Inorganic Chemistry
Article

Inorg. Chem. **2011**, *50*, 1513–1520 **1513**
DOI: 10.1021/ic102119y

Bismuth Coordination Chemistry with Allyl, Alkoxide, Aryloxide, and Tetraphenylborate Ligands and the $\{[2,6\text{-}(\mathrm{Me_2NCH_2})_2\mathrm{C_6H_3}]_2\mathrm{Bi}\}^{+}$ Cation

Ian J. Casely,[†] Joseph W. Ziller,[†] Bruce J. Mincher,[‡] and William J. Evans*[,†]

[†] *Department of Chemistry, University of California, Irvine, California 92697-2025, United States, and*
[‡] *Aqueous Separations and Radiochemistry Department, Idaho National Laboratory, Idaho Falls, Idaho 83415-6180, United States*

Received October 20, 2010

A series of bis(aryl) bismuth compounds containing (*N,C,N*)-pincer ligands, $[2,6\text{-}(\mathrm{Me_2NCH_2})_2\mathrm{C_6H_3}]^-$ (Ar′), have been synthesized and structurally characterized to compare the coordination chemistry of Bi^{3+} with similarly sized lanthanide ions, Ln^{3+}. Treatment of $\mathrm{Ar'_2BiCl}$, **1**, with $\mathrm{ClMg(CH_2CH{=}CH_2)}$ affords the allyl complex $\mathrm{Ar'_2Bi}(\eta^1\text{-}\mathrm{CH_2CH{=}CH_2})$, **2**, in which only one allyl carbon atom coordinates to bismuth. Complex **1** reacts with $\mathrm{KO^tBu}$ and $\mathrm{KOC_6H_3Me_2}$-2,6 to yield the alkoxide $\mathrm{Ar'_2Bi(O^tBu)}$, **3**, and aryloxide $\mathrm{Ar'_2Bi(OC_6H_3Me_2\text{-}2,6)}$, **4**, respectively, but the analogous reaction with the larger $\mathrm{KOC_6H_3{}^tBu_2}$-2,6 forms $\mathrm{[Ar'_2Bi][OC_6H_3{}^tBu_2\text{-}2,6]}$, **6**, in which the aryloxide ligand acts as an outer sphere anion. Chloride is removed from **1** by $\mathrm{NaBPh_4}$ to form $\mathrm{[Ar'_2Bi][BPh_4]}$, **5**, which crystallizes from THF in an unsolvated form with tetraphenylborate as an outer sphere counteranion.

Introduction

Bismuth has many interesting medical and technological applications[1−3] that include treatment of gastrointestinal disorders,[4] applications in radioisotope therapy,[5] and assembly of advanced materials such as superconductors,[6] ferroelectric devices,[7,8] and specialized pigments.[2] Additionally, the use of its oxidative capacity[9] to achieve separations in nuclear waste streams has been investigated.[10,11] Specifically, $\mathrm{NaBiO_3}$ has been examined as a convenient oxidant to convert Am^{3+} to Am^{6+} and allow separation of americium from the trivalent lanthanides in nuclear waste streams.[12]

Surprisingly, in the presence of this bismuth oxidant the separation efficiency has been observed to decrease.[13] It is possible that this is due to interference by the trivalent oxidation byproduct, Bi^{3+}, in competition with Ln^{3+} ions in the separation process. The Shannon ionic radii of Bi^{3+} (1.03 and 1.17 Å for six and eight-coordination, respectively) are similar to those of La^{3+} (1.032 and 1.16 Å, respectively)[14] and consequently these ions have the same charge-to-radius ratio. Accordingly, to a first approximation based on electrostatic and steric factors, analogous complexes of bismuth and the lanthanides could adopt similar coordination geometries.[2,15] However, it is well established that the coordination chemistry of bismuth can be influenced by a stereochemically active lone pair,[16,17] and bismuth has a very different Pauling electronegativity, 1.9, compared to 1.10−1.25 for the lanthanides.[18]

