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Selective Arylation Reactions of Bismuth−Transition Metal Salicylate Complexes

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Heterometallic bismuth−niobium or −tantalum salicylate complexes react with sodium tetraphenylborate to produce complexes in which one or more aryl groups have been transferred from boron to bismuth with the concomitant displacement of a η^2-salicylato ligand. When the previously reported $Bi_2Ta_2(sal)_4(Hsal)_4(OEt)_4$ (**1**) and $BiTa_4(\mu\text{-}O)_4(sal)_4(Hsal)_3(O^iPr)_4$ (**2**) are treated with an alcoholic solution of $NaBPh_4$, the compounds $[PhBi(Hsal)Ta(sal)_2(OEt)_2 \cdot EtOH]_2$ (**3**) and $PhBiTa_4(\mu\text{-}O)_4(Hsal)_2(sal)_4(OEt)_4 \cdot CH_2Cl_2$ (**4**) are produced (sal = $O_2CC_6H_4\text{-}2\text{-}O^{2-}$, Hsal = $O_2CC_6H_4\text{-}2\text{-}OH^-$). The core geometries of the heterometallic complexes are retained. However, if preparations of compound **1** are treated with $NaBPh_4$ without prior isolation of **1**, $[Ph_2BiNb(sal)_2(OMe)_2]_\infty$ (**5**) is produced instead. This compound was characterized both as a solvent-free crystalline form and as one containing a lattice diethyl ether. The compound exhibits a polymeric chain structure that can be viewed as alternating $[Ph_2Bi]^+$ and $[Nb(sal)_2(OMe)_2]^-$ units connected via bridging carboxylate groups. The arylation of the bismuth(III) center proceeds smoothly under mild conditions at room temperature, affording a new means for the mild functionalization of bismuth−transition metal heterometallic complexes.

Introduction

Heterometallic complexes of bismuth with transition metals have been widely investigated, especially because of their interesting structural and reactive features[1−13] as well as their potential utility as precursors for preparing mixed oxide materials,[13−24] and their chemistry remains an active area of research in inorganic and organometallic chemistry. Among these complexes, heterometallic complexes with bridging carboxylate groups have attracted particular interest, owing to their strikingly different structure and reactivity due to the cooperation effects of the metal centers. Hydroxycarboxylate ligands proved useful in producing a large variety of monomers, dimers and other oligomers, and

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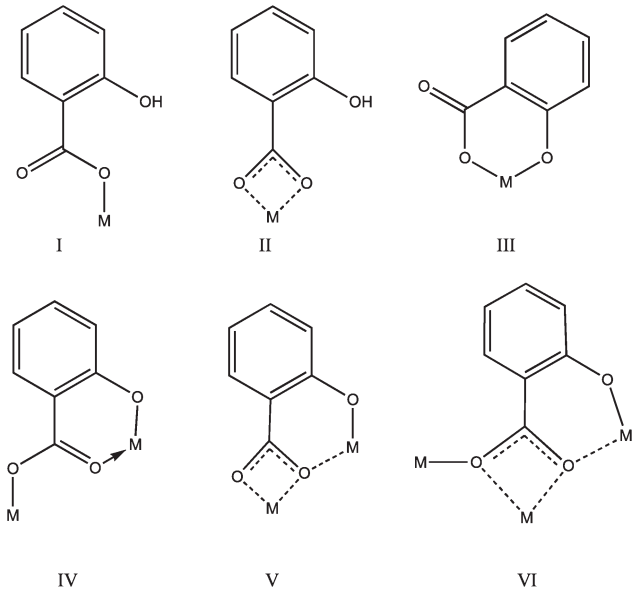
polymers of Bi(III).[25−38] Sometimes these complexes contain additional hydroxide and oxide ligands. The considerable attention to these complexes is mainly due to their relevance to the preparations for the treatment of diverse gastrointestinal disorders, such as Pepto-Bismol (bismuth(III) subsalicylate) and De-Nol (colloidal bismuth subcitrate). In recent work we have reported the syntheses of a variety of heterometallic bismuth−transition metal salicylate complexes which contain additional alkoxide,[16,18,39] β-diketonate,[15] or salen[17] ligands. Salicylic acid ($HO_2CC_6H_4$-2-OH, H_2sal) affords flexibility in binding in that it may be a monoanion with only the carboxylate group deprotonated ($Hsal^- = {}^-O_2CC_6H_4$-2-OH) or a dianion with deprotonation of the phenol OH as well ($sal^{2-} = {}^-O_2CC_6H_4$-2-$O^-$), and a variety of binding modes have been observed, as illustrated in I−VI.



In our attempts to produce more complicated heterometallic complexes containing a third type of metal ion for use as single-source precursors, we treated some of our known bimetallic precursors with $NaBPh_4$.[40] Instead of achieving Na^+ ion incorporation,[41] Ph group substitution for a salicylate ligand attached to bismuth was observed. Subsequently, the reaction of $Bi(O_2CR)_3$ with $NaBAr_4$ (Ar = Ph, C_6H_4-*p*-Me, C_6H_4-*p*-F) was found to be a convenient and general method for the production of $BiAr_3$ complexes.[42] There are multiple examples in the literature in which metal ions abstract aryl groups from BAr_4^- anions,[43−57] although it had not been previously observed for bismuth. These data encouraged us to study the reactivity of bismuth−transition metal heterometallic complexes toward $NaBPh_4$, and three examples are presented herein.

