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Organobismuth(III) and Organobismuth(V) Complexes Containing Pyridyl and Amino Functional Groups. Syntheses and Characterizations of $Bi^{III}Ar_3$ (Ar = *p*-$C_6H_4(NMe_2)$, *p*-$C_6H_4CH_2(NPr^i_2)$, *p*-$C_6H_4[CH_2N(2\text{-}Py)_2]$), $Bi^VAr_3L_2$, $[Bi^VAr_3Cl]_2O$, $[Bi^VAr_4][PF_6]$, and $[Bi^VAr_4]_2[Ag_2Cl_4]$ (Ar = *p*-$C_6H_4(NMe_2)$ or *p*-$C_6H_4[CH_2N(2\text{-}Py)_2]$, L = Cl, $CH_3CO_2^-$, $CF_3CO_2^-$)

Abdi Hassan, Steven R. Breeze, Silke Courtenay, Chris Deslippe, and
Suning Wang*

Department of Chemistry, Queen's University, Kingston, Ontario, Canada K7L 3N6

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The synthesis of tertiary bismuth(III) complexes containing amino or pyridyl functional groups has been investigated. An improved synthesis for Bi[*p*-$C_6H_4(NMe_2)]_3$ (**1**) has been achieved. Two new complexes, Bi[*p*-$C_6H_4CH_2(NPr^i_2)]_3$ (**2**) and Bi[*p*-$C_6H_4CH_2N(2\text{-}Py)_2]_3$ (**3**), have been obtained. The bismuth(V) derivatives of compounds **1** and **3** have been synthesized via chlorine oxidation of **1** and **3** and the subsequent substitution reactions. Compounds Bi[*p*-$C_6H_4(NMe_2)]_3(O_2CCF_3)_2$ (**5**) and Bi{*p*-$C_6H_4[CH_2N(2\text{-}Py_2)]\}_3(O_2CCH_3)_2$ (**7**) were obtained from the reactions of the corresponding dichloride complexes, $BiAr_3Cl_2$, with the appropriate silver salt. NMR spectroscopic studies established that in solution, compound **5** is fluxional while compound **7** is rigid. A dinuclear complex Bi_2[*p*-$C_6H_4(NMe_2)]_6Cl_2(O)$ (**6**) was isolated as the major product when the dichloride complex Bi[*p*-$C_6H_4(NMe_2)]_3Cl_2$ was reacted with NaOH in nondistilled reagent grade dichloromethane. A quaternary bismuth(V) complex, Bi[*p*-$C_6H_4(NMe_2)]_4[PF_6]$ (**8**), was obtained in good yield when Bi[*p*-$C_6H_4(NMe_2)]_3Cl_2$ was reacted with $TlPF_6$ in a 1:2 ratio. A closely related quaternary bismuth(V) complex {Bi[*p*-$C_6H_4(NMe_2)]_4\}_2[Ag_2Cl_4]$ (**9**), which contains an unusual three-coordinate dinuclear anion $Ag_2Cl_4^{2-}$, was obtained as a trace product from the reactions of Bi[*p*-$C_6H_4(NMe_2)]_3Cl_2$ with silver salts. The crystal structures of compounds **1** and **5**−**9** were determined by single-crystal X-ray diffraction analyses.

Introduction

There has been much interest in bismuth compounds due to their various applications in medicines, catalysis, and materials.[1] The exploration and information on the chemistry of organobismuth complexes are still very limited. We have been interested in the syntheses of bismuth complexes containing functional groups such as pyridyl and hydroxo because of their potential use as precursors for the formation of polynuclear mixed metal complexes, e.g., BiCu complexes. Our effort has focused on two types of organobismuth complexes, bismuth(III) complexes, $BiAr_3$, and bismuth(V) complexes, $BiAr_3L_2$, where Ar is a phenyl derivative containing a donor functional group such as amino or pyridyl. Although a few triarylbismuth(III) complexes, $BiAr_3$, and triarylbismuth(V) complexes, $BiAr_3X_2$ (X = halide or carbonate), containing an −OR or $-NO_2$ group are known,[1a,g,j] triarylbismuth(III) and triarylbismuth(V) complexes containing amino or pyridyl donor functional groups are still scarce. The only previously known example of $BiAr_3$ complexes containing an amino functional group is Bi[*p*-$C_6H_4(NMe_2)]_3$ (**1**), reported some 45 years ago by Gilman and Yablunky.[2] The yield of compound **1** reported in the original synthesis was poor, and the chemistry and structure of **1** have hardly been investigated. We therefore decided to reinvestigate the synthesis and chemistry of compound **1**. In addition, we have explored the syntheses of new $BiAr_3$ complexes containing amino or pyridyl functional groups. Two new complexes, Bi[*p*-$C_6H_4CH_2(NPr^i_2)]_3$ (**2**) and Bi{*p*-C_6H_4-$[CH_2N(2\text{-}Py)_2]\}_3$ (**3**), have been obtained. Several interesting bismuth(V) complexes derived from compounds **1** and **3** have been characterized. The details are presented herein.

Experimental Section

All reactions were performed by using the Schlenk vacuum line techniques under a nitrogen atmosphere. All solvents were freshly distilled over the appropriate drying reagents

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[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1996.

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(2) Gilman, H.; Yablunky, H. L. *J. Am. Chem. Soc.* **1941**, *63*, 207.

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prior to use, unless specified otherwise. $BiCl_3$, $Ag(O_2CCH_3)$, $Ag(O_2CCF_3)$, $TlPF_6$, 4-bromo-*N*,*N*-dimethylaniline, 4-bromobenzyl bromide, *n*-butyllithium, di-2-pyridylamine, 4-bromo-*N*,*N*-diisopropylbenzylamine, and trifluoroacetic acid were purchased from Aldrich Chemical Co. Bis(2-pyridylmethyl)amine was synthesized by a modified procedure reported in literature.[3] $PhI{\cdot}Cl_2$ was prepared by the reaction of phenyl iodide with chlorine gas in diethyl ether. NMR spectra were recorded on a Brüker AC 300 spectrometer. Elemental analyses were performed by Canadian Microanalytical Service, Delta, BC.

Preparation of (4-Bromobenzyl)di-2-pyridylamine. 4-Bromobenzyl bromide (8 g, 32 mmol), di-2-pyridylamine (5 g, 29 mmol), and sodium hydroxide pellets (approximately 10 g) were mixed in a 1 L flask containing 300 mL of reagent grade THF. The mixture was refluxed for 5 h and stirred for an additional 16 h at 23 °C. The solution was then filtered and evaporated to dryness. Water was added to the residue. The product was extracted with several portions of diethyl ether. After the diethyl ether solution was concentrated, the product was obtained by crystallization at 0 °C in 62% yield. Mp 95 °C. Anal. Calcd for $BrC_{17}H_{14}N_3$: C, 60.02; H, 4.12; N, 12.35. Found: C, 59.92; H, 4.17; N, 12.34. ^1H NMR (δ, ppm, $CDCl_3$): 5.42 (s, 2H, CH_2), 6.83 (m, 2H, Py), 7.13, 7.34 (AA′BB′, 2H, 2H, phenyl, $J_{AB} = 8.4$ Hz), 7.23 (d, 2H, Py), 7.48 (m, 2H, Py), 8.30 (m, 2H, Py). ^{13}C NMR (δ, ppm, $CDCl_3$): 50.78 (CH_2), 114.55, 117.42, 120.46, 129.22, 131.43, 137.35, 138.74, 148.47, 157.02 (aromatic). MS: 340 (molecular ion).

(4-Bromobenzyl)bis(2-pyridylmethyl)amine. The ligand was prepared by the same procedure as above. The resulting oily compound was purified by distillation under vacuum (250 °C, 0.02 mmHg). The purified ligand is a yellowish orange oil. Anal. Calcd for $BrC_{19}H_{18}N_3$: C, 61.97; H, 4.89; N, 11.42. Found: C, 60.91; H, 5.05; N, 11.06. The poor agreement of carbon and nitrogen content with the calculated value is believed to be caused by impurities, such as water, since it has a high affinity to water via hydrogen bonds. ^1H NMR (δ, ppm, $CDCl_3$): 3.59 (s, 2H, CH_2), 3.75 (s, 4H, CH_2), 7.09 (m, 2H, Py), 7.24, 7.38 (AA′BB′, 2H, 2H, phenyl, $J_{AB} = 8.4$ Hz), 7.49 (d, 2H, Py), 7.60 (m, 2H, Py), 8.47 (m, 2H, Py). ^{13}C NMR (δ, ppm, $CDCl_3$): 57.77 (CH_2), 59.93 (CH_2), 120.84, 122.05, 122.85, 130.58, 131.40, 136.47, 138.03, 149.06, 159.43 (aromatic). MS: 368 (molecular ion).

General Procedure for the Synthesis of $BiAr_3$ Complexes. The $BiAr_3$ complexes were obtained by a modified literature procedure.[2] The synthesis of $Bi[p\text{-}C_6H_4(NMe_2)_2]_3$ given below represents the typical procedure and reaction conditions employed for the $BiAr_3$ complexes described in this report. The experimental details for the synthesis of other $BiAr_3$ complexes are therefore omitted.