We report here synthetic and structural results in organobismuth chemistry that allow comparisons to be made between the coordination geometries of bismuth and the lanthanides. Specifically, we have examined Bi^{3+} complexes ligated by the (*N*,*C*,*N*)-pincer ligand, $[2,6\text{-}(\mathrm{Me_2NCH_2})_2\mathrm{C_6H_3}]^-$ (Ar′), originally studied with the transition metals by van Koten et al.[19−26] The bismuth chemistry of the Ar′ ligand was initially investigated by Cowley and co-workers,[27] and subsequent

---

*To whom correspondence should be addressed. E-mail: wevans@uci.edu.

(1) Briand, G. G.; Burford, N. *Chem. Rev.* **1999**, *99*, 2601.
(2) Mehring, M. *Coord. Chem. Rev.* **2007**, *251*, 974.
(3) Hanna, T. A. *Coord. Chem. Rev.* **2004**, *248*, 429.
(4) Sadler, P. J.; Li, H.; Sun, H. *Coord. Chem. Rev.* **1999**, *185−186*, 689.
(5) Deb, S.; Abdulghani, S.; Behiri, J. C. *Biomaterials* **2002**, *23*, 3387.
(6) Rao, G. V. R.; Swaminathan, K.; Sreedharan, O. M.; Venkadesan, S.; Mannan, S. L.; Varadaraju, U. V. *J. Mater. Sci.* **1998**, *33*, 1511.
(7) Isupov, V. A. *Ferroelectrics* **1996**, *189*, 211.
(8) Park, B. H.; Kang, B. S.; Bu, S. D.; Noh, T. W.; Lee, J.; Jo, W. *Nature* (*London*) **1999**, *401*, 682.
(9) Postel, M.; Dunach, E. *Coord. Chem. Rev.* **1996**, *155*, 127.
(10) Hara, M.; Suzuki, S. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 1041.
(11) Hara, M.; Suzuki, S. J. *Radioanal. Chem.* **1977**, *36*, 95.
(12) Mincher, B. J.; Martin, L. R.; Schmitt, N. C. *Inorg. Chem.* **2008**, *47*, 6984.
(13) Mincher, B. J.; Schmitt, N. C.; Case, M. E. *Solvent Extr. Ion Exch.* **2011**, in press.
(14) Shannon, R. D. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1976**, *32*, 751.
(15) Mansfield, D.; Mehring, M. Z. *Anorg. Allg. Chem.* **2005**, *631*, 2429.
(16) Norman, N. C. *Chemistry of Arsenic, Antimony and Bismuth*, 1st ed.; Blackie Academic Professional: London, 1998.
(17) Silvestru, C.; Breunig, H. J.; Althaus, H. *Chem. Rev.* **1999**, *99*, 3277.
(18) Lide, D. R., Ed.; *CRC Handbook of Chemistry and Physics*, 90th ed.; CRC Press/Taylor and Francis: Boca Raton, FL, Internet Version 2010.
(19) van Koten, G. *Pure Appl. Chem.* **1989**, *61*, 1681.
(20) van Koten, G. *Pure Appl. Chem.* **1990**, *62*, 1155.
(21) van Koten, G.; Jastrzebski, J. T. B. H.; Noh, J. G.; Spek, A. L.; Shoone, I. C. *J. Organomet. Chem.* **1978**, *148*, 233.