Experimental Section

All manipulations were carried out under a dinitrogen or argon atmosphere using standard Schlenk and glovebox techniques. The solvents methanol (MeOH), toluene, and dichloromethane were dried prior to use. All reagents and chemicals, unless otherwise stated, were purchased from commercial sources. Commercial $BiPh_3$ and H_2sal were dried for 4 h in vacuo and then transferred to the drybox. $Bi_2Ta_2(sal)_4(Hsal)_4(OEt)_4$ (**1**) and $BiTa_4(\mu\text{-}O)_4(sal)_4(Hsal)_3(O^iPr)_4$ (**2**) were obtained according to previously published procedures.[58,59] NMR spectra were recorded at room temperature in d_6-dmso and d_8-THF on a Bruker Avance 400 spectrometer, and the ^{1}H and chemical shifts are reported relative to tetramethylsilane (TMS). The reported infrared data were recorded on a Nicolet 670 FT-IR spectrometer using attenuated total reflectance. C and H analyses were performed at Galbraith Laboratories.

Synthesis of $[PhBi(Hsal)Ta(sal)_2(OEt)_2]_2 \cdot 2EtOH$ (3). A solution of **1** (0.25 g, 0.12 mmol) in CH_2Cl_2 (25 mL) was treated with a solution of $NaBPh_4$ (0.021 g, 0.075 mmol) in 10 mL of absolute ethanol. The resulting colorless solution was stirred at room temperature overnight and then concentrated and stored

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Table 1. Crystallographic Data for **3**−**5** and **5**·Et_2O

	3	**4**	**5**	**5**·Et_2O
formula	$C_{66}H_{68}Bi_2Ta_2O_{24}$	$C_{58}H_{55}BiTa_4Cl_4O_{26}$	$[C_{28}H_{24}BiNbO_8]_2$	$C_{32}H_{34}BiNbO_9$
fw	2025.06	2242.60	790.36	864.48
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$C2/c$	$P2_1$	$P2_1/c$
a (Å)	13.121(3)	26.746(5)	11.9757(8)	10.648(2)
b (Å)	19.459(4)	12.872(3)	18.3032(10)	25.083(5)
c (Å)	14.121(3)	19.769(4)	13.0747(8)	12.195(2)
β (deg)	103.99(3)	94.00(3)	90.225(2)	92.97(3)
V (Å^3)	3498.6(12)	6789.2(9)	2865.9(3)	3252.8(11)
Z	2	4	2	4
D_{calcd} (g cm^{-3})	1.920	2.194	1.832	1.765
λ(Mo Kα) (Å)	0.710 73	0.710 73	0.710 73	0.710 73
T (K)	295	295	193	295
$2\theta_{max}$ (deg)	46.56	46.58	54.94	46.74
abs coeff, mm^{-1}	8.208	9.242	6.578	5.806
no. of data collected	15 138	15 002	20 022	14 382
no. of unique rflns	5032	4889	13 011	4730
no. of params refined	430	390	687	376
F(000)	1936	4216	2072	1688
R1 ($I > 2\sigma(I)$)	0.0218	0.0285	0.0481	0.0486
cryst size (mm)	0.18 × 0.15 × 0.13	0.28 × 0.23 × 0.18	0.32 × 0.21 × 0.13	0.10 × 0.10 × 0.10
wR2 ($I > 2\sigma(I)$)	0.0492	0.0871	0.0968	0.1097
GOF	1.043	1.013	1.069	0.793

at −20 °C for several weeks. Colorless well-formed crystals of **3** that deposited in the flask were collected by filtration in 65% yield. The compound is moisture-sensitive, which has prevented obtaining better elemental analyses. Anal. Calcd (found) for **3**, $C_{33}H_{34}BiTaO_{12}$: C, 39.14 (40.35); H, 3.38 (2.92). NMR (δ, d_6-dmso): 1.06 (t, 6H, CH_3), 1.19 (t, 6H, CH_3), 3.35 (q, 4H, CH_2), 3.43 (q, 4H, CH_2), 6.67−6.74 (m, 4H, Hsal), 7.16−7.43 (m, sal + Ph), 7.76−7.97 (m, sal+Ph), 8.81 (d, 2H, Ph), 12.10 (s, 1H, Hsal). IR (ATR CdSe, cm^{-1}): 3287, 3045, 1628, 1596, 1566, 1530, 1473, 1437, 1404, 1387, 1352, 1247, 1225, 1190, 1146, 1091, 1062, 1004, 992, 927, 883, 856, 824, 757, 713, 690, 649, 556.

Synthesis of $PhBiTa_4(\mu\text{-}O)_4(Hsal)_2(sal)_4(OEt)_4\cdot{}_2CH_2Cl_2$ (4). A solution of **2** (0.18 g, 0.1 mmol) in dry CH_2Cl_2 (25 mL) was treated with a solution of $NaBPh_4$ (0.034 g, 0.1 mmol) in 10 mL of absolute ethanol. The resulting colorless solution was stirred at room temperature overnight and then concentrated and stored at −20 °C for several weeks. Colorless crystals of **4** deposited in the flask and were collected by filtration. The compound is moisture sensitive, which has prevented obtaining better elemental analyses. Yield 52%. Anal. Calcd (found) for **4**, $C_{28}H_{24}BiNbO_8$: C, 31.72 (30.06); H, 2.47 (1.99). NMR (δ, d_8-THF): 1.08 (t, 6H, CH_3), 3.49 (q, 4H, CH_2), 6.68−6.89 (m, 4H, Hsal), 7.31−7.40 (m, sal+Ph), 7.84−7.94 (m, sal+Ph), 8.79 (d, 2H, Ph), 11.01 (2H, OH, Hsal). IR (ATR CdSe, cm^{-1}): 3249, 3052, 1637, 1587, 1569, 1540, 1468, 1421, 1398, 1377, 1361, 1274, 1230, 1183, 1152, 1063, 1012, 985, 892, 868, 805, 741, 702, 691, 638, 552.

