analysis are presented in the context of structural comparisons to the rare-earth analogues and potential catalytic function. In addition, preliminary results of a catalytic asymmetric Michael addition using the title complexes are reported.

2. EXPERIMENTAL

2.1. MATERIALS

All operations were performed under dry argon atmosphere using standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from sodium/benzophenone [38] or purified by sequential elution over activated alumina and copper catalyst (R3-11) columns [39], followed by storage under dry argon. Pentane was degassed and dried over freshly activated 5 Å molecular sieves, followed by storage under dry argon. All reagents were purchased from Aldrich Chemical Co., Inc. (Gillingham, United Kingdom) unless otherwise noted and used without further purification. (*R*)-2,2'-dihydroxy-1,1'-binaphthyl (BINOL) was purchased from RCA Separations (Freiburg, Germany). Tris(*tert*-butoxy)bismuth, [Bi(OC(CH₃)₃)₃] [40], was prepared using a previously reported procedure. Tetrahydrofuran-*d*₈ (THF-*d*₈) and dimethylformamide-*d*₇ (DMF-*d*₇) were purchased from Aldrich Chemical Co., Inc. (Gillingham, United Kingdom) and dried over freshly activated 5 Å molecular sieves prior to use.

2.2. SYNTHESSES & REACTIONS

2.2.1. Synthesis of [Li₃Bi(*R*-O₂C₂₀H₁₀)₃(THF)₆] (1)

A sample of (*R*)-2,2'-dihydroxy-1,1'-binaphthyl (2.00 g, 6.98 mmol) in 40 mL of THF was cooled to 0 °C as *n*-butyllithium (4.65 mL of a 1.5 M solution in hexanes, 7.0 mmol) was added dropwise via syringe. The white slurry was stirred for 30 min as a solution of [Bi(OC(CH₃)₃)₃] (0.98 g, 2.3 mmol) in THF was added via cannula. The orange mixture was stirred overnight and evacuated to dryness affording an orange powder. The crude material was dissolved in 50 mL of THF, filtered over a pad of Celite, and layered with pentane. On standing for two days at room temperature, yellow-orange plates of **1** suitable for X-ray analysis was isolated (CCDC 611474). The filtrate produced a second crop of crystals on standing overnight (2.65 g, 75.7%).

2.2.2. Synthesis of [Na₃Bi(*R*-O₂C₂₀H₁₀)₃(THF)₆] (2)

A sample of (*R*)-2,2'-dihydroxy-1,1'-binaphthyl (2.00 g, 6.98 mmol) in 40 mL of THF was cooled to 0 °C as sodium bis(trimethylsilyl)amide (7.0 mL of a 1.0 M solution in THF, 7.0 mmol) was added dropwise via cannula. The white slurry was stirred for 30 min and then evacuated to dryness affording a white residue. The solid was dissolved in 40 mL of THF and cooled to 0 °C as a solution of [Bi(OC(CH₃)₃)₃] (0.98 g, 2.3 mmol) in THF was added via cannula. A yellow precipitate was observed and the mixture was slowly warmed to rt and

stirred for 8 hours. The solvent was removed under vacuum affording a bright yellow solid that was slightly soluble in THF. A 1.75 gram portion was suspended in 15 mL of THF and heated to 80 °C in a sealed tube. On cooling, yellow needles of **2** suitable for X-ray diffraction analysis was produced (CCDC 611474). The remaining crude material was rinsed with cold THF (3 x 5 mL) and dried under reduced pressure (3.35 g, 94%). Calculated elemental analysis for C₈₄H₈₄O₁₂Na₃Bi: C, 64.53, H, 5.42. Found: C, 64.18, H, 5.38.

2.2.3. Synthesis of [K₃Bi(R-O₂C₂₀H₁₀)₃(THF)₆] (**3**)

A sample of (*R*)-2,2'-dihydroxy-1,1'-binaphthyl (2.00 g, 6.98 mmol) in 40 mL of THF was cooled to 0 °C as potassium bis(trimethylsilyl)amide (1.4 g, 7.0 mmol) in 30 mL of THF was added dropwise via cannula. The white slurry was stirred for 30 min. and then evacuated to dryness affording a white residue. The solid was suspended in 40 mL of THF and cooled to 0 °C as a solution of [Bi(OC(CH₃)₃)₃] (0.98 g, 2.3 mmol) in THF was added via cannula. The bright yellow solution was slowly warmed to room temperature and stirred for 8 hours. The solvent was removed under vacuum affording a bright yellow solid that was dissolved in 50 mL of THF, filtered over Celite, and layered with pentane. On standing for days, yellow plates of **3** were isolated. The filtrate produced two additional crops of crystals on standing for days (3.08 g, 84%).

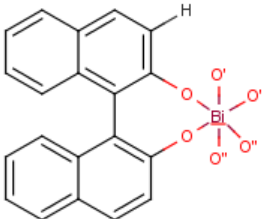
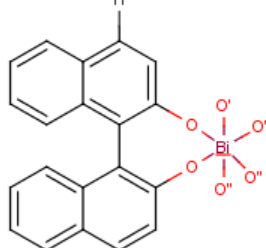
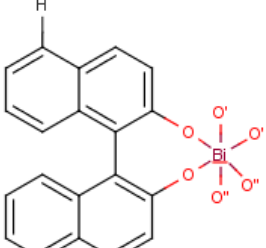
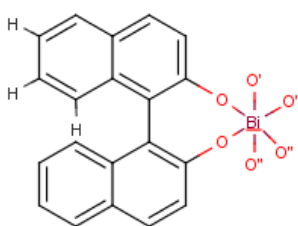
2.2.4. General procedure for the catalytic synthesis of 3-[bis(methoxycarbonyl)methyl]cylco-hexanone

A solution of the bismuth complex (0.16 mmol) in THF (20 mL) was cooled to 0°C under an argon atmosphere, as 2-cyclohexen-1-one (350 µL, 3.1 mmol) and dimethyl malonate (290 µL, 3.1 mmol) were sequentially added dropwise via syringe. The solution was slowly warmed to room temperature over a period of 2 h and stirred an additional 6 h. The reaction mixture was quenched with H₂O and extracted with ethyl acetate (3 x 30 mL). The combined extracts were washed with saturated NaHCO₃, H₂O, and brine, followed by drying over MgSO₄. The solvent was removed by rotary evaporation to afford a yellow oil that was purified by flash column chromatography (silica gel: 10% v/v acetone/hexanes). The ¹H and ¹³C NMR spectra of the clear oil were identical to the previously reported spectral data. Enantiomeric purity was determined by high performance liquid chromatography (HPLC) using a Daicel Chiralpak AS-H chiral stationary phase and 10% 2-propanol in hexanes as the mobile phase with an elution rate of 0.5 ml/minute. Spectroscopic detection of the eluted sample was monitored at a wavelength of 210 nm and retention times (t_R) of the (+) and (-) enantiomers were determined: t_R(+) = 62 min, t_R(-) = 73 min. The absolute configurations (*R,S*) of the eluted isomers were established by comparison to literature data [41].