studies have been reported by Breunig, Silvestru, and coworkers.[28−30] This ligand was chosen for our comparative studies since it provides a favorable bismuth-aryl bond with chelating nitrogen donor groups that can fill the coordination sphere of bismuth if needed. The synthesis of the bis(aryl) Bi^{3+} complexes, $(Ar')_2BiX$, was examined since the two Ar′ ligands provide a stable coordination environment for bismuth while leaving a single anionic X site for evaluation.[31] Comparisons will be made with $(C_5Me_5)_2LnX$ lanthanide complexes since the bis(pentamethylcyclopentadienyl) ligand set also provides a stable coordination environment to lanthanides with one X site, and an extensive set of complexes is known with lanthanum through lutetium. Lanthanide complexes of the $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]^-$ ligand are known,[32,33] but the set of compounds is insufficient for the comparisons of X ligand binding desired in this study. In fact, crystallographically characterized complexes are known only for species containing one of these ligands: $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]LuCl_2(\mu\text{-}Cl)[\mu\text{-}Li(THF)_2]\}_2$, $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Lu(\mu\text{-}Cl)(CH_2SiMe_3)\}_2$, and $(\eta^5\text{-}C_5H_5)_2La[2,6\text{-}(Me_2NCH_2)_2C_6H_3]$.[32,33] It has previously been noted that the bis(dimethylaminomethyl)phenyl (*N,C,N*) ligand may be considered as a replacement for cyclopentadienyl-based ligands in terms of both the number of coordination sites it can occupy and the bonding electrons it provides.[32]

Experimental Section

All manipulations and syntheses described below were conducted with the rigorous exclusion of air and water using standard Schlenk line and glovebox techniques, under an argon or dinitrogen atmosphere. Solvents were sparged with UHP argon and dried by passage through columns containing Q-5 and molecular sieves prior to use. Deuterated NMR solvents were purchased from Cambridge Isotope Laboratories, dried over NaK alloy, degassed by three freeze−pump−thaw cycles and vacuum transferred before use. ^1H NMR spectra were recorded on Bruker DR400, GN500, or CRYO500 MHz spectrometers (^{13}C spectra on 500 MHz spectrometer operating at 125 MHz) at 298 K unless otherwise stated and referenced internally to residual protio-solvent resonances. Elemental analyses were conducted on a Perkin-Elmer 2400 Series II CHNS elemental analyzer. Melting point measurements were determined on a Thomas Scientific Unimelt capillary melting point apparatus. $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2BiCl$, **1**, was synthesized according to literature procedures.[28] $KOC_6H_3Me_2\text{-}2,6$ and $KOC_6H_3{}^tBu_2\text{-}2,6$ were synthesized by treatment of the parent phenol with 1 equiv of $KN(SiMe_3)_2$ in toluene. $[HNEt_3][BPh_4]$ was synthesized by treatment of $NEt_3 \cdot HCl$ with $NaBPh_4$ in water followed by filtration, washing, and drying under vacuum (10^{-5} Torr) overnight. $ClMg(CH_2CH{=}CH_2)$ (2.0 M solution in THF) and all other reagents were purchased from Aldrich and used as received. KO^tBu was sublimed and $NaBPh_4$ placed under vacuum (10^{-5} Torr) overnight prior to use.

$[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi(CH_2CH{=}CH_2)$, 2. A tetrahydrofuran (THF) solution of $ClMg(CH_2CH{=}CH_2)$ (0.40 mL, 0.80 mmol) was added to a stirred THF (10 mL) solution of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2BiCl$ (500 mg, 0.80 mmol) at room temperature. The yellow reaction mixture was stirred for 12 h, and the solvent was removed under reduced pressure to afford an off-white solid that was subsequently stirred in hexanes (10 mL) for 0.5 h. Following centrifugation, filtration, and removal of the volatiles, **2** was obtained as a yellow solid (495 mg, 98%). This crude product was analytically pure. Single crystals suitable for an X-ray diffraction study were grown by slow evaporation of a hexane solution at room temperature. ^1H NMR (CD_3CN): δ 7.25 (d, 4H, $^3J_{H-H}$ = 7.4 Hz, *m*−Ar-C*H*), 7.15 (t, 2H, $^3J_{H-H}$ = 7.4 Hz, *p*−Ar-C*H*), 5.96 (m, 1H, $CH_2CH{=}CH_2$), 4.43 (dd, 1H, $^3J_{trans}$ = 16.8 Hz, $^2J_{H-H}$ = 2.4 Hz, $CH_2CH{=}CH_2$), 4.23 (dd, 1H, $^3J_{cis}$ = 10.0 Hz, $^2J_{H-H}$ = 2.4 Hz, $CH_2CH{=}CH_2$), 3.33 and 3.14 (d, 4H each, $^2J_{H-H}$ = 13.2 Hz, NCH_2), 2.75 (d, 2H, $^3J_{H-H}$ = 8.6 Hz, $CH_2CH{=}CH_2$), 1.97 [s, 24H, $N(CH_3)_2$]. ^{13}C (CD_3CN): δ 167.7 [Bi-*C*(Ar)], 147.7 (quaternary *o*-Ar-*C*), 138.6 ($CH_2CH{=}CH_2$), 128.5 and 126.5 (Ar-*C*H), 110.2 ($CH_2CH{=}CH_2$), 68.4 (NCH_2), 44.4 [$N(CH_3)_2$], 35.7 ($CH_2CH{=}CH_2$). Mp 89−90 °C. Anal. Calcd for $C_{27}H_{43}BiN_4$: C, 51.25; H, 6.86; N, 8.86. Found: C, 51.22; H, 6.59; N, 8.77.