Synthesis of $[Ph_2BiNb(sal)_2(OMe)_2]_\infty$ (5). $Bi(Hsal)_3$ was generated in situ from the reaction of $BiPh_3$ (0.44 g, 1.0 mmol) and salicylic acid (0.55 g, 4.0 mmol) in refluxing toluene for 90 min. Afterward, the solvent was removed under vacuum and the yellow paste was dissolved in 20 mL of anhydrous MeOH to give a clear solution. This solution was treated dropwise with niobium ethoxide (240 μL, 1.0 mmol) and stirred at room temperature for 1 h. The reaction was accompanied by the appearance of a yellow color. A solution of $NaBPh_4$ (0.33 g, 1.0 mmol) in 10 mL of anhydrous MeOH was added slowly to the reaction mixture. The solution was stirred overnight at room temperature and then concentrated to one-fourth of its original volume and left for crystallization. Colorless crystals of **5** were obtained in 57% yield. Additional amounts of the complex could be obtained by further concentration of the filtrate. When a concentrated solution of **5** was layered with dry Et_2O and kept overnight at −20 °C, crystals of the polymeric compound **5**·Et_2O were isolated. Anal. Calcd (found) for **5**, $C_{28}H_{24}BiNbO_8$: C, 42.55 (42.61); H, 3.06 (3.04). NMR (δ, d_8-THF, 25 °C): 3.30 (s, 6H, CH_3), 6.65−6.90 (m, Hsal), 7.30−7.39 (m, Hsal+Ph), 7.67 (t, 4H, Ph), 7.85 (m, sal) 8.32 (d, 4H, Ph). IR (ATR CdSe, cm^{-1}): 3249, 3049, 1647, 1593, 1572, 1552, 1495, 1417, 1372, 1344, 1285, 1242, 1198, 1143, 1082, 1005, 989, 897, 841, 801, 739, 675, 624, 563.

X-ray Crystallography. Single-crystals of **3**−**5** and **5**·Et_2O suitable for X-ray crystallography were separated as small plates or blocks either directly from the aforementioned reactions or recrystallized from the corresponding solvents. X-ray crystallographic data are given in Table 1. The structures are shown in Figures 1−3, with the most important bond distances and angles provided in the figure captions. The data for **5** were collected at 173 K on a Rigaku SCXmini diffractometer with 10 s exposure time. The data for **3, 4**, and **5**·Et_2O were collected at 293 K on a Bruker SMART 1000 CCD diffractometer equipped with graphite-monochromated Mo Kα radiation in a hemisphere with 10 or 20 s exposure times. Cell refinement and data reduction for **5** were performed with PROCESS-AUTO (Rigaku, 1998). Data reduction and integration for **3**, **4**, and **5**·Et_2O were performed with the SAINT software, and absorption corrections were applied using the program SADABS. The structures were solved using direct methods and refined by full-matrix least squares on F^2 using SHELXL. Hydrogen atoms were idealized throughout the convergence process. In **3** the molecule possesses crystallographic inversion symmetry, while **4** exhibits crystallographic C_2 symmetry. In **4** one of the alkoxide ligands in the compound was found to be disordered, with the methyl carbon occupying two locations in the crystal lattice. This disorder was modeled with each potential location of the carbon atom receiving partial occupancy. The bond lengths and angles of the two parts of the disordered part of the ligand were constrained to be equal. The disordered alkoxide ligand was refined isotropically. In compound **5**, there are two of the formula units $[Ph_2BiNb(sal)_2(OMe)_2]$ per asymmetric unit.

Results and Discussion

The synthesis of heterometallic arylbismuth−transition metal complexes is performed by treatment of the corresponding heterometallic salicylates $Bi_2Ta_2(sal)_4(Hsal)_4(OEt)_4$

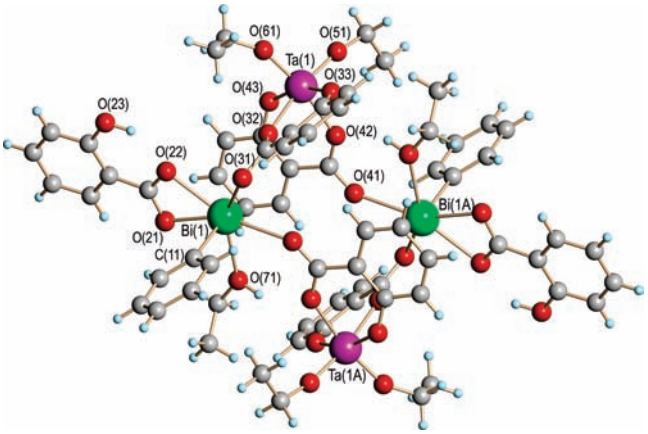


Figure 1. Coordination environment of Bi(III) and Ta(V) in **3**.

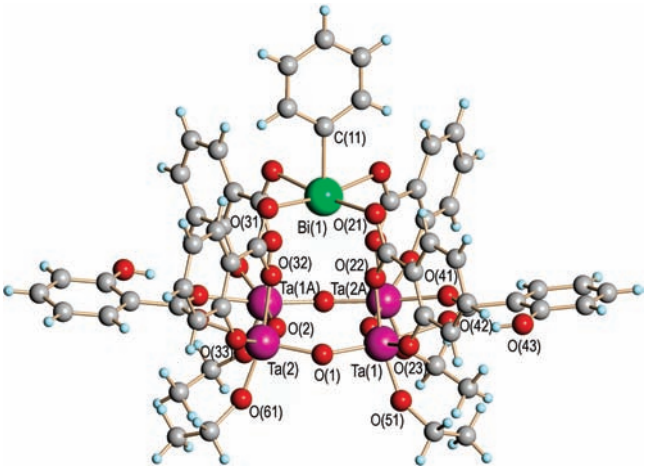


Figure 2. Coordination environment of Bi(III) and Ta(V) in **4**. Lattice solvent molecules have been omitted for clarity.