2.3. INSTRUMENTS & METHODS

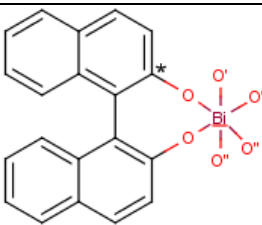
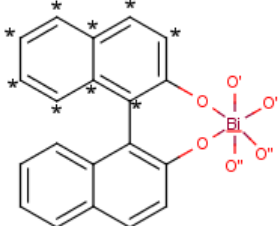
The ¹H and ¹³C NMR spectra were acquired using a Bruker Advance 300 spectrometer and referenced to the protio impurities of the solvents as internal standards. The ⁷Li NMR spectra were acquired using a Bruker Advance 400 spectrometer and referenced to lithium chloride. Thermogravimetric analysis was performed using a Perkin Elmer Thermogravimetric Analyzer TGA 7. Elemental analysis was obtained from Elemental Microanalysis Limited (Okehampton, United Kingdom). Mass spectra, using matrix-assisted laser desorption-ionization (MALDI) were acquired from the EPSRC National Mass Spectrometry Service Center, Swansea, United Kingdom.

Table 1. ^1H and ^7Li NMR (THF- d_8 , 21°C) chemical shift data for 1- 3.

Nuclei	1	2*	3
	δ 7.36, doublet $^3J(^1\text{H}-^1\text{H}) = 7.6$ Hz	δ 7.02, doublet $^3J(^1\text{H}-^1\text{H}) = 8.7$ Hz	δ 7.36, doublet $^3J(^1\text{H}-^1\text{H}) = 7.6$ Hz
	δ 7.72, doublet $^3J(^1\text{H}-^1\text{H}) = 7.8$ Hz	δ 7.64, doublet $^3J(^1\text{H}-^1\text{H}) = 7.8$ Hz	δ 7.72, doublet $^3J(^1\text{H}-^1\text{H}) = 7.6$ Hz
	δ 7.65, doublet $^3J(^1\text{H}-^1\text{H}) = 7.7$ Hz	δ 7.50, doublet $^3J(^1\text{H}-^1\text{H}) = 8.4$ Hz	δ 7.65, doublet $^3J(^1\text{H}-^1\text{H}) = 7.7$ Hz
	δ 6.91-6.78, multiplet	δ 6.88-6.82, multiplet	δ 6.91-6.78, multiplet
Li^+	δ 1.97	NA	NA

* ^1H NMR analysis performed using DMF- d_7 (21°C).

Table 2. ^{13}C NMR (THF- d_8 , 21°C) chemical shift data for 1 and 3.

Nuclei	1	3
	δ 160.1	δ 160.1
	δ 136.3, 129.5, 128.4, 128.0, 127.6, 127.1, 124.9, 123.0, 121.5	δ 136.3, 129.5, 128.4, 128.0, 127.6, 127.1, 124.9, 123.0, 121.5

Molecular structures were obtained through the University of Bath departmental facilities. Crystallography data were collected on a Nonius KappaCCD area detector diffractometer using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$), and all structures were solved by direct methods and refined on all F^2 data using the SHELXL-97 suite of programs hydrogen atoms, with the exception of those involved in hydrogen bonding, were included in idealized positions and refined using the riding model [42]. Completed X-ray crystal structure data were deposited in electronic CIF format to the Cambridge Crystallographic Data Centre (CCDC).

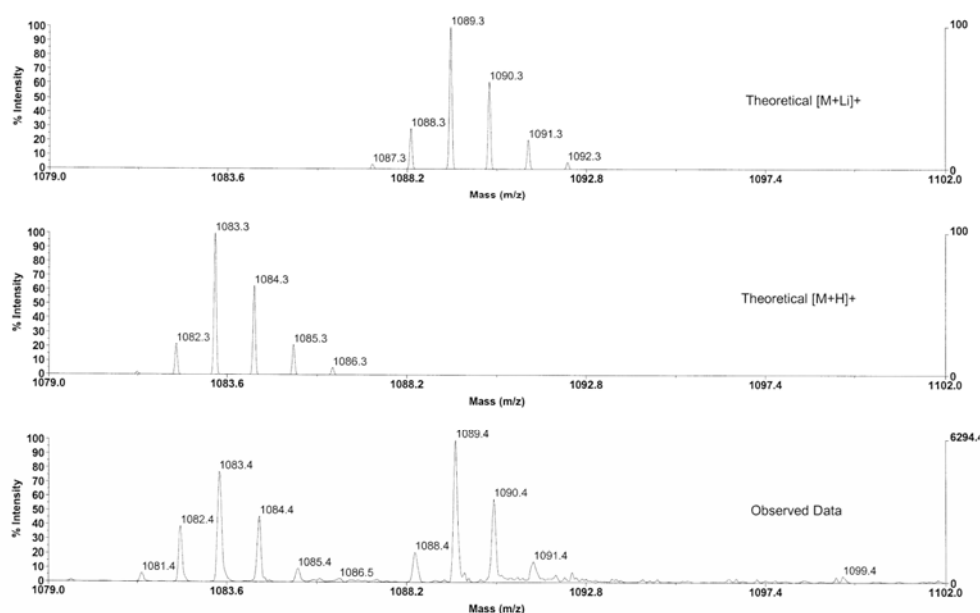


Fig. 1. Theoretical (*top, middle*) and observed (*bottom*) laser desorption/ionization time-of-flight mass spectra for complex 1.