Preparation of $Bi[p\text{-}C_6H_4(NMe_2)]_3$ (1). A 1.00 g (5.00 mmol) sample of 4-bromo-*N*,*N*′-dimethylaniline was dissolved in 20 mL of THF. This solution was then cooled to −78 °C by using a dry ice/acetone bath. *n*-Butyllithium (3.12 mL of 1.6 M, 1.60 mmol) in hexane was added. After the solution was stirred for 30 min at −78 °C, a 0.500 g, (1.59 mmol) sample of $BiCl_3$ dissolved in 10 mL of THF was added. The mixture was stirred for 1 h at −78 °C and was allowed to warm up to 23 °C. After being stirred for an additional 12 h, the THF solvent was removed in vacuo and the residue was extracted with 20 mL of toluene. The toluene extract was filtered and concentrated to about 10 mL. After the solution was allowed to stand at 0 °C for a few days, colorless crystals of **1** were obtained (0.96 g, yield 86%). More crystals can be isolated by further concentrating the mother liquor. Mp 200 °C, dec. Anal. Calcd for $BiC_{24}H_{30}H_3$: C, 50.62; H, 5.31; N, 7.38. Found: C, 50.76; H, 5.18; N, 7.30. ^1H NMR (δ, ppm, $CDCl_3$): 2.91 (s, 6H, CH_3), 6.72, 7.57 (AA′BB″, 2H, 2H, $J_{AB} = 8.1$ Hz, phenyl). ^{13}C NMR (δ, ppm, $CDCl_3$): 51.85 (CH_3), 130.78, 136.89, 144.99, 151.37 (phenyl).

$Bi[p\text{-}C_6H_4CH_2(NPr^i_2)]_3$ (2). The colorless compound **2** was crystallized from acetonitrile. Yield 43%. Mp 85 °C, dec. Anal. Calcd for $BiC_{39}H_{60}N_3$: C, 60.08; H, 7.70; N, 5.39. Found: C, 59.71; H, 7.80; N, 5.42. ^1H NMR (δ, ppm, $CDCl_3$): 0.98 (d, 6H, CH_3, $^3J = 6.6$ Hz), 2.98 (septet, 1H, CH), 3.58 (s, 2H, CH_2), 7.36, 7.63 (AA′BB″, 2H, 2H, $J_{AB} = 7.8$ Hz, phenyl). ^{13}C NMR (δ, ppm, $CDCl_3$): 20.89 (CH_3), 47.79 (CH), 49.00 (CH_2), 130.12, 137.37, 142.79, 152.07 (phenyl).

$Bi[p\text{-}C_6H_4CH_2N(2\text{-}Py)_2]_3$ (3). The colorless crystals of compound **3** were obtained by crystallization in acetonitrile. Yield 15%. Mp 115−120 °C, dec. Anal. Calcd for $BiC_{51}H_{42}N_9$: C, 61.88; H, 4.28; N, 12.73. Found: C, 61.13; H, 4.22; N, 12.60. ^1H NMR (δ, ppm, $CDCl_3$): 5.43 (s, 2H, CH_2), 6.82 (m, 2H, Py), 7.12, 7.27 (AA′BB′, 2H, 2H, phenyl, $J_{AB} = 8.1$ Hz), 7.49 (m, 4H, Py), 8.28 (m, 2H, Py). ^{13}C NMR (δ, ppm, $CDCl_3$): 51.56 (CH_3), 114.71, 117.29, 148.19, 157.12 (pyridyl), 129.17, 138.87, 152.72 (phenyl), 137.41, 137.67 (pyridyl, phenyl).

Preparation of $Bi[p\text{-}C_6H_4(NMe_2)]_3Cl_2$ (4). A 0.100 g (0.176 mmol) sample of compound **1** was dissolved in 20 mL of CH_2Cl_2. The solution was cooled to −78 °C by using a dry ice/acetone bath. $PhI{\cdot}Cl_2$ (0.058 g, 0.211 mmol) was added. The mixture was stirred for 3 h and was allowed to warm up to 23 °C. The solvent and phenyl iodide were removed *in vacuo*. The residue was redissolved in CH_2Cl_2. Concentration of the solution yielded orange crystals of compound **4** in 88% yield. Compound **4** cocrystallizes with the CH_2Cl_2 solvent molecule. Anal. Calcd for the vacuum dried sample, $BiCl_2C_{24}H_{30}N_3$: C, 45.00; H, 4.69; N, 4.65. Found: C, 44.02; H, 4.65; N, 6.30. The low observed carbon and nitrogen content can be attributed to the presence of 0.20 CH_2Cl_2 per molecule of **4** (calcd for $BiCl_2C_{24}H_{30}N_3/0.2\ CH_2Cl_2$: C, 44.21; H, 4.63; N, 6.39). ^1H NMR (δ, ppm, $CDCl_3$): 3.01 (s, 6H, CH_3), 7.78, 8.24 (AA′BB′, 2H, 2H, phenyl, $J_{AB} = 9.3$ Hz).

$Bi[p\text{-}C_6H_4CH_2N(2\text{-}Py)_2]_3Cl_2$ was obtained by the same procedure in 74% yield.

Preparation of $Bi[p\text{-}C_6H_4(NMe_2)]_3(O_2CCF_3)_2$ (5). Silver trifluoroacetate (0.083 g, 0.375 mmol) was added to a 20 mL THF solution containing 0.120 g (0.186 mmol) of compound **4**. The reaction mixture was stirred for 17 h at 23 °C. The solution was filtered and concentrated *in vacuo*. Orange crystals of compound **5** were obtained at 0 °C in 71% yield. Mp 120 °C. Anal. Calcd for $C_{28}H_{30}N_3BiO_4F_6$: C, 42.25; H, 3.77; N, 5.28. Found: C, 42.24; H, 3.80; N, 5.42. ^1H NMR (δ, ppm, $CDCl_3$): 3.01 (s, 6H, CH_3), 6.83, 7.89 (AA′BB′, 2H, 2H, phenyl, $J_{AB} = 8.8$ Hz).

Preparation of $Bi_2[p\text{-}C_6H_4(NMe_2)]_6Cl_2(O)$ (6). A 0.100 g (0.156 mmol) sample of compound **4** was dissolved in 20 mL of reagent grade dichloromethane in the presence of 1.5 equiv of NaOH (5 mg). This solution was stirred for 3 h and filtered. The filtrate was concentrated to about 4 mL and kept at 0 °C. After a few days, yellow crystals of compound **6** were obtained in 35% yield. Mp 159 °C, dec. Compound **6** cocrystallizes with one H_2O and one CH_2Cl_2 solvent molecule. Anal. Calcd for the CH_2Cl_2 free sample, $C_{49}H_{62}Bi_2ON_6Cl_2/H_2O$: C, 46.30; H, 5.14; N, 6.75. Found: C, 45.67; H, 5.26; N, 6.80. ^1H NMR (δ, ppm, $CDCl_3$): 3.01 (s, 6H, CH_3), 6.81, 8.19 (AA′BB′, 2H, 2H, phenyl, $J_{AB} = 9.1$ Hz).

Preparation of $Bi[p\text{-}C_6H_4CH_2N(2\text{-}Py)_2]_3(O_2CCH_3)_2$ (7). A sample of 80 mg (0.075 mmol) of $Bi[p\text{-}C_6H_4CH_2N(2\text{-}Py)_2]_3Cl_2$ was dissolved in 10 mL of THF. $Ag(O_2CCH_3)$ (25 mg, 0.151 mmol) was added to the solution. The mixture was stirred for 16 h at 23 °C. The solution was filtered and concentrated to about 4 mL. Hexane (0.5 mL) was added. After being allowed to stand a few days at 0 °C, colorless crystals of compound **7** were obtained (89 mg, 80% yield). Compound **7** cocrystallizes with two THF solvent molecules. Mp 95−97 °C. Anal. Calcd for the vacuum dried sample, $C_{55}H_{54}N_9BiO_4$: C, 59.62; H, 4.73; N, 11.33. Found: C, 59.19; H, 4.83; N, 10.40. ^1H NMR (δ, ppm, $CDCl_3$, 296 K): 1.71 (s, 6H, CH_3), 5.49, 5.51 (s, 6H, CH_2), 6.83, 7.15, 7.50, 7.92, 8.02, 8.29 (m, 36H, aromatic). ^{13}C NMR (δ, ppm, $CDCl_3$, 296 K): 29.80 (CH_3), 50.89, 50.97, 51.08 (CH_2), 114.48, 117.48, 137.40, 148.47,

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[3] Romary, J. K.; Zachariasen, R. D.; Barger, J. D.; Schiesser, H. *J. Chem. Soc. C* **1968**, 2884.