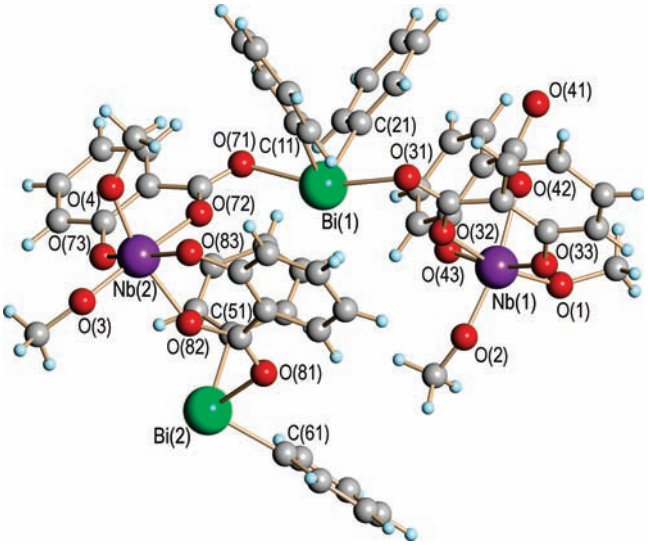
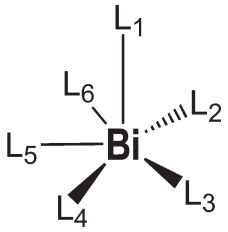


Figure 3. Asymmetric unit in the crystal structure of **5**.

(**1**) and $BiTa_4(\mu\text{-}O)_4(sal)_4(Hsal)_3(O^iPr)_4$ (**2**) with $NaBPh_4$ in either MeOH or EtOH. The products are $[PhBi(Hsal)Ta(sal)_2(OEt)_2 \cdot EtOH]_2$ (**3**) and $PhBiTa_4(\mu\text{-}O)_4(Hsal)_2(sal)_4(OEt)_4 \cdot CH_2Cl_2$ (**4**) and show retention of the fundamental metal salicylate framework. In the case of **4**, the starting material **2** was dissolved first in CH_2Cl_2, which was found incorporated into the crystal lattice. However, if preparations of compound **1** are treated with $NaBPh_4$ without prior isolation of **1**, $[Ph_2BiNb(sal)_2(OMe)_2]_\infty$ (**5**) is produced instead, which suggests in the initial preparation of **1** that the cyclic ring structure is not present. Once the ring structure is formed, however, it would appear to be stable to dissociation or oligomerization.

Scheme 1. Diagram of the Pseudopentagonal-Pyramidal Stereochemistry around Bi(III) in **3**



Regardless of the alkoxide present in the starting materials, the final alkoxides present in the products are derived from the solvent used, indicating facile exchange between the bound ligands and solvent during the synthesis. Use of excess $NaBPh_4$ was avoided to prevent the presence of byproduct or large amounts of unreacted starting materials. The exact stoichiometry of the arylation reaction is not known, and we were not able to determine the fate of the boron-containing product(s). In the case of the reaction to produce $BiAr_3$ using $NaBAr_4$ and $Bi(O_2CR)_3$, it appeared that the stoichiometry was 3:1: i.e., only one aryl group was transferred from the tetraarylborate anion to the bismuth center per carboxylate replaced. It is possible that more than one phenyl group could be available, as the presumed byproduct BPh_3 could also serve as an arylation agent.

The reaction of **1** with $NaBPh_4$ results in the isolation of the product **3** (Figure 1), which is monoarylated at each bismuth center. Increasing the amount of $NaBPh_4$ did not result in bis(arylation) at the bismuth centers or in higher yields.[60] The structural integrity of the complex is preserved on substitution of the salicylate ligand. The bismuth center in the complex is six-coordinate and adopts a distorted-pentagonal-pyramidal geometry (Scheme 1). In terms of the terminology introduced by Shimoni-Livny et al.[61] for Pb(II), the geometry of Bi(III) can be assigned as *hemidirected*. The aryl ligand occupies the apical position of the bismuth coordination sphere, while the basal plane is completed by interactions with a residual terminal salicylate ligand, two dative interactions with the carboxyl groups of adjacent tantalum−salicylate complexes, and a coordinated ethanol molecule. The $Bi-C_{aryl}$ bond distance is 2.234(5) Å, which is slightly shorter than the $Bi-C_{aryl}$ bond distance reported for $BiPh_3$ (2.268 Å). The Bi(III) center also exhibits weak π interactions with an aryl ring of a salicylate ligand. This π interaction is found trans to the Ph group. A similar π interaction is observed in **1**. The Bi−centroid distance in **3** is 3.655 Å and is significantly longer than what is observed for **1** ($d_{Bi-centroid}$ = 3.393 Å). The weakening of the π interaction of the bismuth center with the salicylate ligand is consistent

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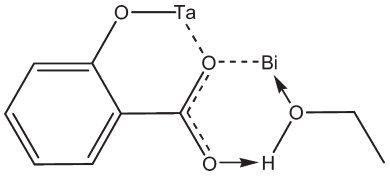
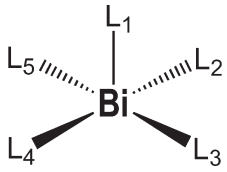
Scheme 2. Diagram of the Hydrogen-Bonding Interaction of the Coordinated Ethanol Molecule in **2**