$[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi(O^tBu)$, 3. Separate solutions of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2BiCl$ (200 mg, 0.32 mmol) and KO^tBu (36 mg, 0.32 mmol) in THF (5 mL each) were cooled to −30 °C, and the KO^tBu solution was added dropwise to the stirred bismuth solution. The reaction mixture was allowed to warm to room temperature and stirred for 2.5 h. The solution remained colorless, and a fine white precipitate formed which was removed by filtration before solvent evaporation. The resulting colorless solids were extracted by stirring in hexane (10 mL) for 0.5 h, after which centrifugation, filtration, and removal of the volatiles under reduced pressure yielded crude **3** (150 mg, 70%). Recrystallization from hexanes (2 mL) at −30 °C afforded colorless **3** (133 mg, 62%) as single crystals suitable for an X-ray diffraction study. ^1H NMR (C_6D_6): δ 7.43 (bd, 4H, *m*−Ar-C*H*), 7.21 (t, 2H, $^3J_{H-H}$ = 7.4 Hz, *p*−Ar-C*H*), 3.75 (bs, 4H, NCH_2), 3.39 (bd, 4H, $^2J_{H-H}$ = 12.3 Hz, NCH_2), 2.06 [s, 24H, $N(CH_3)_2$], 1.39 [s, 9H, $OC(CH_3)_3$]. ^{13}C (C_6D_6): δ 185.4 (Bi-*C*), 148.6 (quaternary *o*-Ar-*C*), 129.4 (*m*-Ar-*C*H), 126.8 (*p*-Ar-*C*H), 71.1 (NCH_2), 66.8 [$OC(CH_3)_3$], 45.2 [$N(CH_3)_2$], 33.4 [$OC(CH_3)_3$]. Mp 99−100 °C. Purple color observed at 75 °C. Anal. Calcd for $C_{28}H_{47}BiN_4O$: C, 50.59; H, 7.14; N, 8.43. Found: C, 50.29; H, 7.05; N, 8.36.

$[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi(OC_6H_3Me_2\text{-}2,6)$, 4. Separate solutions of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2BiCl$ (200 mg, 0.32 mmol) and $KOC_6H_3Me_2\text{-}2,6$ (51 mg, 0.32 mmol) in THF (5 mL each) were cooled to −30 °C, and the $KOC_6H_3Me_2\text{-}2,6$ solution was added dropwise to the stirred bismuth solution. The reaction mixture was allowed to warm to room temperature, whereupon a pale yellow solution and fine white precipitate formed. The mixture was stirred for 12 h, centrifuged, and the solution filtered. The solvent was removed under reduced pressure yielding a yellow solid. Recrystallization from hexanes (2 mL) at −30 °C afforded yellow **4** (163 mg, 71%) as single crystals suitable for an X-ray diffraction study. ^1H NMR (CD_3CN): δ 7.53 (d, 4H, $^3J_{H-H}$ = 7.5 Hz, *m*−Ar-C*H*), 7.36 (t, 2H, $^3J_{H-H}$ = 7.5 Hz, *p*−Ar-C*H*), 6.72 (d, 2H, $^3J_{H-H}$ = 7.3

---

[22] van Koten, G.; Terheijden, J.; van Beek, J. A. M.; Wehman-Ooyevaar, I. C. M.; Muller, F.; Stan, C. H. *Organometallics* **1990**, *9*, 903.