Table 1. Crystallographic Data

	1	5	6	7	8	9
formula	$C_{24}H_{30}N_3Bi$	$C_{28}H_{30}N_3O_4F_6Bi$	$C_{49}H_{64}N_6O_2Cl_4Bi_2$	$C_{63}H_{64}N_9O_6Bi$	$C_{32}H_{40}N_4F_6PBi$	$C_{32}H_{40}N_4Cl_2AgBi$
fw	569.50	795.53	1328.86	1252.24	834.64	868.45
space group	$P\bar{1}$	$C2/c$	$P2_1/n$	$P2_1/n$	$P2_1/n$	$C2/c$
a, Å	11.478(4)	12.427(6)	13.219(5)	8.743(3)	15.864(5)	26.789(9)
b, Å	11.495(3)	12.461(8)	19.875(6)	38.33(1)	12.789(7)	17.534(3)
c, Å	11.394(4)	19.616(4)	21.043(8)	17.744(4)	15.975(6)	18.144(5)
α, deg	103.38(3)	90	90	90	90	90
β, deg	110.43(3)	99.14(2)	103.17(3)	101.90(3)	90.59(3)	127.47
γ, deg	111.82(3)	90	90	90	90	90
V, Å^3	1189.9(9)	2999(2)	5383(3)	5818(2)	3240(2)	6764(3)
Z	2	4	4	4	4	8
D, g cm^{-3}	1.59	1.76	1.64	1.43	1.71	1.71
T, °C	23	23	23	23	0	23
radiation, λ, Å	Mo Kα, 0.710 69	Mo Kα, 0.710 69	Mo Kα, 0.710 69	Mo Kα, 0.710 69	Ag Kα, 0.560 83	Mo Kα, 0.710 69
μ, cm^{-1}	73.98	59.43	67.57	30.83	22.33	59.47
trans. coeff.	0.21−1.00	0.81−1.00	0.89−1.00	0.90−1.00	0.65−0.89	0.85−1.00
$2\theta_{max}$, deg	50	50	50	45	40	45
reflns measured	4204	2786	7778	7519	6120	3335
reflns observed	$I > 3.00\sigma(I)$, 2297	$I > 2.70\sigma(I)$, 803	$I > 1.80\sigma(I)$, 2224	$I > 2.30\sigma(I)$, 2075	$I > 3.00\sigma(I)$, 2904	$I > 2.70\sigma(I)$, 1142
no. of variables	253	126	318	322	397	181
largest shift/esd in final cycle	0.00	0.00	0.01	0.01	0.00	0.00
largest electron density peak, e$^-$/Å^3	1.61	1.34	1.29	1.12	0.61	0.50
R^a	0.047	0.058	0.076	0.064	0.027	0.043
$R_w{}^b$	0.044	0.051	0.064	0.062	0.023	0.036
goodness of fit^c	1.64	1.39	1.48	1.28	1.09	1.21

^{a} $R = \sum|F_o| - |F_c|/\sum|F_o|$. ^{b} $R_w = (\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)^{-1/2}$, $w = 1/\sigma^2(F_o)$. ^{c} $S = \sum(|F_o| - |F_c|)/\sigma(N_o - N_v)$.

156.85 (pyridyl), 129.74, 130.20, 130.38, (CH, phenyl), 133.65, 133.89, 134.38 (CH, phenyl), 142.51, 143.27, 143.82 (C, phenyl), 154.17, 155.95, 159.09 (phenyl, the carbon atom bonded to bismuth).

Preparation of Bi[*p*-$C_6H_4(NMe_2)]_4[PF_6]$ (8). A 0.100 g, (0.156 mmol) sample of compound **4** was dissolved in 20 mL of CH_2Cl_2 at 23 °C. $TlPF_6$ (0.110 g, 0.312 mmol) was added to the solution. The mixture was stirred for 16 h. The solution was then filtered and concentrated to about 4 mL. After the addition of 2 mL of hexane and allowing the solution to stand at 0 °C for a few days, green crystals of compound **8** were obtained (117 mg, 90% yield). Mp 140 °C, dec. Anal. Calcd for $C_{32}H_{40}N_4BiPF_6$: C, 46.04; H, 4.79; N, 6.71. Found: C, 45.97; H, 4.57; N, 6.70. ^{1}H NMR (δ, ppm, CD_2Cl_2, 180 K): 2.98 (s, 6H, CH_3), 6.78 (d, 2H, J = 8.4 Hz, phenyl), 7.38 (broad, 2H, phenyl). ^{13}C NMR (δ, ppm, CD_2Cl_2, 180 K): 39.81 (CH_3), 113.34, 116.33, 135.83, 151.24 (aromatic).

Bi[*p*-$C_6H_4(NMe_2)]_4[AgCl_2]$ (9). This compound was obtained as a trace yellow crystalline product from the reactions of compound **4** with silver salts, such as $Ag(O_2CCF_3)$. Independent synthesis for this compound has not yet been achieved. Its poor solubility in common organic solvents, such as CD_2Cl_2, THF, and acetone, prevented us from taking NMR spectra. The elemental analysis was not performed due to the lack of a sufficient amount of sample. Mp 178 °C, dec.

X-ray Diffraction Analyses. The crystals of compound **1** were obtained from a concentrated toluene solution at 0 °C, while the crystals of **5**−**9** were obtained from the mixed solvents of CH_2Cl_2/hexane or THF/hexane at 0 °C. They were mounted on glass fibers and sealed with epoxy glue. Data were collected at 23 °C on a Rigaku AFC6S diffractometer with graphite-monochromated Mo Kα radiation for compounds **1**, **5**−**7**, and **9**. The data for compound **8** were collected at −79 °C on a Siemens P3 diffractometer with a graphite-monochromated Ag Kα radiation. All data were processed on a Silicon Graphics computer using the TEXSAN crystallographic software package[4] and corrected for decay and Lorentz-polarization effects. An empirical absorption correction based on azimuthal scans of several reflections was applied to all crystals. Neutral atom scattering factors were taken from Cromer and Waber.[5]

The crystal of **1** belongs to the triclinic space group $P\bar{1}$. The crystals of **6**−**8** belong to the monoclinic space group $P2_1/n$, uniquely determined by the systematic absences ($0k0$, $k = 2n + 1$; $h0l$, $h + l = 2n + 1$) while the crystals of **5** and **9** belong to the monoclinic space group $C2/c$, determined by the systematic absences (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$) and the successful structural solution and refinement. The positions of the metal atoms in all structures were determined either by the heavy atom method or by direct methods. Nonhydrogen atoms were located by subsequent difference Fourier syntheses. A THF solvent molecule and a H_2O molecule located in the lattice of compound **6** were refined successfully. Two THF solvent molecules, co-crystallized with compound **7**, were located in the lattice. Both solvent molecules show some degree of disorder, which could not be modeled successfully due to the limitation of the data. All non-hydrogen atoms in **1** and **8** were refined anisotropically. Due to the lack of a sufficient number of reflections, only bismuth, fluorine, oxygen, nitrogen, and one carbon atom in **5**, bismuth, chlorine, oxygen, and nitrogen atoms in **6**, bismuth in **7**, and bismuth, silver, and chlorine atoms in **9** were refined anisotropically. The positions of the hydrogen atoms were calculated wherever possible and their contributions were included in the structural factor calculation. Further details of the crystallographic analyses can be found in Table 1.

Results and Discussion

Syntheses and Structures of Tertiary Bismuth(III) Complexes, Bi^{III}[*p*-$C_6H_4(NMe_2)]_3$ (1), Bi^{III}[*p*-$C_6H_4(CH_2NPr^i{}_2)]_3$ (2), and Bi^{III}[*p*-$C_6H_4CH_2N(2\text{-}Py)_2]_3$ (3). Most of the previously investigated organobismuth(III) complexes involve simple aromatic or aliphatic ligands. Compound **1** is the only known example of a tertiary aromatic bismuth(III) complex containing an amino functional group. Although the synthesis of compound **1** was reported many years ago, its crystal structure has not been reported. In addition, perhaps

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[4] TEXSAN-TEXRAY Structure Analysis Package, Molecular Structure Corporation, Houston, TX, 1985 and 1992.

[5] Cromer, D. T.; Waber, J. T. *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, Al, 1974; Vol. 4, Table 2.2A.

due to the poor yield reported in the original synthesis, the chemistry involving this compound has been hardly investigated. We therefore conducted the investigation on an improved synthetic method for compound **1** and its solid state structure. By modifying a previously reported procedure[2] for compound **1**, we have been able to obtain this compound in very good yield from the reaction of $BiCl_3$ with $Li(p\text{-}C_6H_4NMe_2)$ in an approximate 1:3 ratio. The structure of compound **1** has been determined by a single-crystal X-ray diffraction analysis. Important bond lengths and angles for **1** are listed in Table 2. As shown in Figure 1, compound **1** has a pyramidal geometry, resembling that of $BiPh_3$. The Bi−C bond lengths (2.22(2)−2.25(2) Å) and C−Bi−C angles (93.7(6)−95.6(5)°) are very similar to those observed[6] in $BiPh_3$. One notable feature of compound **1** is the conjugation of the nitrogen lone pair with the phenyl ring, as indicated by the planar geometry of the nitrogen atom (the sum of the angles surrounding each nitrogen atom is nearly 360°) and the short bond distance between the nitrogen atom and the carbon atom of the phenyl ring (1.36(2)−1.41(2) Å). The lone pair conjugation is not a desirable feature for the bismuth complex because it will make the coordination of the nitrogen atom to a metal center, such as a copper(II) ion, difficult.

To prevent the conjugation of the lone pair, we synthesized compound **2**, $Bi^{III}(p\text{-}C_6H_4CH_2NPr^i{}_2)_3$, where the amino group is separated from the phenyl ring by a methylene group, from the reaction of $BiCl_3$ with 3 equiv of $Li(p\text{-}C_6H_4CH_2NPr^i{}_2)$. Compound **2** was characterized by NMR spectroscopic and elemental analyses. The lack of suitable single crystals for X-ray diffraction analysis prevented the crystal structural determination, but we believe that the structure of **2** is similar to that of **1** and $BiPh_3$.