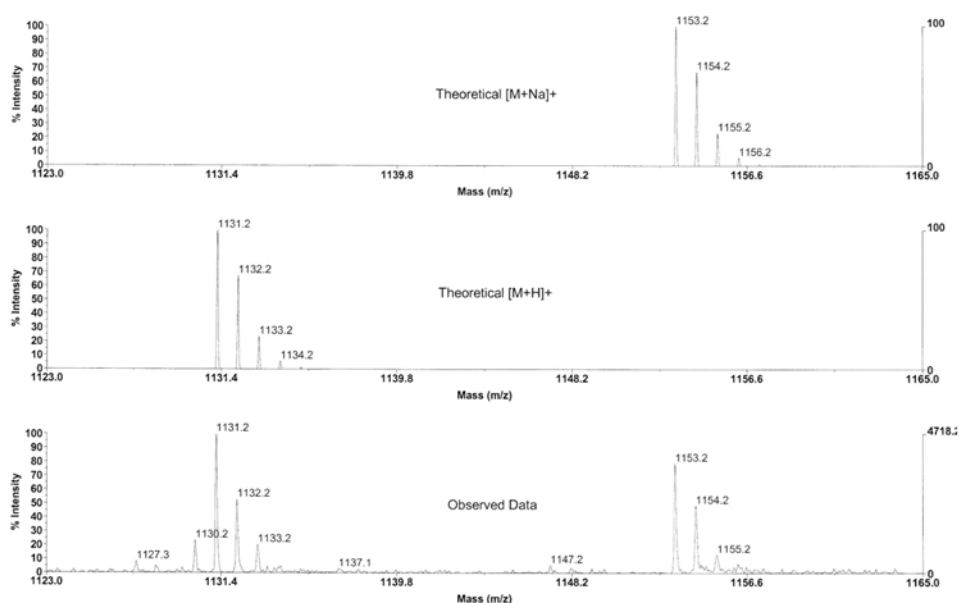


Fig. 2. Theoretical (*top, middle*) and observed (*bottom*) laser desorption/ionization time-of-flight mass spectra for complex 2.

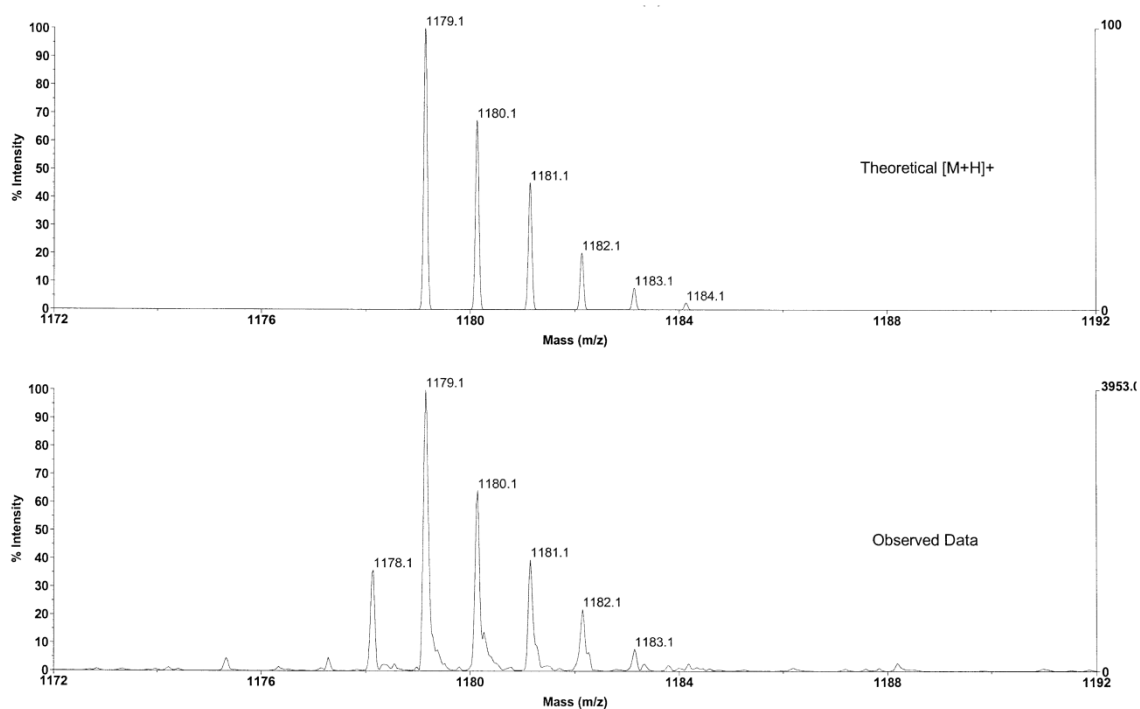


Fig. 3. Theoretical (*top*) and observed (*bottom*) laser desorption/ionization time-of-flight mass spectra for complex 3.

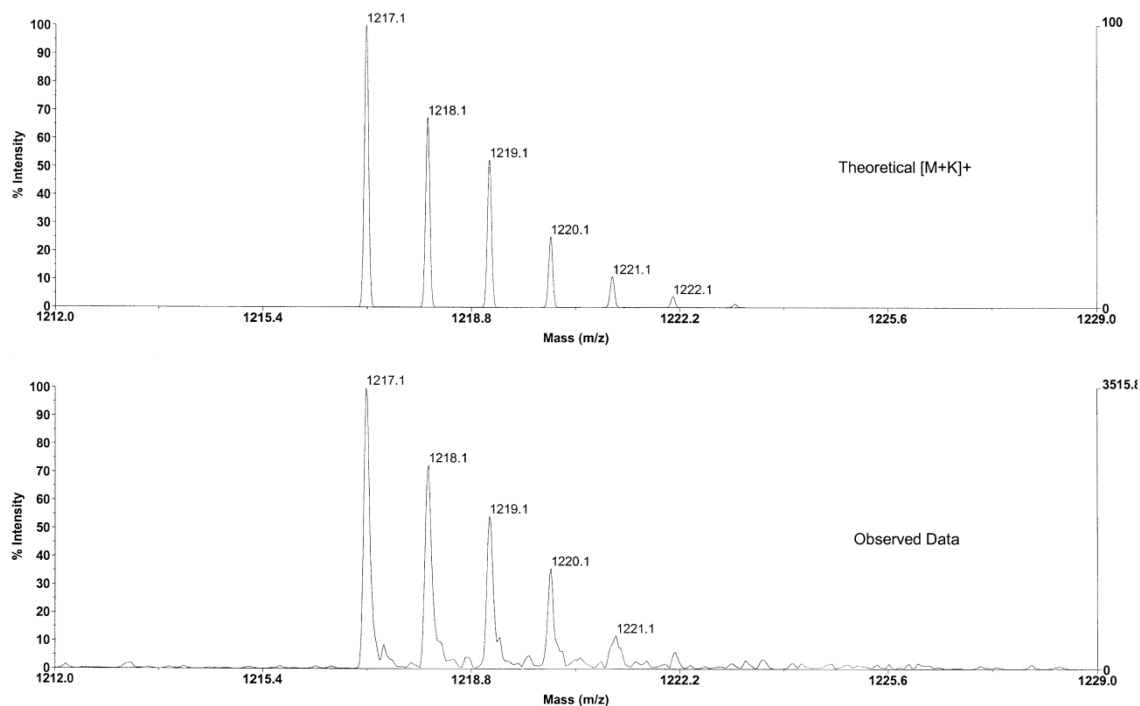


Fig. 4. Theoretical (*top*) and observed (*bottom*) laser desorption/ionization time-of-flight mass spectra for complex 3.