Scheme 3. Diagram of the Pseudosquare-Pyramidal Stereochemistry around Bi(III) in **4**



with what is expected from the replacement of a salicylate ligand with the more electron-rich phenyl moiety. The Bi−O bond distances in the complex range from 2.393(3) to 2.528(4) Å. The identity of the coordinated solvent molecule as ethanol and not ethoxide has been confirmed both by structural analysis and by charge balance considerations of the overall molecule. The $Bi-O_{ethanol}$ bond distance ($d = 2.490(4)$ Å) is significantly longer than the Bi−O bonds found for terminally bound bismuth alkoxides (d_{Bi-O} = 2.07−2.17 Å)[62−67] and is at the shorter end of the range for the few other structurally characterized examples of an alcohol coordinated to a bismuth(III) metal ion.[68,69] For example, in $Bi(Hsal)_3(phen)(HOMe)$ (phen = 1,10-phenanthroline) the distance is 2.929(4) Å, while in the cation $[Bi(HOCH_2CH_2OCH_2CH_2O)_3(HOCH_2CH_2OCH_2CH_2OH)]^{3+}$ the values of chelating alcohol groups are in the range 2.61(2)−2.73(2) Å[68] and in $BiCl_3$(MeOH)(18-crown-6) the distance is 2.549(9) Å. The proton on the coordinated ethanol molecule was located from the residual electron density map during refinement of the single-crystal X-ray diffraction data and is oriented toward a carbonyl oxygen atom of an adjacent salicylate ligand (O···O separation 2.769(5)Å). A diagram of the ethanol coordination mode to the bismuth center, including hydrogen bonds is provided in Scheme 2. Compound **3**, as for the majority of the crystallographically characterized aryl−bismuth complexes, displays a *hemidirected* pentagonal-bipyramidal geometry. Thus, the related monometallic aryl−bismuth(*bis*)-salicylate adducts with bipyridine and phenanthroline contain the aryl group in the apical position of the Bi(III) coordination sphere, the base of the pentagonal pyramid being completed by three carboxylate oxygen atoms of one monodentate and one bidentate salicylate ligand and two nitrogen atoms of the chelating diamine ligand.[67] Other structurally characterized $PhBi(O_2CR)_2$ complexes, including $[PhBi(O_2CCH_2Cl)_2]$,[70] $[PhBi(O_2CCH(CH_3)CH_2GePh_3)_2]$,[71] $[PhBi(O_2CC_6H_2F_3\text{-}3,4,5)_2]$,[72] and $[PhBi\{(2\text{-}C_5H_4N)CO_2\}_2]$[73] adopt similar coordination geometries around each Bi center.

Like **1**, reaction of **2** with $NaBPh_4$ results in retention of the overall metal framework of the parent complex and formation of the monoarylated complex **4**. This illustrates the specificity of the substitution for salicylate bound to the bismuth center. The structure of **4** consists of a tetrameric Ta_4O_4 ring system, capped by a bismuth−aryl unit by means of bridging carboxylate groups of the fully deprotonated

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complexes **3** and **4**

3		**4**	
Bi(1)−C(11)	2.234(5)	Bi(1)−C(11)	2.246(10)
Bi(1)−O(21)	2.434(3)	Bi(1)−O(21)	2.384(5)
Bi(1)−O(22)	2.439(3)	Bi(1)−O(31)	2.470(5)
Bi(1)−O(31)	2.393(3)	Ta(1)−O(22)	2.073(5)
Bi(1)−O(71)	2.489(3)	Ta(1)−O(23)	1.970(5)
Bi(1)−O(41A)	2.528(4)	Ta(1)−O(1)	1.909(5)
Ta(1)−O(32)	2.104(3)	Ta(1)−O(41)	2.138(5)
Ta(1)−O(33)	1.950(4)	Ta(1)−O(51)	1.836(5)
Ta(1)−O(42)	2.092(3)	Ta(2)−O(32)	2.062(5)
Ta(1)−O(43)	1.944(4)	Ta(2)−O(33)	1.967(5)
Ta(1)−O(51)	1.838(4)	Ta(2)−O(61)	1.844(5)
Ta(1)−O(61)	1.838(4)	Ta(2)−O(2)	1.887(5)
C(11)−Bi(1)−O(21)	87.85(16)	C(11)−Bi(1)−O(21)	85.08(15)
C(11)−Bi(1)−O(22)	89.37(14)	C(11)−Bi(1)−O(31)	86.84(13)
C(11)−Bi(1)−O(31)	84.30(15)	O(21)−Bi(1)−O(31)	85.2(2)
C(11)−Bi(1)−O(41A)	89.31(16)	O(21)−Bi(1)−O(31A)	94.3(2)
C(11)−Bi(1)−O(71)	84.15(16)	O(21)−Bi(1)−O(21A)	170.2(3)
O(21)−Bi(1)−O(31)	134.44(11)	O(31)−Bi(1)−O(31A)	173.7(3)
O(31)−Bi(1)−O(22)	81.50(11)	O(23)−Ta(1)−O(22)	80.4(2)
O(21)−Bi(1)−O(22)	53.55(11)	O(22)−Ta(1)−O(41)	82.0(2)
O(31)−Bi(1)−O(71)	144.90(12)	O(23)−Ta(1)−O(41)	82.3(2)
O(21)−Bi(1)−O(71)	77.98(11)	O(51)−Ta(1)−O(1)	99.8(2)
O(22)−Bi(1)−O(71)	131.33(11)	O(1)−Ta(1)−O(23)	101.7(2)
O(31)−Bi(1)−O(41A)	71.13(11)	O(51)−Ta(1)−O(22)	166.5(2)
O(21)−Bi(1)−O(41A)	153.68(12)	O(51)−Ta(1)−O(41)	87.7(2)
O(22)−Bi(1)−O(41A)	152.59(12)	O(1)−Ta(1)−O(41)	171.5(2)
O(71)−Bi(1)−O(41A)	75.70(12)	O(1)−Ta(1)−O(2A)	92.1(2)
O(32)−Ta(1)−O(33)	80.88(13)	O(51)−Ta(1)−O(2A)	100.9(2)
O(42)−Ta(1)−O(32)	80.68(13)	O(23)−Ta(1)−O(2A)	161.0(2)
O(32)−Ta(1)−O(43)	81.64(14)	O(22)−Ta(1)−O(2A)	86.4(2)
O(51)−Ta(1)−O(61)	100.13(17)	O(61)−Ta(2)−O(1)	100.4(2)
O(61)−Ta(1)−O(43)	93.71(17)	O(61)−Ta(2)−O(2)	99.0(2)
O(51)−Ta(1)−O(43)	99.29(17)	O(2)−Ta(2)−O(1)	97.1(2)
O(61)−Ta(1)−O(33)	97.02(17)	O(61)−Ta(2)−O(33)	88.3(2)
O(51)−Ta(1)−O(33)	96.08(17)	O(2)−Ta(2)−O(33)	161.1(2)
O(43)−Ta(1)−O(33)	159.39(14)	O(1)−Ta(2)−O(33)	98.7(2)
O(61)−Ta(1)−O(42)	169.51(15)	O(61)−Ta(2)−O(32)	165.6(2)
O(51)−Ta(1)−O(42)	89.67(15)	O(2)−Ta(2)−O(32)	88.8(2)
O(43)−Ta(1)−O(42)	80.90(14)	O(1)−Ta(2)−O(32)	90.5(2)
O(33)−Ta(1)−O(42)	85.56(14)	O(33)−Ta(2)−O(32)	80.7(2)
O(61)−Ta(1)−O(32)	89.67(15)	O(2)−Ta(2)−O(42A)	82.43(19)
O(51)−Ta(1)−O(32)	170.05(16)	O(1)−Ta(2)−O(42A)	171.9(2)