To further increase the versatility of the tertiary aromatic bismuth(III) complexes containing functional groups, we synthesized the chelating ligands, (4-bromobenzyl)di-2-pyridylamine (bbdpa) and (4-bromobenzyl)bis(2-pyridylmethyl)amine (bbdpma). The bbdpa and bbdpma ligands were obtained from the reactions of the corresponding secondary amines with 4-bromobenzyl bromide by utilizing the reactivity difference of the two bromo sites, as shown in Scheme 1. We have been able to convert the bbdpa ligand to the corresponding lithium salt, $Li[p\text{-}C_6H_4CH_2N(2\text{-}Py)_2]$, by the reaction of *n*-butyllithium with bbdpa at −78 °C. The subsequent reaction of $Li[p\text{-}C_6H_4CH_2N(2\text{-}Py)_2]$ with $BiCl_3$ yielded compound **3**, $Bi^{III}[p\text{-}C_6H_4CH_2N(2\text{-}Py)_2]_3$, which was characterized by elemental and NMR spectroscopic analyses. The crystal structure of compound **3** has not been determined due to the lack of single crystals. Molecular modeling,[7] however, showed that the basic structural features of compound **3** should be similar to that of **1**. Compound **3** is the first example of a tertiary organobismuth(III) complex containing a chelating functional group. We examined the utility of the chelating group of compound **3** in binding to a metal center by performing the reaction of compound **3** with 3 equiv of anhydrous $CuCl_2$ in CH_2Cl_2. An insoluble light green powder product was obtained. The elemental analysis results for this green powder are, however, deviated significantly from those of the anticipated product, $Bi[p\text{-}C_6H_4CH_2N(2\text{-}Py)_2CuCl_2]_3$. The composition of the green compound still remains unknown.

We have not been able to convert the bbdpma to the corresponding lithium salt, which is attributed to the high reactivity of the methylene protons in the bbdpma ligand toward *n*-butyllithium. The attempted synthesis of the corresponding bismuth(III) complex was therefore unsuccessful.

Syntheses and Structures of $Bi[p\text{-}C_6H_4(NMe_2)]_3(O_2CCF_3)_2$ (5), $Bi_2[p\text{-}C_6H_4(NMe_2)]_6Cl_2(O)$ (6), and $Bi[p\text{-}C_6H_4CH_2N(2\text{-}Py)_2]_3(O_2CCH_3)_2$ (7). It has been established earlier that tertiary aromatic bismuth(III) complexes undergo oxidative addition reactions readily with halogens, such as the chlorine molecule,[1a,8] to form the bismuth(V) complex $Bi^VAr_3X_2$, which is a good starting material for the synthesis of new bismuth(V) derivatives. We therefore performed the oxidation reactions of compounds **1**−**3** by using the chlorine delivery reagent, $PhI{\cdot}Cl_2$. At −78 °C, both compounds **1** and **3** can be oxidized cleanly to form the corresponding dichloride products, $Bi[p\text{-}C_6H_4(NMe_2)]_3Cl_2$ and $Bi[p\text{-}C_6H_4CH_2N(2\text{-}Py)_2]_3Cl_2$, respectively, while the reaction of compound **2** with $PhI{\cdot}Cl_2$ appeared to generate several products which have not been isolated at this time. The $Bi[p\text{-}C_6H_4(NMe_2)]_3Cl_2$ complex was reported[8] by Keck and Klar in 1972. The structure of this compound, however, has not been determined. The crystal structure of the analogous complex $BiPh_3Cl_2$ has been reported earlier to be a distorted trigonal bipyramid.[9] Our preliminary X-ray diffraction analysis results[10] for the $Bi[p\text{-}C_6H_4(NMe_2)]_3Cl_2$ complex revealed that this compound has a trigonal bipyramidal geometry with the bismuth and the two chlorine atoms lying on the crystallographically imposed C_3 axis. The two Bi−Cl bond lengths, 2.46(3) and 2.73(3) Å, are significantly different, but the average 2.59 Å bond length is comparable to that found in $BiPh_3Cl_2$. The Bi−C bond length of 2.20(2) Å is similar to that found in compound of **1**. The C−Bi−Cl angles range from 84.8(9)° to 95.2(9)°, similar to those observed in the $BiPh_3Cl_2$ compound. Molecular modeling showed that the structure of $Bi[p\text{-}C_6H_4CH_2N(2\text{-}Py)_2]_3Cl_2$ resembles those of $BiPh_3Cl_2$ and $Bi[p\text{-}C_6H_4(NMe_2)]_3Cl_2$ (**4**). We therefore did not conduct the X-ray diffraction analysis for this compound.

The $Bi[p\text{-}C_6H_4(NMe_2)]_3Cl_2$ and $Bi[p\text{-}C_6H_4CH_2N(2\text{-}Py)_2]_3Cl_2$ compounds react readily with silver salts, AgL, where L is a carboxylate derivative, RCO_2^-, to form the substituted complexes $Bi[p\text{-}C_6H_4(NMe_2)]_3(O_2CR)_2$ and $Bi[p\text{-}C_6H_4CH_2N(2\text{-}Py)_2]_3(O_2CR)_2$, respectively. Compounds $Bi[p\text{-}C_6H_4(NMe_2)]_3(O_2CCF_3)_2$ (**5**) and $Bi[p\text{-}C_6H_4\text{-}CH_2N(2\text{-}Py)_2]_3(O_2CCH_3)_2$ (**7**) have been fully characterized by NMR, elemental, and X-ray diffraction analyses. In the absence of silver salt and in the presence of moisture and NaOH, the $Bi[p\text{-}C_6H_4(NMe_2)]_3Cl_2$ compound is converted to the dinuclear complex, $Bi_2[p\text{-}C_6H_4(NMe_2)]_6Cl_2(O)$ (**6**) in good yield. Compound **6** was also commonly found as a trace product from the reactions of compound **1** with silver salts.

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(6) Hawley, D. M.; Ferguson, G. *J. Chem. Soc. A* **1968**, 2059.

(7) CACHe Scientific, Inc., USA, 1994.

(8) (a) Challenger, F. *J. Chem. Soc.* **1916**, *109*, 250. (b) Keck, J. M.; Klar, G. *Z. Naturforsch. (B)* **1972**, *27*, 596.

(9) Hawley, D. M.; Ferguson, G. *J. Chem. Soc. (A)* **1968**, 2539.

(10) Crystal data for $Bi[p\text{-}C_6H_4(NMe_2)]_3Cl_2/2$ THF: hexagonal space group $R3c$ (# 161), $a = 12.521(3)$ Å, $c = 33.834(7)$ Å, $V = 4593(2)$ Å^3, $Z = 6$. The satisfactory refinement for this compound was not achieved due to the disorder of the two THF molecules.

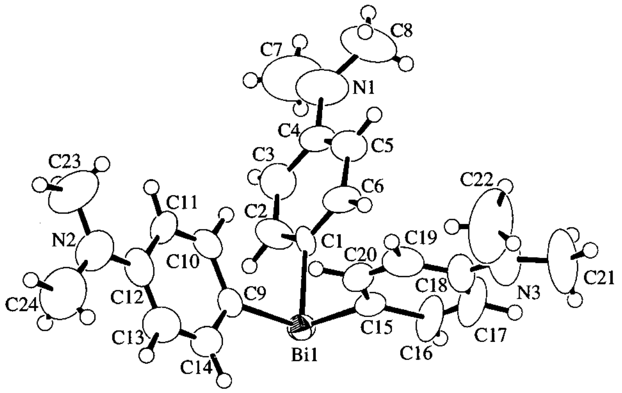
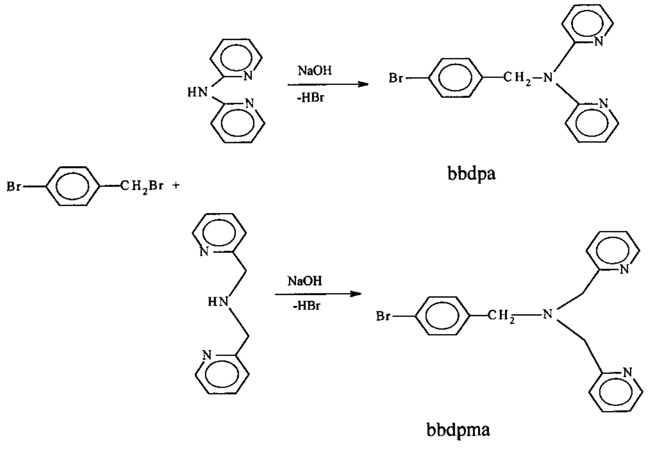


Figure 1. ORTEP diagram showing the molecular structure of compound **1** with 50% thermal ellipsoids and labeling scheme.

Scheme 1



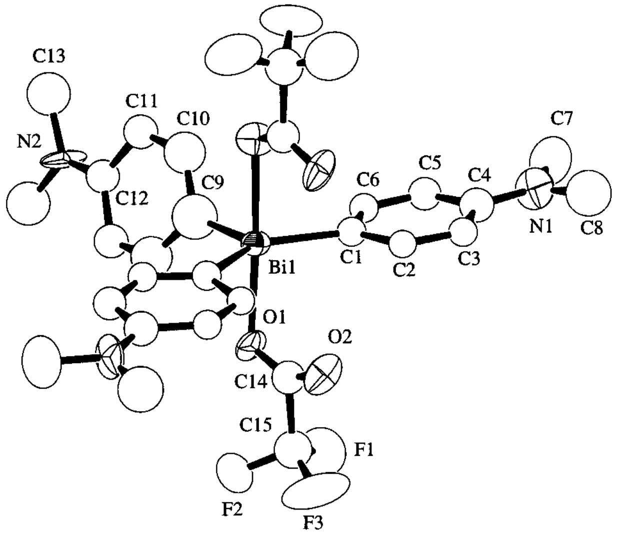


Figure 2. ORTEP diagram showing the molecular structure of compound **5** with 50% thermal ellipsoids and labeling scheme.