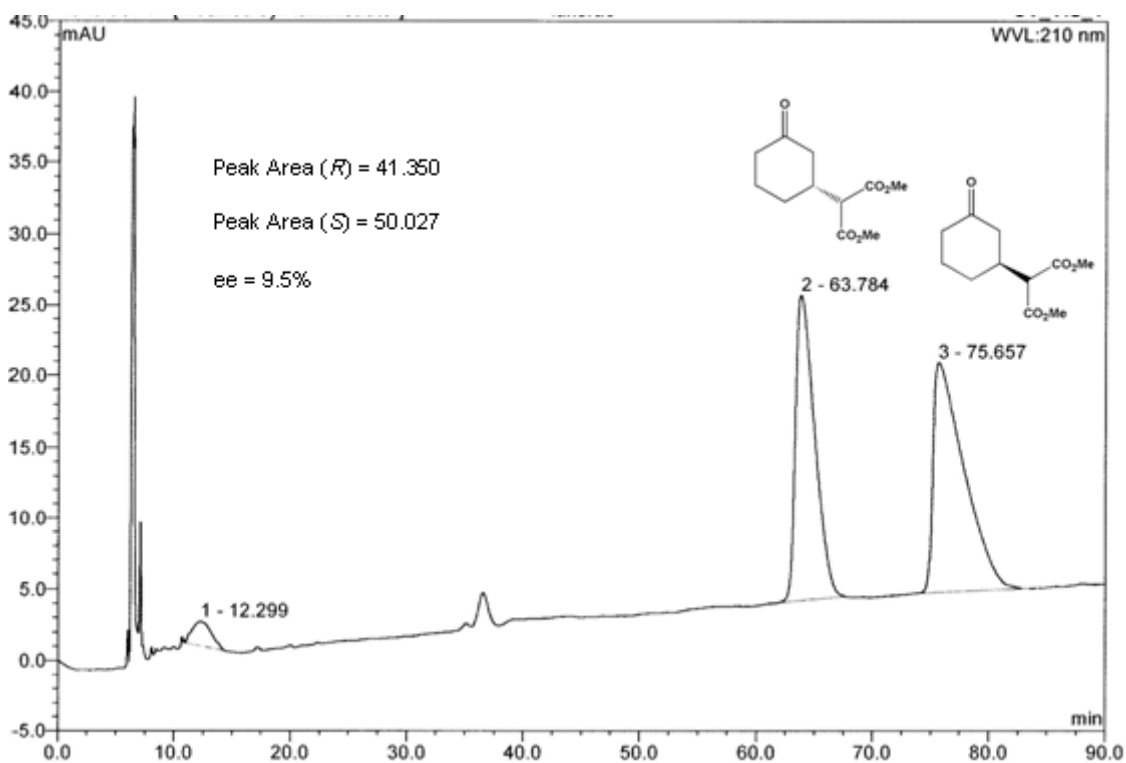


Fig. 5. HPLC analysis of 3-[bis(methoxycarbonyl)methyl]cyclohexanone produced from the Michael addition of dimethyl malonate to 2-cyclohexen-1-one catalyzed by $[\text{Li}_3\text{Bi}(\text{R}-\text{O}_2\text{C}_{20}\text{H}_{10})_3(\text{THF})_6]$ (1).

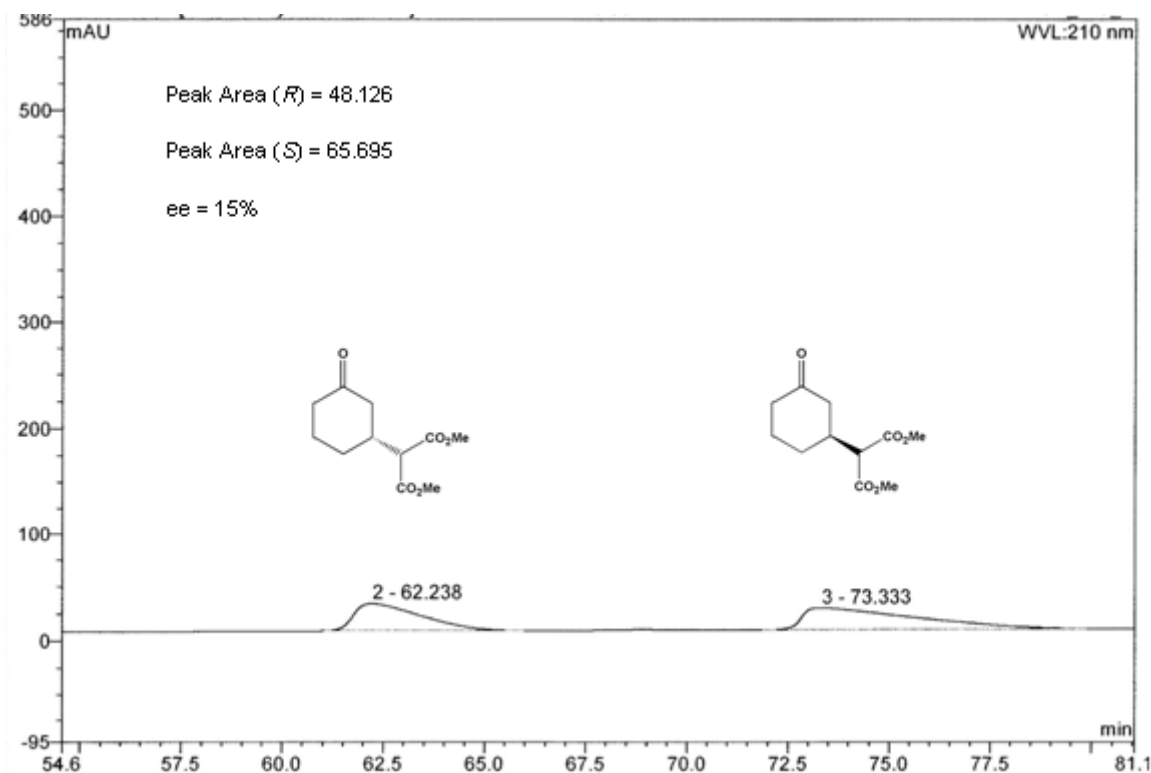


Fig. 6. HPLC analysis of 3-[bis(methoxycarbonyl)methyl]cyclohexanone produced from the Michael addition of dimethyl malonate to 2-cyclohexen-1-one catalyzed by $[\text{Na}_3\text{Bi}(\text{R}-\text{O}_2\text{C}_{20}\text{H}_{10})_3(\text{THF})_6]$ (2).