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Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complexes **5** and **5**·Et_2O

	5				
Bi(1)/Nb(1)		Bi(2)/Nb(2)		**5**·Et_2O	
Bi(1)−C(11)	2.236(7)	Bi(2)−C(51)	2.219(9)	Bi(1)−C(11)	2.181(9)
Bi(1)−C(21)	2.246(9)	Bi(2)−C(61)	2.265(10)	Bi(1)−C(21)	2.237(12)
Bi(1)−O(31)	2.387(7)	Bi(2)−O(81)	2.429(6)	Bi(1)−O(31)	2.423(9)
Bi(1)−O(71)	2.385(7)	Bi(2)−O(41A)	2.374(6)	Bi(1)−O(41A)	2.391(8)
Nb(1)−O(1)	1.858(7)	Nb(2)−O(3)	1.861(7)	Nb(1)−O(1)	1.822(9)
Nb(1)−O(2)	1.862(6)	Nb(2)−O(4)	1.884(7)	Nb(1)−O(2)	1.829(9)
Nb(1)−O(32)	2.081(6)	Nb(2)−O(72)	2.096(6)	Nb(1)−O(32)	2.057(9)
Nb(1)−O(33)	1.988(6)	Nb(2)−O(73)	1.983(7)	Nb(1)−O(33)	1.983(9)
Nb(1)−O(42)	2.098(6)	Nb(2)−O(82)	2.080(6)	Nb(1)−O(42)	2.097(8)
Nb(1)−O(43)	1.979(7)	Nb(2)−O(83)	1.981(6)	Nb(1)−O(43)	1.916(9)
C(11)−Bi(1)−C(21)	94.1(3)	C(51)−Bi(2)−C(61)	92.2(4)	C(11)−Bi(1)−C(21)	92.2(4)
C(11)−Bi(1)−O(71)	87.1(3)	C(51)−Bi(2)−O(41A)	86.7(3)	C(11)−Bi(1)−O(41A)	87.8(4)
C(21)−Bi(1)−O(71)	82.0(3)	C(61)−Bi(2)−O(41A)	82.1(3)	C(21)−Bi(1)−O(41A)	84.1(4)
C(11)−Bi(1)−O(31)	81.0(3)	C(51)−Bi(2)−O(81)	84.0(3)	C(11)−Bi(1)−O(31)	83.4(4)
C(21)−Bi(1)−O(31)	86.3(3)	C(61)−Bi(2)−O(81)	86.4(3)	C(21)−Bi(1)−O(31)	85.7(4)
O(71)−Bi(1)−O(31)	162.7(2)	O(41A)−Bi(2)−O(81)	164.8(2)	O(41A)−Bi(1)−O(31)	166.3(3)
O(1)−Nb(1)−O(2)	99.0(3)	O(3)−Nb(2)−O(4)	98.9(3)	O(1)−Nb(1)−O(2)	99.7(4)
O(1)−Nb(1)−O(43)	97.8(3)	O(3)−Nb(2)−O(83)	102.9(3)	O(1)−Nb(1)−O(43)	90.4(4)
O(2)−Nb(1)−O(43)	88.0(3)	O(4)−Nb(2)−O(83)	86.9(3)	O(2)−Nb(1)−O(43)	98.6(4)
O(1)−Nb(1)−O(33)	87.6(3)	O(3)−Nb(2)−O(73)	88.6(3)	O(1)−Nb(1)−O(33)	87.4(4)
O(2)−Nb(1)−O(33)	104.3(3)	O(4)−Nb(2)−O(73)	96.7(3)	O(2)−Nb(1)−O(33)	103.2(4)
O(43)−Nb(1)−O(33)	165.8(3)	O(83)−Nb(2)−O(73)	167.3(3)	O(43)−Nb(1)−O(33)	164.1(3)
O(1)−Nb(1)−O(32)	163.5(3)	O(4)−Nb(2)−O(82)	164.9(3)	O(1)−Nb(1)−O(32)	166.2(3)
O(2)−Nb(1)−O(32)	94.4(3)	O(3)−Nb(2)−O(82)	93.0(3)	O(2)−Nb(1)−O(32)	90.1(3)
O(43)−Nb(1)−O(32)	92.3(3)	O(73)−Nb(2)−O(82)	92.7(3)	O(43)−Nb(1)−O(32)	91.0(3)
O(33)−Nb(1)−O(32)	79.7(3)	O(83)−Nb(2)−O(82)	81.5(2)	O(33)−Nb(1)−O(32)	80.9(3)
O(1)−Nb(1)−O(42)	86.5(3)	O(4)−Nb(2)−O(72)	88.2(3)	O(1)−Nb(1)−O(42)	89.2(3)
O(2)−Nb(1)−O(42)	167.8(3)	O(3)−Nb(2)−O(72)	168.2(3)	O(2)−Nb(1)−O(42)	168.4(4)
O(43)−Nb(1)−O(42)	80.5(3)	O(73)−Nb(2)−O(72)	81.2(3)	O(43)−Nb(1)−O(42)	81.0(3)
O(33)−Nb(1)−O(42)	86.7(3)	O(83)−Nb(2)−O(72)	86.8(3)	O(33)−Nb(1)−O(42)	84.4(3)
O(32)−Nb(1)−O(42)	82.2(2)	O(82)−Nb(2)−O(72)	81.6(3)	O(32)−Nb(1)−O(42)	82.4(3)