An ORTEP diagram showing the molecular structure of compound **5** is given in Figure 2. Important bond lengths and angles are listed in Table 2. Compound **5** has an approximately trigonal bipyramidal geometry with a crystallographically imposed C_2 axis where the Bi(1), N(2), C(9), and C(12) atoms lie. The Bi–C bond lengths (2.00(6)–2.15(2) Å) are shorter than those observed in compound **1**, but comparable with those observed in $BiPh_3(O_2CCF_3)_2$. The Bi(1)–O(1) bond length of 2.32(1) Å is similar to that[11] in $BiPh_3(O_2CCF_3)_2$. The noncoordinating O(2) and O(2′) atoms are 3.16 Å away from the Bi(1) center. The C–Bi–C angles range from 110.9(7)° to 138(1)°, indicative of the significant distortion from the ideal trigonal bipyramidal geometry. There are two distinct environments for the three aromatic ligands of **5** in the solid state, two of which (C(1) and C(1′) rings) are perpendicular to the Bi–O vector and are on the same side as the noncoordinating O(2) and O(2′) atoms while the third one is parallel to the Bi–O vector and is on the opposite side from the O(2) and O(2′) atoms. However, in solution, only one aromatic ligand environment is observed, as established by ^{13}C and ^{1}H NMR spectroscopic analysis, which can be attributed to the relatively low energy required for the rotation of the Bi(1)–O(1) and Bi(1)–O(1′) bonds.

An ORTEP diagram showing the structure of the dinuclear complex, $Bi_2[p\text{-}C_6H_4(NMe_2)]_6Cl_2(O)$ (**6**), is given in Figure 3. Important bond lengths and angles are given in Table 2. Compound **6** contains two $Bi[p\text{-}C_6H_4(NMe_2)]_3Cl$ units linked together by an oxygen atom. The Bi(1)–O(1) and Bi(2)–O(1) bond lengths, 2.12(3) and 2.02(3) Å, are comparable to those observed in $Bi_2Ph_6(ClO_4)_2(O)$, reported by Ferguson and coworkers.[12b] The Bi(1)–O(1)–Bi(2) angle (166(1)°) deviated from linearity by 14°, however, is much larger than that (142.2(7)°) in $Bi_2Ph_6(ClO_4)_2(O)$, possibly caused by the increased steric bulkiness in **6**. The geometry surrounding each bismuth center is very close to the ideal trigonal bipyramidal geometry, as evidenced by the O–Bi–Cl angles (175.9(6)° and 179.5(8)°) and the C–Bi–C angles ranging from 117(1)° to 123(1)°. The Bi–Cl bond lengths (2.79(1) and 2.77(1) Å) are much longer than those observed in $Bi[p\text{-}C_6H_4(NMe_2)]_3Cl_2$ and $BiPh_3Cl_2$, perhaps due to the stronger *trans* effect induced by the oxo lingand than that by the chloro ligand. Although several oxo-bridged dinuclear bismuth(V) complexes are known, few of them have been characterized structurally. In fact, to our knowledge, compound **6** is only the second example of a structurally characterized oxo-bridged dinuclear bismuth complex.[12]

The ORTEP diagram showing the structure of compound **7** is given in Figure 4. Selected bond lengths and angles are listed in Table 2. The structure of **7** bears some resemblance to that of compound **5**, i.e., five-coordinate with three carbon and two oxygen coordinating atoms. There are, however, several structural features in **7** which are significantly different from those in **5**. First of all, the Bi(1)–O(1) and Bi(1)–O(3) bond lengths, 2.19(2) and 2.25(2) Å, are considerably shorter than those in **5**. The noncoordinating O(2) and O(4) atoms are at 2.80 and 2.81 Å, respectively, from the bismuth center, much closer than those in **5**, indicating that some weak bonding interactions between the bismuth and the noncoordinating oxygen atoms may exist. Secondly, the geometry of the bismuth center in **7** is much more distorted from the trigonal planar geometry than that in **5**, as indicated by the C(22)–Bi(1)–C(39) angle of 146(1)°, the C(5)–Bi(1)–C(22) angle of 109(1)°, and the C(5)–Bi(1)–C(39) angle of 104(1)°. The geometry of compound **7** can therefore be

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[11] Ferguson, G.; Kaitner, B. *J. Organomet. Chem.* **1991**, *419*, 283.

[12] (a) Goel, R. G.; Prasad, H. S. *J. Organomet. Chem.* **1972**, *36*, 323. (b) March, F. C.; Ferguson, G. *J. Chem. Soc., Dalton Trans.* **1975**, 1291.

Table 2. Selected Bond Lengths (Å) and Angles (deg)

Compound **1**

atom	atom	distance	atom	atom	distance	atom	atom	distance	atom	atom	distance
Bi(1)	C(1)	2.25(1)	Bi(1)	C(9)	2.22(2)	N(2)	C(12)	1.36(2)	N(2)	C(23)	1.45(2)
Bi(1)	C(15)	2.25(2)	N(1)	C(4)	1.41(2)	N(2)	C(24)	1.44(2)	N(3)	C(18)	1.41(3)
N(1)	C(7)	1.42(2)	N(1)	C(8)	1.52(3)	N(3)	C(21)	1.42(3)	N(3)	C(22)	1.46(3)

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C(1)	Bi(1)	C(9)	95.6(5)	Bi(1)	C(9)	C(14)	122(1)	C(18)	N(3)	C(21)	115(2)	C(18)	N(3)	C(22)	122(2)
C(1)	Bi(1)	C(15)	94.1(5)	Bi(1)	C(9)	C(10)	121(1)	C(21)	N(3)	C(22)	120(2)	Bi(1)	C(15)	C(16)	120(1)
C(9)	Bi(1)	C(15)	93.7(6)	Bi(1)	C(9)	C(14)	122(1)	Bi(1)	C(1)	C(2)	118(1)	Bi(1)	C(15)	C(20)	123(1)
C(4)	N(1)	C(7)	123(2)	C(4)	N(1)	C(8)	118(2)	Bi(1)	C(1)	C(6)	122(1)	N(3)	C(18)	C(17)	124(2)
C(7)	N(1)	C(8)	118(2)	C(12)	N(2)	C(23)	119(2)	N(1)	C(4)	C(3)	118(2)	N(3)	C(18)	C(19)	119(2)
C(12)	N(2)	C(24)	119(2)	C(23)	N(2)	C(24)	121(2)	N(1)	C(4)	C(5)	121(2)				

Compound **5**

atom	atom	distance	atom	atom	distance	atom	atom	distance	atom	atom	distance
Bi(1)	O(1)	2.32(1)	N(2)	C(13)	1.45(3)	O(2)	C(14)	1.24(3)	N(1)	C(4)	1.31(3)
Bi(1)	C(1)	2.15(2)	Bi(1)	C(9)	2.00(6)	N(1)	C(7)	1.43(4)	C(2)	C(3)	1.37(3)
F(1)	C(15)	1.24(4)	F(2)	C(15)	1.36(3)	N(1)	C(8)	1.43(4)	C(14)	C(15)	1.63(4)
F(3)	C(15)	1.30(4)	O(1)	C(14)	1.16(3)	N(2)	C(12)	1.28(5)			

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
O(1)	Bi(1)	O(1′)	176(1)	N(1)	C(4)	C(3)	123(3)	C(4)	N(1)	C(8)	123(3)	Bi(1)	C(1)	C(6)	120(2)
O(1)	Bi(1)	C(1)	92.0(8)	N(1)	C(4)	C(5)	121(3)	C(7)	N(1)	C(8)	113(3)	O(1)	C(14)	O(2)	137(3)
O(1′)	Bi(1)	C(1)	89.6(8)	O(1)	Bi(1)	C(9)	87.8(5)	C(12)	N(2)	C(13)	124(2)	O(1)	C(14)	C(15)	115(3)
C(1)	Bi(1)	C(1′)	138(1)	C(1)	Bi(1)	C(9)	110.9(7)	C(12)	N(2)	C(13′)	124(2)	O(2)	C(14)	C(15)	107(3)
Bi(1)	C(9)	C(10)	127(2)	Bi(1)	C(9)	C(10′)	127(2)	C(13)	N(2)	C(13′)	112(3)	F(1)	C(15)	F(2)	105(3)
Bi(1)	O(1)	C(14)	109(2)	N(2)	C(12)	C(11)	122(2)	Bi(1)	C(1)	C(2)	120(2)	F(1)	C(15)	F(3)	110(3)
C(4)	N(1)	C(7)	124(3)	N(2)	C(12)	C(11)	122(2)	F(2)	C(15)	F(3)	103(3)				

Compound **6**

atom	atom	distance	atom	atom	distance	atom	atom	distance	atom	atom	distance
Bi(1)	Cl(1)	2.79(1)	N(5)	C(40)	1.56(6)	Bi(2)	C(33)	2.20(3)	N(2)	C(15)	1.46(5)
Bi(1)	O(1)	2.12(3)	N(6)	C(44)	1.41(5)	Bi(2)	C(41)	2.24(4)	N(2)	C(16)	1.42(5)
Bi(1)	C(1)	2.24(4)	N(6)	C(47)	1.38(5)	Cl(3)	C(49)	1.71(7)	N(3)	C(20)	1.41(4)
Bi(1)	C(9)	2.14(4)	N(6)	C(48)	1.48(5)	Cl(4)	C(49)	1.79(8)	N(3)	C(23)	1.40(5)
Bi(1)	C(17)	2.15(3)	N(1)	C(4)	1.40(5)	N(3)	C(24)	1.42(6)	N(4)	C(28)	1.37(5)
Bi(2)	Cl(2)	2.77(1)	N(1)	C(7)	1.40(5)	N(4)	C(31)	1.38(5)	N(4)	C(32)	1.44(5)
Bi(2)	O(1)	2.02(3)	N(1)	C(8)	1.43(7)	N(5)	C(36)	1.27(5)	N(5)	C(39)	1.45(5)
Bi(2)	C(25)	2.24(4)	N(2)	C(12)	1.41(4)						