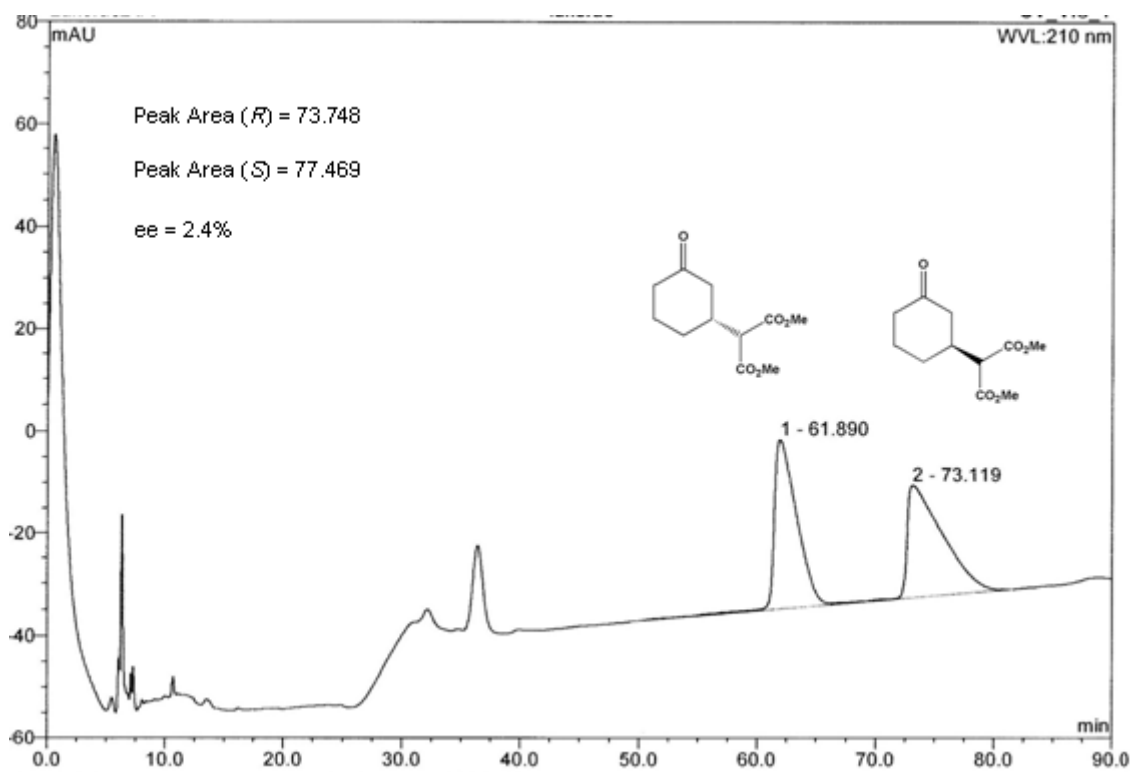


Fig. 7. HPLC analysis of 3-bis(methoxycarbonyl)methylcyclohexanone produced from the Michael addition of dimethyl malonate to 2-cyclohexen-1-one catalyzed by $[K_3Bi(R-O_2C_{20}H_{10})_3(THF)_6]$ (3).

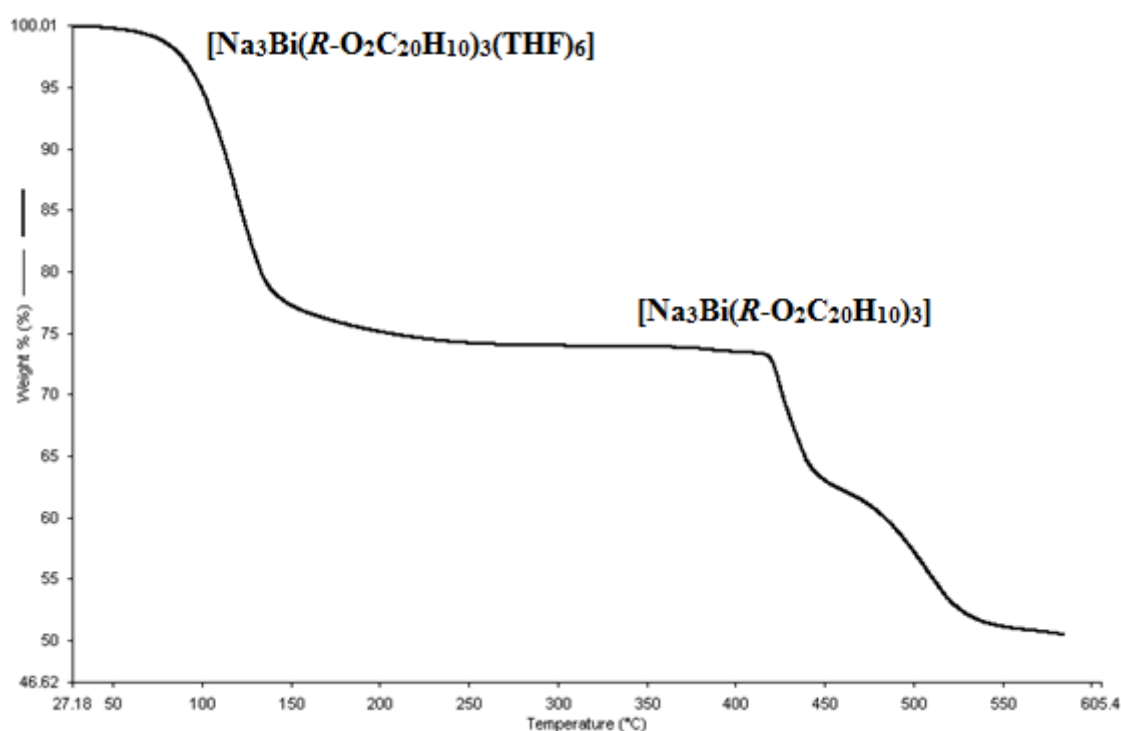


Fig. 8. Thermogravimetric analysis of complex 3.