Scheme 4. Diagram of the Seesaw-Shaped Stereochemistry around Bi(III) in **5** with the Lone Pair Hypothetically at One of the Equatorial Positions

salicylate ions. The coordination environment of the hexacoordinate Ta atoms include two cis-oxide ligands, two O atoms from a chelating sal^{2-} ion, one oxygen atom from the carboxylate of a $Hsal^{-}$ ligand, and an oxygen atom of the ethoxide ligand (Figure 2). All four sal^{2-} ligands are oriented so that the oxygen atoms of the carboxylate groups not bound to Ta point toward the Bi atom. The coordination polyhedron of Ta atoms can be presented as a distorted octahedron with Ta−O bond lengths ranging from 1.848(6) to 2.199(6) Å. The Bi(III) atom is coordinated to the four O atoms of the bridging carboxylate groups as described above, in addition to the C atom of the Ph group, giving the Bi atom a slightly distorted square pyramidal geometry. It is known that in cases where there are six electron pairs around an atom, of which five are bonding and one is a lone pair, the VSEPR model predicts an octahedral distribution that produces a square-based pyramid with the SALEP opposite to the apical position. In the case of **4**, the void in the coordination sphere of Bi(III) is clearly observable and suggests a SALEP and a *hemidirected* stereochemistry for Bi(III) (Scheme 3). As in **3**, the phenyl group occupies the apical position of the coordination sphere, while the basal plane is defined by dative interactions between Bi(III) and bridging carbonyl oxygen atoms. The Bi−O bond distances range from 2.378(7) to 2.464(6) Å, while the $Bi-C_{aryl}$ bond length is 2.268(14) Å. A comparison of the bond distances and angles of complexes **3** and **4** is presented in Table 2. Compound **4** represents a relatively rare example of square-pyramidal geometry in aryl−bismuth complexes with oxygen donor ligands. The gross structural features are similar to those described previously for $[PhBi\{OP(NMe_2)_3\}_4][PF_6]_2$;[74] however, in the latter case there is a Bi···F contact of 3.28(3) Å between Bi(III) and one fluorine atom of the PF_6 anion, which, if considered as part of the Bi(III) coordination environment, results in a distorted-octahedral geometry.

Compound **5** is a polymeric structure made of alternating $[Ph_2Bi]^{+}$ and $[Nb(sal)_2(OMe)_2]^{-}$ units, two of each of these units being present in the asymmetric unit of the crystal lattice. The structure is very similar to that observed for $[Et_2BiOAr]_\infty$[75] (Ar = Ph, C_6F_5), in which $[Et_2Bi]^{+}$ groups are bridged by the phenoxide ligands with unique Bi−O distances of 2.382(7) Å for $[Et_2BiOPh]_\infty$ and 2.4105(7) Å for $[Et_2BiOC_6F_5]_\infty$. These correlate well with the Bi−O bonds of 2.385(7) and 2.387(7) Å found in **5**. Slightly shorter Bi−O bonds of 2.317(5) and 2.355(5) Å are present in the crystal structure of the ionic compound $[Ph_2Bi\{OP(NMe_2)_3\}_2][PF_6]$, in which the $[Ph_2Bi\{OP(NMe_2)_3\}_2]^{+}$

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cation may be viewed as a ligand-stabilized $[Ph_2Bi]^+$ species.[74] Complex **5** and its diethyl ether solvate **5**·Et_2O display similar structures; a comparison of their bond distances and angles is presented in Table 3.