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
Cl(1)	Bi(1)	O(1)	175.9(6)	C(15)	N(2)	C(16)	121(4)	O(1)	Bi(2)	C(41)	90(1)	N(1)	C(4)	C(3)	120(5)
Cl(1)	Bi(1)	C(1)	83(1)	C(20)	N(3)	C(23)	124(4)	C(25)	Bi(2)	C(33)	120(1)	N(1)	C(4)	C(5)	117(5)
Cl(1)	Bi(1)	C(9)	87(1)	C(20)	N(3)	C(24)	117(4)	C(25)	Bi(2)	C(41)	120(1)	N(4)	C(28)	C(27)	126(5)
Cl(1)	Bi(1)	C(17)	89(1)	C(23)	N(3)	C(24)	119(4)	C(33)	Bi(2)	C(41)	120(1)	N(4)	C(28)	C(29)	115(4)
O(1)	Bi(1)	C(1)	93(1)	C(28)	N(4)	C(31)	117(4)	Bi(1)	O(1)	Bi(2)	167(1)	C(4)	N(1)	C(7)	123(5)
O(1)	Bi(1)	C(9)	93(1)	C(28)	N(4)	C(32)	126(4)	C(4)	N(1)	C(8)	124(5)	Bi(2)	C(25)	C(30)	117(3)
O(1)	Bi(1)	C(17)	94(1)	C(31)	N(4)	C(32)	117(4)	C(7)	N(1)	C(8)	112(5)	Bi(1)	C(9)	C(10)	129(3)
C(1)	Bi(1)	C(9)	118(1)	C(36)	N(5)	C(39)	123(4)	C(12)	N(2)	C(15)	118(4)	Bi(1)	C(9)	C(14)	116(3)
C(1)	Bi(1)	C(17)	124(1)	C(36)	N(5)	C(40)	124(4)	C(12)	N(2)	C(16)	121(4)	Bi(2)	C(33)	C(34)	121(3)
C(9)	Bi(1)	C(17)	117(1)	C(39)	N(5)	C(40)	113(4)	N(2)	C(12)	C(11)	122(4)	Bi(2)	C(33)	C(38)	119(3)
Cl(2)	Bi(2)	O(1)	179.5(8)	C(44)	N(6)	C(47)	124(4)	N(2)	C(12)	C(13)	123(4)	N(5)	C(36)	C(35)	122(5)
Cl(2)	Bi(2)	C(25)	89(1)	C(44)	N(6)	C(48)	120(4)	Bi(1)	C(17)	C(18)	121(3)	N(5)	C(36)	C(37)	120(5)
Cl(2)	Bi(2)	C(33)	83(1)	C(47)	N(6)	C(48)	115(4)	Bi(1)	C(17)	C(22)	123(3)	Bi(2)	C(41)	C(42)	119(3)
Cl(2)	Bi(2)	C(41)	90(1)	Bi(1)	C(1)	C(2)	123(3)	N(3)	C(20)	C(19)	123(4)	Bi(2)	C(41)	C(46)	118(3)
O(1)	Bi(2)	C(25)	91(1)	Bi(1)	C(1)	C(6)	117(3)	N(3)	C(20)	C(21)	120(4)	N(6)	C(44)	C(43)	116(4)
O(1)	Bi(2)	C(33)	97(1)	C(2)	C(1)	C(6)	120(4)	Bi(2)	C(25)	C(26)	125(3)	N(6)	C(44)	C(45)	119(5)

Compound **7**

atom	atom	distance	atom	atom	distance	atom	atom	distance	atom	atom	distance
Bi(1)	O(1)	2.19(2)	N(5)	C(33)	1.39(5)	N(2)	C(12)	1.29(4)	N(9)	C(55)	1.36(4)
Bi(1)	O(3)	2.25(2)	N(6)	C(34)	1.33(4)	C(1)	C(2)	1.45(4)	C(3)	C(4)	1.48(4)
Bi(1)	C(5)	2.26(3)	N(6)	C(38)	1.44(4)	N(2)	C(16)	1.46(5)	N(3)	C(17)	1.36(3)
Bi(1)	C(22)	2.19(3)	N(7)	C(45)	1.50(3)	N(1)	C(11)	1.47(3)	N(3)	C(21)	1.28(4)
Bi(1)	C(39)	2.24(3)	N(7)	C(46)	1.39(3)	N(1)	C(12)	1.44(4)	N(4)	C(28)	1.54(3)
O(1)	C(1)	1.26(3)	N(7)	C(51)	1.39(3)	N(1)	C(17)	1.35(3)	N(4)	C(29)	1.41(4)
O(2)	C(1)	1.31(3)	N(8)	C(46)	1.31(4)	N(4)	C(34)	1.43(3)	N(5)	C(29)	1.35(4)
O(3)	C(3)	1.32(3)	N(8)	C(50)	1.35(5)	C(8)	C(11)	1.49(4)	C(25)	C(28)	1.60(4)
O(4)	C(3)	1.25(3)	N(9)	C(51)	1.34(3)	C(42)	C(45)	1.54(4)			

Table 2. (Continued)

Compound **7**

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
O(1)	Bi(1)	O(3)	170.6(8)	C(29)	N(4)	C(34)	127(3)	C(28)	N(4)	C(29)	115(3)	N(1)	C(11)	C(8)	115(3)
O(1)	Bi(1)	C(5)	86(1)	C(29)	N(5)	C(33)	120(4)	C(28)	N(4)	C(34)	118(3)	N(1)	C(12)	N(2)	110(4)
O(1)	Bi(1)	C(22)	88.7(9)	C(34)	N(6)	C(38)	115(3)	N(1)	C(12)	C(13)	120(4)	N(5)	C(29)	C(30)	119(4)
O(1)	Bi(1)	C(39)	94.9(9)	C(45)	N(7)	C(46)	123(3)	N(2)	C(12)	C(13)	130(4)	N(5)	C(33)	C(32)	122(4)
O(3)	Bi(1)	C(5)	85(1)	C(45)	N(7)	C(51)	112(3)	N(2)	C(16)	C(15)	113(4)	N(4)	C(34)	N(6)	109(4)
O(3)	Bi(1)	C(22)	91.8(6)	C(46)	N(7)	C(51)	122(3)	N(1)	C(17)	N(3)	118(3)	N(4)	C(34)	C(35)	125(4)
O(3)	Bi(1)	C(39)	89.9(9)	C(46)	N(8)	C(50)	120(4)	N(1)	C(17)	C(18)	122(4)	N(6)	C(34)	C(35)	126(4)
C(5)	Bi(1)	C(22)	109(1)	C(51)	N(9)	C(55)	116(4)	N(3)	C(17)	C(18)	119(3)	N(6)	C(38)	C(37)	119(4)
C(5)	Bi(1)	C(39)	105(1)	O(1)	C(1)	O(2)	116(3)	N(3)	C(21)	C(20)	127(4)	Bi(1)	C(39)	C(40)	115(3)
C(22)	Bi(1)	C(39)	146(1)	O(1)	C(1)	C(2)	131(3)	Bi(1)	C(22)	C(23)	115(2)	Bi(1)	C(39)	C(44)	122(3)
Bi(1)	O(1)	C(1)	113(2)	O(2)	C(1)	C(2)	114(3)	Bi(1)	C(22)	C(27)	124(3)	N(7)	C(51)	C(52)	122(4)
Bi(1)	O(3)	C(3)	105(2)	O(3)	C(3)	O(4)	122(3)	N(4)	C(28)	C(25)	113(3)	N(7)	C(46)	N(8)	117(4)
O(3)	C(3)	C(4)	117(4)	O(4)	C(3)	C(4)	121(4)	N(4)	C(29)	N(5)	121(4)	N(7)	C(46)	C(47)	121(4)
Bi(1)	C(5)	C(6)	118(3)	Bi(1)	C(5)	C(10)	119(2)	N(4)	C(29)	C(30)	120(4)	N(8)	C(46)	C(47)	122(4)
C(11)	N(1)	C(12)	118(3)	C(11)	N(1)	C(17)	121(3)	N(8)	C(50)	C(49)	118(5)	N(9)	C(51)	C(52)	116(3)
C(12)	N(1)	C(17)	120(3)	C(12)	N(2)	C(16)	117(4)	N(7)	C(51)	N(9)	121(4)	N(9)	C(55)	C(54)	129(5)
C(17)	N(3)	C(21)	120(3)	N(7)	C(45)	C(42)	113(3)								

Compound **8**

atom	atom	distance	atom	atom	distance	atom	atom	distance	atom	atom	distance
Bi	C(1)	2.167(10)	N(3)	C(20)	1.36(2)	N(1)	C(4)	1.37(2)	N(4)	C(31)	1.43(1)
Bi	C(9)	2.194(8)	N(3)	C(23)	1.43(1)	N(1)	C(7)	1.46(1)	N(4)	C(32)	1.43(1)
Bi	C(17)	2.181(9)	N(3)	C(24)	1.45(1)	N(1)	C(8)	1.46(1)	N(2)	C(15)	1.48(1)
Bi	C(25)	2.192(8)	N(4)	C(28)	1.37(1)	N(2)	C(12)	1.37(1)	N(2)	C(16)	1.45(1)