3. RESULTS AND DISCUSSION

Our previous work toward the synthesis of tripodal bismuth amine tris(phenoxide) complexes [43] has shown that selection of an appropriate bismuth starting material is critical to achieve product conversion in high yield and minimal side reactions. For example, the use of tris(disilylamido)amido bismuth complexes such as $[\text{Bi}(\text{N}(\text{SiMe}_3)_2)_3]$ is undesirable as a significant side reaction occurs involving the silylation of the phenol substrate, as reported by Hanna et al in the synthesis of a bismuth calixarene complex [44]. Alternatively, tris(dialkyl)amido bismuth materials such as $[\text{Bi}(\text{NMe}_2)_3]$ are light sensitive, as well as difficult to synthesize and purify [45]. The metathesis of alkali metal aryloxides with bismuth halides can be complicated by salt coproducts that are incorporated in the resultant complex [35, 46, 47]. In addition, the oxidative coupling of lithiated phenols in the presence of $[\text{BiCl}_3]$ is known and could prove problematic for ortho or para unprotected arene substrates [48]. Whilst $[\text{BiPh}_3]$ reacts cleanly with carboxylic acids and thiols in the absence of solvent [49], only complex mixtures were obtained upon reaction of $[\text{BiPh}_3]$ with monometallated BINOL. The use of metal alkoxides as precursors to aryloxide derivatives has been established for a range of main group and transition metals [50], and our recent success using $[\text{Bi}(\text{OC}(\text{CH}_3)_3)_3]$ for the preparation of bismuth tripodal amine tris(phenoxide)s [38] provided a basis for our exploration of heterobimetallic complexes. Monometallation (Li, Na, K) of three equivalents of (*R*)-2,2-dihydroxy-1,1'-binaphthyl (BINOL) with the appropriate base followed by the addition of $[\text{Bi}(\text{OC}(\text{CH}_3)_3)_3]$ affords the optically pure alkali bismuth tris(binaphthoxide) in high yield (Fig. 9).

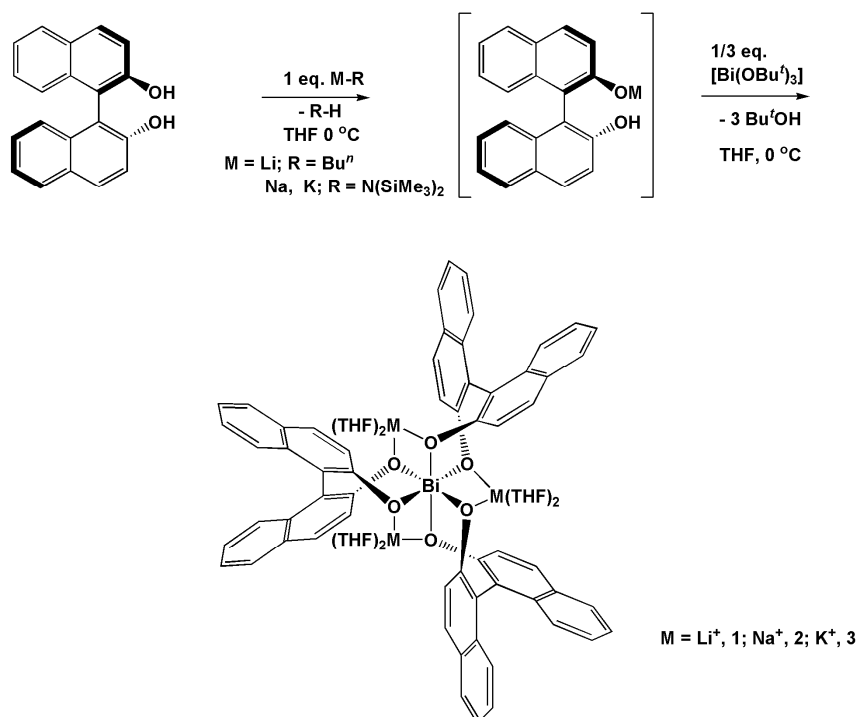


Fig. 9. Synthesis of complexes 1-3.

The lithium and potassium complexes are soluble in THF and were purified by recrystallization from THF/pentane, the sodium adduct is only sparingly soluble in ethereal solvents and was recrystallized from hot THF. The complexes have been analyzed

spectroscopically by NMR (Tables 1 and 2) and contain only one isomer in solution, as confirmed by a single set of signals in the proton and carbon spectra. Decomposition of the heterobimetallic complexes in solution was not observed by ^1H NMR under anhydrous conditions over a period of weeks, the alkali aryloxy fragments do not undergo the oxidative coupling reported for lithium phenoxides. Mass spectrometric (MALDI) analysis of the series of compounds confirms the presence of a trimetallic bismuth tris(binaphthoxide) species (Figs. 1-4), as observed in the previously reported spectra for the analogous rare-earth complexes [51]. The complexes are moderately stable to air and moisture in the solid state and can be manipulated under ambient conditions without decomposition for several hours.

Recrystallization of complexes **1** and **2** produced crystals suitable for X-ray diffraction analysis. The molecular structures are shown in Figs 10 and 11 and collection parameters are outlined in Table 3 [52].

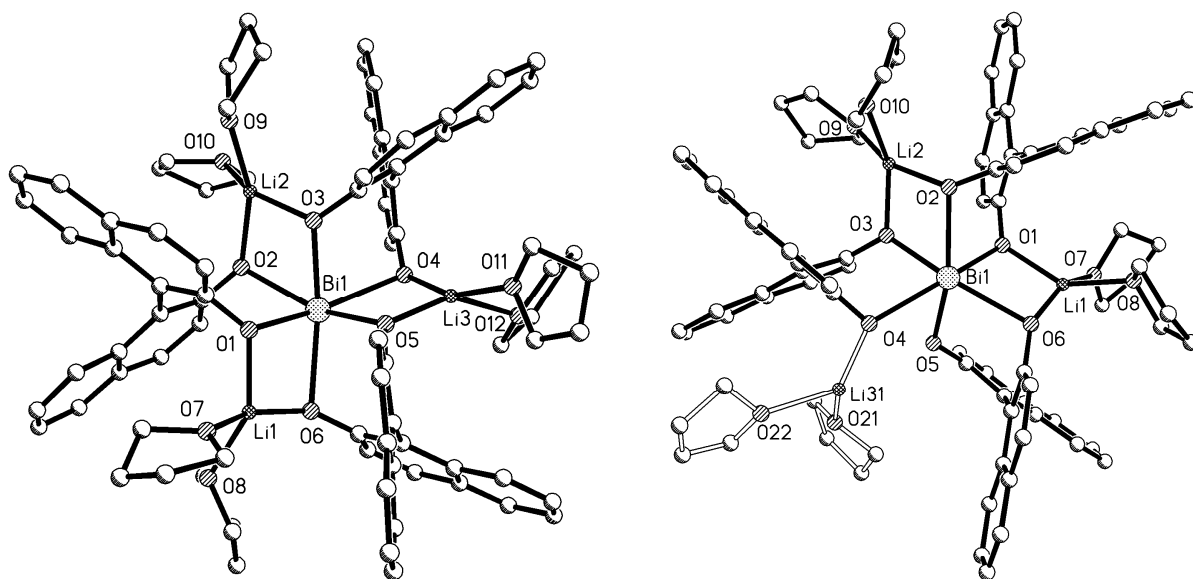


Fig. 10. Molecular structure of complex **1** with each lithium occupying a bridging binaphthoxide position (*left*) and with a $[\text{Li}^+]$ unit in a terminal binaphthoxide position (*right*). H atoms have been omitted for clarity.