The environment of Nb in **5** has a distorted-octahedral geometry with four coplanar bonds of nearly equivalent length and two slightly longer apical bonds (Figure 3). The equatorial atoms deviate slightly from the plane, the Nb atom being close to the center. The bismuth atom in **5** is four-coordinate with bonds to two phenyl groups and two carboxylate oxygen atoms from the doubly deprotonated salicylate groups. Bi(III) adopts a highly distorted seesaw geometry predicted by classical VSEPR theory, with the lone pair of electrons hypothetically at an equatorial position (Scheme 4). As in the case of complexes **3** and **4**, in terms of the terminology introduced by Shimoni-Livny et al.,[61] the geometry of Bi(III) can be assigned as *hemidirected*. The void in the coordination sphere of Bi(III) is clearly observable in the structure and is positioned opposite to the Ph groups. The axis passing through the lone pair should bisect the angle between these two bonds in the equatorial plane of the pseudotrigonal bipyramid. As the result of the presence of a SALEP, the geometry at the bismuth center is distorted with a O−Bi−O bond angle of 162.7(2)° and a C−Bi−C bond angle of 94.1(3)°, values that deviate significantly from the expected angles of 180 and 120° for this geometry predicted by VSEPR theory. Similar deviations were observed for the complex cations $[Ph_2Bi\{OP(NMe_2)_3\}_2]^+$ in $[Ph_2Bi\{OP(NMe_2)_3\}_2][BF_4]$ and $[Ph_2Bi\{OP(NMe_2)_3\}_2][PF_6]$, with O−Bi−O and C−Bi−C angles of 167.5(3) and 93.2(5)°.[74] The surprisingly low coordination number (CN) of the Bi(III) center is unique for bismuth-containing heterometallic salicylate−alkoxide complexes. The alternating $[Ph_2Bi]^+$ and metal anions results in the coordination polymer acquiring a helical structure as found in $[Et_2BiOAr]_\infty$.[75]

As can be seen from the data presented above, significant structural differences are observed if the heterobimetallic coordination complex is first isolated and then allowed to react with $NaBPh_4$. Compund **5** can be viewed as a ring-opened isomeric form of **3** with an additional salicylate ligand attached to Bi replaced by Ph. The essential connectivity of the Bi and transition metal centers remains unchanged. Both possess $[M(sal)_2(OR)_2]^-$ groups that are connected to bridging BiX_2^+ functions through oxygen atoms of the salicylate carboxylate groups. In the polymeric case, the X_2Bi^+ groups are Ph_2Bi^+, while in the cyclic structure these are present as Ph(Hsal)Bi^+ units. The structural changes can be understood as arising from the reconciliation of two geometric constraints in the compound. The bismuth atom in **3** is four-coordinate and has adopted a highly distorted disphenoidal geometry. The geometry at the bismuth center, in which the O−Bi−O bond angle is 162.7(2)°, as opposed to **5**, in which the O−Bi−O bond angle is 71.12(11)°, can be one of the reasons for the structural reorganization of the complex and for the preference of the coordination polymer in the solid state.

The mechanism of the ligand exchange reactions is not completely clear. Attempts to probe this for the production of $BiAr_3$ met with only limited success. No boron−salicylate complexes were formed, and it appeared that BPh_3 was a byproduct of those reactions. The arylation reactions represent attractive alternatives for the derivatization of bismuth heterometallic coordination complexes. The lability of carboxylate ligands in Bi(III) complexes and their participation in ligand exchange reactions is well documented in the literature.[13,76] The use of tetraarylborate salts as arylation agents is convenient, because such reactions can occur spontaneously under very mild conditions.

An interesting comparison in the synthesis of compounds **3** and **5** is that the starting conditions for **5** are essentially the same as for **3** but without the prior isolation of **1**. This suggests that the ring structure of **1** may not exist in the solution prior to its isolation but that, once the ring structure forms, it is stable.

The ^1H and NMR spectra of **3**−**5** in d_8-THF and d_6-dmso revealed only a single salicylate environment, consistent with fluxional salicylate ligands on the NMR time scale. The spectra exhibit the ortho, meta, and para protons of the phenyl group centered between 7.3 and 8.8 ppm. In addition to the signals of the aromatic hydrogens of the salicylate groups between 6.7 and 7.4, the spectra of **3** and **4** also contain a broad peak around 12 ppm of the protonated phenoxy group of the salicylate ligand. In all three complexes the NMR data revealed a significant downfield shift of the resonance for the *o*-H atoms of the phenyl group, as observed in other arylbismuth(III) salicylates.[60] The mechanism by which the salicylate ligands are equilibrating is unclear. For **3** and **5**, dissociation equilibria into heterobimetallic units are possible and may be the most likely route to achieve exchange, but this is not a very likely pathway for **4**, where the bridging oxo ligands would be expected to maintain the core structure. Because of the fluxionality of the ligands, the NMR data do not allow more detailed comments about the solution structures of the molecules.

Conclusions

Heterometallic bismuth−transition metal complexes with salicylate and alkoxide ligands have been shown to undergo facile and selective arylation reactions using $NaBPh_4$. The single-crystal X-ray studies revealed that the metal stoichiometry as well as core framework structures of the complexes are preserved upon the substitution of nonbridging salicylate ligands with a more electron-rich aryl group. The reactions presented illustrate the feasibility of introducing one or two aryl groups coordinated to Bi(III) in the heterobimetallic coordination complexes through the use of $NaBAr_4$. The preservation of both the structure and the stoichiometry of the complexes under most of the conditions presented here is a significant advantage and allows for facile selective derivatization of complex main group element−transition metal architectures.

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Supporting Information Available: CIF files giving crystallographic data and figures giving thermal ellipsoid plots for all structures and spectroscopic results. This material is available free of charge via the Internet at http://pubs.acs.org.

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