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C(1)	Bi	C(9)	106.1(3)	C(15)	N(2)	C(16)	117.0(7)	Bi	C(9)	C(14)	119.6(6)	C(4)	N(1)	C(7)	120(1)
C(1)	Bi	C(17)	112.0(3)	C(20)	N(3)	C(23)	120(1)	C(4)	N(1)	C(8)	122(1)	N(2)	C(12)	C(11)	122.1(9)
C(1)	Bi	C(25)	107.7(3)	C(20)	N(3)	C(24)	119.2(9)	C(7)	N(1)	C(8)	117.4(9)	N(2)	C(12)	C(13)	121(1)
C(9)	Bi	C(17)	109.0(3)	C(23)	N(3)	C(24)	117.7(9)	C(12)	N(2)	C(15)	119.5(8)	N(3)	C(20)	C(21)	124(1)
C(9)	Bi	C(25)	110.0(3)	C(28)	N(4)	C(31)	121.1(8)	C(12)	N(2)	C(16)	120.4(8)	Bi	C(25)	C(26)	118.2(6)
C(17)	Bi	C(25)	111.9(3)	C(28)	N(4)	C(32)	119.3(9)	Bi	C(17)	C(18)	119.7(7)	Bi	C(25)	C(30)	120.4(7)
Bi	C(1)	C(2)	119.7(7)	C(31)	N(4)	C(32)	117.4(8)	Bi	C(17)	C(22)	120.0(6)	N(3)	C(20)	C(19)	120(1)
Bi	C(1)	C(6)	121.2(7)	N(1)	C(4)	C(3)	123(1)	N(4)	C(28)	C(27)	119(1)	N(4)	C(28)	C(29)	124(1)
Bi	C(9)	C(10)	119.0(7)	N(1)	C(4)	C(5)	120(1)								

Compound **9**

atom	atom	distance	atom	atom	distance	atom	atom	distance	atom	atom	distance
Bi(1)	C(1)	2.15(2)	N(1)	C(4)	1.35(3)	Ag(1)	Cl(1)	2.367(8)	N(2)	C(16)	1.46(3)
Bi(1)	C(9)	2.16(2)	N(1)	C(7)	1.43(3)	Ag(1)	Cl(2)	2.571(9)	N(3)	C(20)	1.39(3)
Bi(1)	C(17)	2.18(3)	N(1)	C(8)	1.44(4)	Ag(1)	Cl(2′)	2.540(8)	N(3)	C(23)	1.48(3)
Bi(1)	C(25)	2.14(2)	N(2)	C(12)	1.38(3)	N(3)	C(24)	1.46(3)	N(4)	C(28)	1.39(3)
Ag(1)	Ag(1′)	3.211(5)	N(2)	C(15)	1.39(3)	N(4)	C(31)	1.41(4)	N(4)	C(32)	1.44(3)

atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle	atom	atom	atom	angle
C(1)	Bi(1)	C(9)	109.8(9)	Bi(1)	C(1)	C(6)	124(2)	C(4)	N(1)	C(7)	122(3)	N(3)	C(20)	C(21)	123(2)
C(1)	Bi(1)	C(17)	106(1)	Bi(1)	C(17)	C(18)	118(2)	C(4)	N(1)	C(8)	122(3)	N(2)	C(12)	C(11)	119(3)
C(1)	Bi(1)	C(25)	109.8(9)	Bi(1)	C(17)	C(22)	123(2)	C(7)	N(1)	C(8)	116(3)	N(2)	C(12)	C(13)	122(3)
C(9)	Bi(1)	C(17)	107(1)	Bi(1)	C(1)	C(2)	119(2)	C(12)	N(2)	C(15)	121(3)	C(12)	N(2)	C(16)	119(3)
C(9)	Bi(1)	C(25)	110.2(9)	N(1)	C(4)	C(3)	123(3)	C(15)	N(2)	C(16)	118(3)	C(20)	N(3)	C(23)	121(2)
C(17)	Bi(1)	C(25)	113(1)	N(1)	C(4)	C(5)	121(3)	C(20)	N(3)	C(24)	120(3)	C(23)	N(3)	C(24)	117(3)
Cl(1)	Ag(1)	Cl(2)	129.1(3)	Bi(1)	C(9)	C(10)	123(2)	C(28)	N(4)	C(31)	119(3)	C(28)	N(4)	C(32)	120(3)
Cl(1)	Ag(1)	Cl(2′)	130.9(4)	Bi(1)	C(9)	C(14)	123(2)	C(31)	N(4)	C(32)	120(3)	N(3)	C(20)	C(19)	119(3)
Cl(2)	Ag(1)	Cl(2′)	99.9(3)	Bi(1)	C(25)	C(26)	120(2)	N(4)	C(28)	C(27)	123(3)	N(4)	C(28)	C(29)	120(3)
Ag(1)	Cl(2)	Ag(1′)	77.8(3)	Bi(1)	C(25)	C(30)	126(2)								

described best as an intermediate between a trigonal bipyramid and a square pyramid. Thirdly, the environment surrounding each of the aromatic ligands, p-$\mathrm{C_6H_4CH_2N(2\text{-}Py)_2}$, is not identical. The environments of two of the aromatic ligands, C(22) and C(39), which are on the same side as the noncoordinating O(2) and O(4) atoms, are much closer than that of the third aromatic ligand, C(5), which is on the opposite side of the O(2) and O(4) atoms and occupies the axial position of the distorted square pyramid. However, the pyridyl groups of the C(39) ligand are oriented away from the pyridyls of the C(5) ligand, while the pyridyls of the C(22) ligand are oriented toward the pyridyls of the C(5) ligand. If compound **7** retains the same structure in solution, one would expect to observe three sets of chemical shifts due to the three p-$\mathrm{C_6H_4CH_2N(2\text{-}Py)_2}$ ligands. Indeed, the proton NMR spectrum of compound **7** in the aromatic region shows a complicated pattern which cannot be assigned unambiguously. The ^{13}C NMR spectrum of compound **7**, however, shows three well-resolved sets of chemical shifts for each of the unique carbon atoms on the phenyl ring and the carbon atom of the methylene group, where the three chemical shifts due to the quaternary carbon atoms bonded to the bismuth center differ most dramatically (see the Experimental Section). The NMR results lead us to suggest that compound **7**

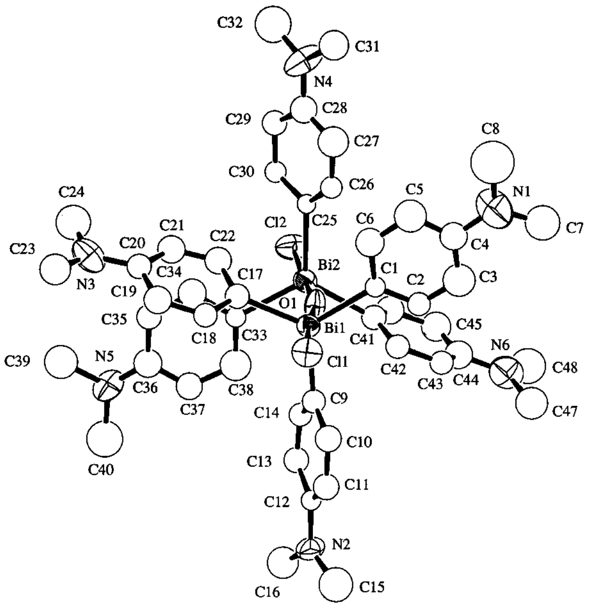

Figure 3. ORTEP diagram showing the molecular structure of compound **6** with 50% thermal ellipsoids and labeling scheme.

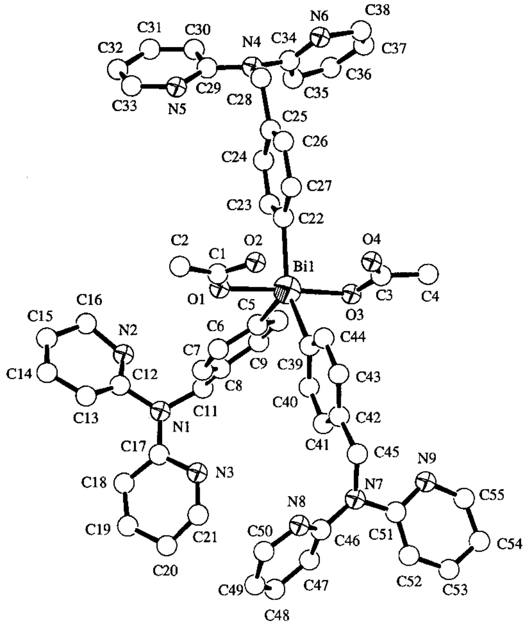

Figure 4. ORTEP diagram showing the molecular structure of compound **7** with 50% thermal ellipsoids and labeling scheme.