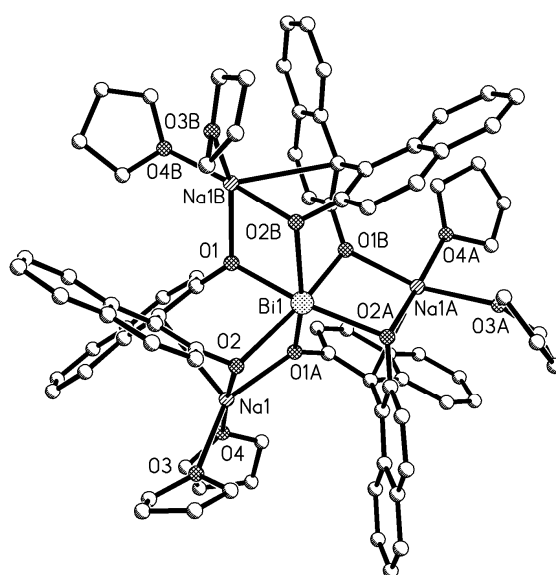


Fig. 11. Molecular structure of complex **2**. H atoms have been omitted for clarity.

Table 3. Crystal data and data collection parameters for 1 and 2.

	1	2
Formula	C ₈₄ H ₈₄ BiLi ₃ O ₁₂	C ₈₄ H ₈₄ BiNa ₃ O ₁₂
FW	1515.31	1563.46
Space Group	<i>P</i> 3 ₂	<i>P</i> 6 ₃
<i>a</i> , Å	14.9083(1)	15.1070(1)
<i>b</i> , Å	14.9082(1)	15.1070(1)
<i>c</i> , Å	28.6778(3)	18.2370(2)
α, deg	90	90
β, deg	90	90
γ, deg	120	120
<i>V</i> , Å ³	5519.88(8)	3604.46(5)
<i>Z</i>	3	2
ρ _{calcd} , g·cm ⁻³	1.368	1.441
<i>T</i> , K	150(2)	150(2)
Radiation, λ	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
<i>R</i>	0.0478	0.0254
<i>R</i> _w	0.0855	0.0590
CCDC No.	611474	611475

The complexes are pseudo-octahedral with Bi-O distances that alternately vary by *ca.* 0.15 Å for each coordinated naphthoxide unit of the bidentate ligands (Tables 4 and 5). The capping alkali metal ions bridge the binaphthoxide ligands and are further coordinated by six THF molecules.

Table 4. Selected bond distances (Å) and angles (°) for [Li₃Bi(R-O₂C₂₀H₁₀)₃(THF)₆] (1).

Bi(1)-O(1)	2.222(3)	Bi(1)-O(2)	2.407(3)
Bi(1)-O(3)	2.231(3)	Bi(1)-O(4)	2.454(4)
Bi(1)-O(5)	2.243(3)	Bi(1)-O(6)	2.441(3)
Li(1)-O(1)	1.913(9)	Li(1)-O(6)	1.884(9)
Li(2)-O(2)	1.948(9)	Li(2)-O(3)	2.00(1)
Li(3)-O(4)	1.94(2)	Li(3)-O(5)	1.94(2)
Li(31)-O(4) ^a	1.84(4)		
O(1)-Bi(1)-O(2)	78.8(1)	O(1)-Bi(1)-O(3)	88.7(1)
O(1)-Bi(1)-O(4)	159.0(1)	O(1)-Bi(1)-O(5)	90.9(1)
O(1)-Bi(1)-O(6)	68.9(1)	O(2)-Bi(1)-O(3)	70.2(1)
O(2)-Bi(1)-O(4)	111.4(1)	O(2)-Bi(1)-O(5)	156.2(1)
O(2)-Bi(1)-O(6)	116.8(1)	O(3)-Bi(1)-O(4)	78.3(1)
O(3)-Bi(1)-O(5)	88.4(1)	O(3)-Bi(1)-O(6)	153.3(1)
O(4)-Bi(1)-O(5)	72.5(1)	O(4)-Bi(1)-O(6)	118.2(1)
O(5)-Bi(1)-O(6)	78.1(1)	O(1)-Li(1)-O(6)	88.2(4)
O(2)-Li(2)-O(3)	85.0(4)	O(4)-Li(3)-O(5)	91.7(7)
Bi(1)-O(1)-Li(1)	104.9(3)	Bi(1)-O(6)-Li(1)	98.0(3)
Bi(1)-O(2)-Li(2)	100.1(3)	Bi(1)-O(3)-Li(2)	104.6(3)
Bi(1)-O(4)-Li(3)	94.4(5)	Bi(1)-O(5)-Li(3)	101.3(5)
Bi(1)-O(4)-Li(31) ^a	144(2)	Li(3)-O(4)-C(31)	139.9(7)
Li(31)-O(4)-C(31) ^a	102(2)		

^aBond distances (Å) and angles (°) for the terminal lithium occupancy.

Table 5. Selected bond distances (Å) and angles (°) for [Na₃Bi(R-O₂C₂₀H₁₀)₃(THF)₆] (2).

Bi(1)-O(1)	2.258(2)	Bi(1)-O(2)	2.415(2)
Na(1)-O(2)	2.292(3)	Na(1)-O(1A)	2.261(3)
O(1)-Bi(1)-O(2)	78.58(8)	O(1)-Bi(1)-O(1A)	87.25(9)
O(1)-Bi(1)-O(2A)	156.27(8)	O(2)-Bi(1)-O(2A)	114.57(4)
O(2)-Na(1)-O(1A)	75.64(9)	Bi(1)-O(2)-Na(1)	101.61(9)
Na(1)-O(2)-C(21)	122.7(2)		

The standard deviations of angles and distances are shown in parentheses.