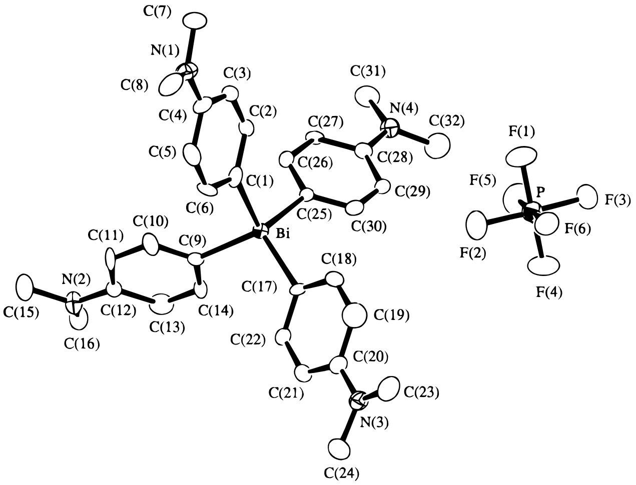

Figure 5. ORTEP diagram showing the structure of compound **8** with 50% thermal ellipsoids and labeling scheme.

indeed retains its asymmetric structure in solution, which is in sharp contrast to the behavior of compound **5**. We believe that the structural rigidity of compound **7** could be caused by two factors, the possible weak bonding interactions between Bi(1) and O(2) and O(4) which would make the rotation of the Bi(1)−O(1) bond and the Bi(1)−O(3) bond more energy demanding than that in **5** and the steric bulkiness of the ligands in **7** which could also prevent the free rotation of the Bi(1)−O(1) and Bi(1)−O(3) bonds by avoiding too many nonbonding interactions. It is very likely that the second factor plays a more important role than the first one because the similar structural rigidity was not observed in the analogous bismuth(V) complexes,[13] Bi[*p*-C_6H_4-$(NMe_2)]_3(O_2CR)_2$, where R is a non-trifluoromethyl group and the distances between the Bi and the noncoordinating oxygen atoms are similar to those observed in **7**. Compound **7** is the first example of a tertiary bismuth(V) complex containing the bidentate dipyridyl functional group.

Syntheses and Structures of Quaternary Bismuth(V) Complexes Bi[*p*-$C_6H_4(NMe_2)]_4[PF_6]$ (8) and {Bi[*p*-$C_6H_4(NMe_2)]_4\}_2[Ag_2Cl_4]$ (9). It has been observed earlier that when the compound $BiPh_3Cl_2$ is reacted with silver salts where the anion is noncoordinating, such as BF_4^- or PF_6^-, or weakly coordinating, such as ClO_4^-, several products including the tetrahedral cation $[BiAr_4]^+$ could be obtained.[14] We performed the reaction of Bi[*p*-$C_6H_4(NMe_2)]_3Cl_2$ (**4**) with $AgBF_4$ or $AgPF_6$ in a 1:2 ratio, which yielded mixed and unidentified products. In contrast, the reaction of Bi[*p*-C_6H_4-$(NMe_2)]_3Cl_2$ with $TlPF_6$ in a 1:2 ratio in CH_2Cl_2 produced the new green crystalline compound Bi[*p*-C_6H_4-$(NMe_2)]_4[PF_6]$ (**8**) in high yield. The mechanism for this reaction has not been understood. Nevertheless, this reaction provides a convenient way for the synthesis of the quaternary bismuth(V) complex containing amino groups. Compound **8** has been fully characterized by NMR, elemental, and X-ray diffraction analyses. At 23 °C, the crystals of compound **8** have a light green color and belong to the tetragonal space group *P*4/*n*. The structure of **8** at 23 °C appeared to be tetrahedral but displayed significant disorders. We therefore determined the structure of **8** by collecting the diffraction data at −79 °C. At −79 °C, compound **8** changed color to blue and the crystal unit cell changed to the monoclinic space group $P2_1/n$, apparently caused by a phase transition.

The ORTEP diagram showing the structure of **8** determined by −79 °C is given in Figure 5. Important bond lengths and angles are listed in Table 2. The geometry of the cation, Bi[*p*-$C_6H_4(NMe_2)]_4^+$, is tetrahedral, as indicated by the C−Bi−C angles ranging from 106.1(3)° to 112.0(3)°. The Bi−C bond lengths, 2.167(10)−2.194(8) Å, are comparable with those observed in the analogous compound $BiPh_4[ClO_4]$ reported

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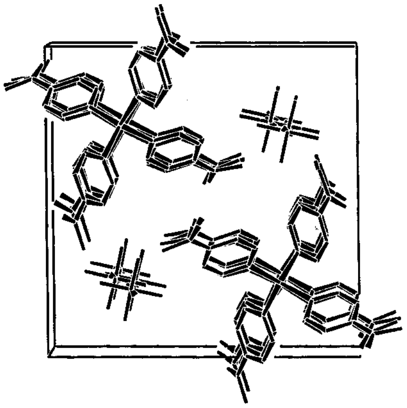

Figure 6. Unit cell packing diagram showing the cation and anion channels of compound **8** down the *b* axis.

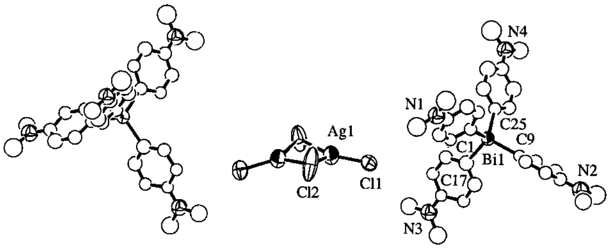

Figure 7. ORTEP diagram showing the structure and the relative location of the cation and anion in compound **9** with 50% thermal ellipsoids and labeling scheme.

by Bordner and Freedman[14c] and $BiPh_4$[tosylate] and $Bi^{V}Ph_4[Bi^{III}Ph_2(O_2CCF_3)_2]$ reported by Barton and coworkers.[1d] However, weak Bi−O bonding interactions appeared to be present in Barton's compounds. In the crystal lattice, the $Bi[p\text{-}C_6H_4(NMe_2)]_4^+$ cations are stacked along one dimension to form a cationic channel. Similarly, the PF_6^- anions are also stacked to form an anionic channel as shown by the unit cell packing diagram (Figure 6). Bismuth(V) complexes containing the $p\text{-}C_6H_4(NMe_2)$ ligand are usually colorless or light yellow. The unusual green color of compound **8** is believed to be caused by ligand to metal charge transfer, possibly involving the lone pair of the nitrogen atom since the analogous compound, $BiPh_4(ClO_4)$, is colorless. In solution, compound **8** appears to undergo some dynamic processes as evident by the broad ^1H and ^{13}C NMR signals of the phenyl group at 293 K. When the solution was cooled to 180 K, relatively sharp and resolved signals were observed. Dynamic processes involving a tetrahedral geometry and a closed d^{10} electronic configuration on the metal center are rare. Further investigation on the electronic structure and the dynamic behavior of compound **8** is in progress.

Compound **8** is closely related to compound **9**, $\{Bi[p\text{-}C_6H_4(NMe_2)]_4\}_2[Ag_2Cl_4]$, obtained as a trace product from the reactions of $Bi[p\text{-}C_6H_4(NMe_2)]_3Cl_2$ with a variety of silver salts, $Ag(O_2CR)$. Attempts to synthesize compound **9** by reacting $Bi[p\text{-}C_6H_4(NMe_2)]_3Cl_2$ with AgCl have not been successful. The structure of **9** was determined by X-ray diffraction analysis. An ORTEP diagram showing the structure and the relative location of the cation and the anion is given in Figure 7. Selected bond lengths and angles are listed in Table 2. The structure of the cation, $Bi[p\text{-}C_6H_4(NMe_2)]_4^+$, is very similar to that in compound **8**. The most interesting feature of compound **9** is the $Ag_2Cl_4^{2-}$ anion which is situated between the cations. The two silver atoms in the anion are bridged by two chlorine atoms with the Ag(1)−Ag(1′) separation distance being 3.211(5) Å. The geometry of the silver atom is approximately trigonal planar. The terminal Cl(1)−Ag(1) bond length, 2.367(8) Å, is significantly shorter than the bridging Cl(2)−Ag(1) and Cl(2′)−Ag(1) bond lengths, 2.571(9) and 2.540(8) Å. Examples of three-coordinate dinuclear silver(I) complexes are not uncommon.[15a] Silver halide complexes have been known to have the tendency to aggregate via the halide bridge forming typically four-coordinate oligomers.[15] To our knowledge, the three-coordinate dinuclear anion $Ag_2Cl_4^{2-}$ is previously unknown, perhaps due to its poor stability. Although the formation mechanism of **9** has not been established, we believe that the unusual $Ag_2Cl_4^{2-}$ anion in compound **9** was trapped and stabilized by the bulky cation $Bi[p\text{-}C_6H_4(NMe_2)]_4^+$.

Conclusion

An improved synthesis and a full characterization for the compound $Bi[p\text{-}C_6H_4(NMe_2)]_3$ (**1**) have been achieved. New tertiary bismuth(III) complexes containing functional groups, $Bi[p\text{-}C_6H_4(CH_2NPr^i_2)]_3$ (**2**) and $Bi\{p\text{-}C_6H_4[CH_2N(2\text{-}Py)_2]\}_3$ (**3**), have been synthesized and characterized. The bismuth(V) derivatives of compounds **1** and **3** can be obtained via oxidation and substitution reactions. The structure and composition of the products obtained from the reaction of $BiAr_3Cl_2$ with AgL are highly dependent on the nature of the anion L and the reaction conditions as demonstrated by the reactions of $Bi[p\text{-}C_6H_4(NMe_2)]_3Cl_2$ with silver salts. The $BiAr_3(O_2CR)_2$ compound can be best described as a distorted trigonal bipyamid. The compound $TlPF_6$ is a better reagent than $AgPF_6$ or $AgBF_4$ for the synthesis of quaternary bismuth(V) complexes. The interactions between the noncoordinate oxygen atoms and the bismuth center are very weak and negligible as demonstrated by the high fluxionality of the $Bi[p\text{-}C_6H_4(NMe_2)]_3(O_2CR)_2$ compounds in solution. The quaternary bismuth(V) complex, $Bi[p\text{-}C_6H_4(NMe_2)]_4[PF_6]$ (**8**), displays an unusual dynamic behavior in solution. The nature and the mechanism of this dynamic process have yet to be established.

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Supporting Information Available: Tables of crystallographic data, atomic coordinates, thermal parameters, and bond lengths and angles (56 pages). Ordering information is given on any current masthead page.

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