The structural characteristics of **1** and **2** are comparable to the previously reported rare-earth trischelates, with the absence of coordinated water molecule. Whilst the molecular structure of **3** could not be obtained, thermogravimetric analysis of the recrystallized complex shows a 27% reduction in mass on heating to 300 °C, which corresponds to the loss of six THF molecules. Only the $\Delta(RRR)$ diastereomer is observed for both trischelate octahedral complexes, consistent with the preference of structurally characterized (*S*)-BINOL/rare-earth (La, Pr, Nd, Eu)/alkali (Na) analogues for the $\Lambda(SSS)$ configuration. The preference of tris(naphthoxide) octahedral complexes for $\Delta(RRR)$ and $\Lambda(SSS)$ configurations likely stems from thermodynamic factors associated with ligand steric effects and torsional strain [53]. The solid state molecular structure of **1** contains a partial occupancy in which a lithium ion resides in both bridging (Fig. 2, *left*) and terminal (Fig. 2, *right*) positions. The ⁷Li NMR spectrum of this complex contains a singlet at -1.97 ppm at ambient temperature, however, on cooling to -80 °C additional resonances are observed (Fig. 4). The appearance of multiple Li environments suggests a fluxional process that could be associated with the “hopping” of [Li⁺] from a terminal to bridging mode as observed in the solid state molecular structure. The shifting of [Li⁺] to the terminal position disrupts the symmetry of the helical trischelate configuration, thus inducing inequivalent lithium environments. The observed solution fluxionality, as well as the partial occupancy of [Li⁺] in the solid state is significant, the migration of [Li⁺] to the terminal position exposes the Bi metal center for chelation of a Lewis base (e.g., carbonyl or imine) while potentially activating the Bronsted basic aryloxide fragment for proton abstraction of an acidic substrate. Shibasaki and workers have conducted mechanistic computational simulations of a catalytic asymmetric Michael addition, which involve enone chelation to the central metal with subsequent nucleophilic attack by sodium enolate [51]. The X-ray diffraction and spectroscopic evidence for the alkali metal migration in **1** could suggest a pathway toward the putative substrate coordination/activation.

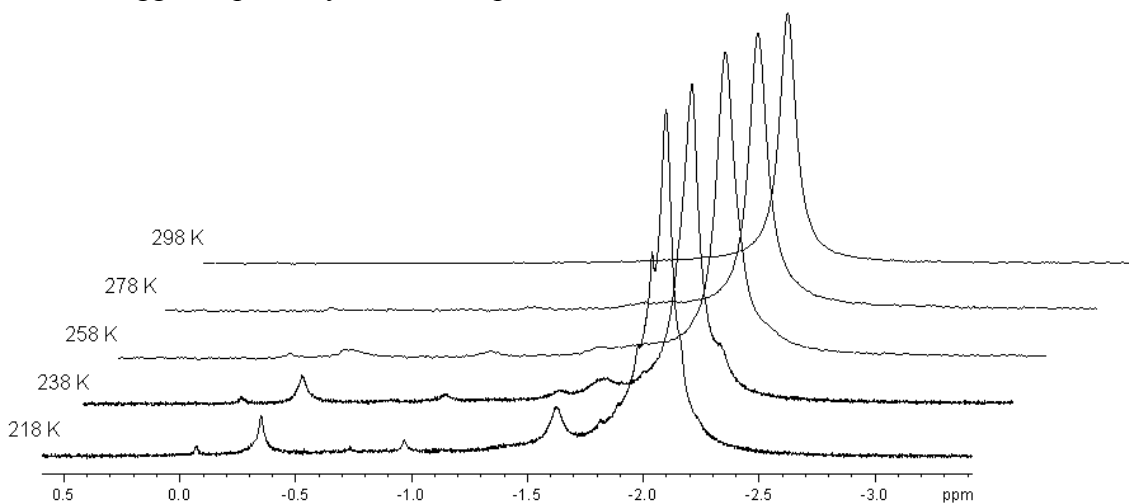


Fig. 12. ⁷Li NMR spectra of **1** on cooling to -100 °C.

The observed fluxionality of the $[Li^+]$ component of **1** prompted investigation of a catalytic transformation requiring Lewis acid and Bronsted base reactants. A survey of the literature suggests the Michael addition of malonates to α,β -unsaturated ketones is a significant reaction in assessing the activity and selectivity of heterobimetallic catalysts [7, 8, 51, 54-57]. The conjugate addition reaction requires activation of the enone π -system, i.e. a Lewis acid, and deprotonation of the malonate to generate the requisite nucleophile. For the title complexes, the 1,4-addition of dimethyl malonate to 2-cyclohexen-1-one in the presence of 5 mol% catalyst was examined (Fig. 13). Whilst the range of catalysts furnished the Michael adduct in high yield (75-84%), minimal enantioselectivity was achieved (Table 4). In contrast, analogous rare-earth catalysts by Shibasaki et al. impart effective stereocontrol ($ee > 90\%$) for a range of synthetic transformations [7, 8, 51, 54-57]. The lack of asymmetric induction may result from the lower oxophilicity of bismuth versus rare-earth metal complexes.

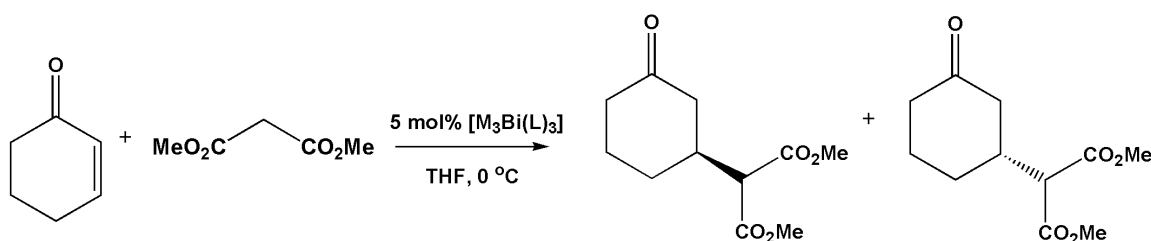


Fig. 13. Catalytic Michael addition of dimethyl malonate to 2-cyclohexen-1-one in the presence of complexes 1-3.

Table 6. Catalytic asymmetric Michael addition of dimethyl malonate to 2-cyclohexen-1-one promoted by complexes 1-3.^a

entry	catalyst	% yield ^b	% ee ^c
1	1	81	10
2	2	75	15
3	3	84	2

^a5 mol% catalyst. ^bIsolated yields after purification. ^cEnantiomeric excess determined by HPLC. Details of the reaction parameters and HPLC conditions provided in the experimental section.

The coordination of the carbonyl moiety to the Bi core is necessary for the cooperative substrate control with adjacent Bronsted basic component, as outlined in the computational model reported by Shibasaki [57]. In addition, small changes in the catalyst structure, e.g. variation of the metal-oxygen bond length by *ca.* 0.1 Å, induce substantial changes in the enantioselectivity of rare-earth (Eu, Nd, Pr, La) metal complexes [51, 57]. The combination of electronic and structural differences in complexes **1-3** versus the rare-earth analogues may account for the lack of asymmetric induction in the investigated Michael addition.

4. CONCLUSIONS

In conclusion we have successfully synthesised and structurally characterized optically active heterobimetallic bismuth complexes containing alkali (Li, Na, K) metal capped binaphthoxides. The solution and solid state analysis of the heterobimetallic complexes confirms the presence of one isomer, $\Delta(RRR)$, consistent with the previously reported rare-earth metal trischelate analogues. Whilst the complexes were found to have minimal asymmetric influence on the Michael addition investigated, further studies of other catalytic transformations will ensue.

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