[23] Mehendale, N. C.; Lutz, M.; Spek, A. L.; Gebbink, R. J. M. K.; van Koten, G. *J. Organomet. Chem.* **2008**, *693*, 2971.

[24] Steenwinkel, P.; Grove, D. M.; Veldman, N.; Spek, A. L.; van Koten, G. *Organometallics* **1998**, *17*, 5647.

[25] Kleij, A. W.; Gossage, R. A.; Gebbink, R. J. M. K.; Brinkmann, N.; Reijerse, E. J.; Kragl, U.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2000**, *122*, 12112.

[26] Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750.

[27] Atwood, D. A.; Cowley, A. H.; Ruiz, J. *Inorg. Chim. Acta* **1992**, *198−200*, 271.

[28] Soran, A. P.; Silvestru, C.; Breunig, H. J.; Balazs, G.; Green, J. C. *Organometallics* **2007**, *26*, 1196.

[29] Balazs, L.; Breunig, H. J.; Lork, E.; Soran, A. P.; Silvestru, C. *Inorg. Chem.* **2006**, *45*, 2341.

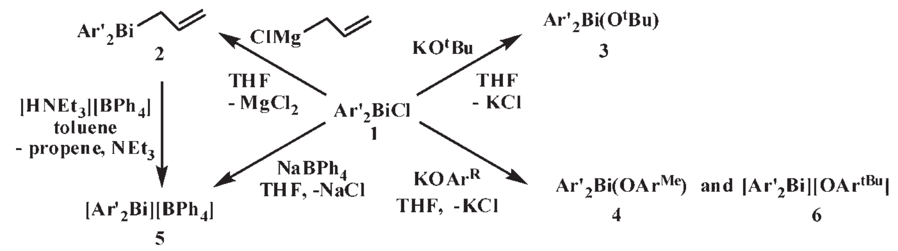
[30] Breunig, H. J.; Koenigsmann, L.; Lork, E.; Nema, M.; Philipp, N.; Silvestru, C.; Soran, A. P.; Varga, R. A.; Wagner, R. *Dalton Trans.* **2008**, 1831.

[31] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 4th ed.; Wiley: New York, 2005. pp 25−35.

[32] Hogerheide, M. P.; Grove, D. M.; Boersma, J.; Jastrzebski, J. T. B. H.; Kooijman, H.; Spek, A. L.; van Koten, G. *Chem.*—*Eur. J.* **1995**, *1*, 343.

[33] Hogerheide, M. P.; Boersma, J.; Spek, A. L.; van Koten, G. *Organometallics* **1996**, *15*, 1505.

Scheme 1. Synthesis of Ar′$_2$BiX Complexes



Ar′ = 2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$; Ar^{Me} = C$_6$H$_3$Me$_2$-2,6; Ar^{tBu} = C$_6$H$_3{}^t$Bu$_2$-2,6

Hz, *m*-OAr−C*H*), 6.21 (t, 1H, $^3J_{H-H}$ = 7.3 Hz, *p*-OAr−C*H*), 3.60 (s, 8H, NC*H*$_2$), 2.08 [s, 6H, OAr-(C*H*$_3$)$_2$], 2.03 [s, 24H, N(C*H*$_3$)$_2$]. ^{13}C (CD$_3$CN): *δ* 192.0 (Bi-*C*), 162.1 and 127.3 (quaternary *i*/*o*-OAr-*C*), 149.4 (quaternary *o*-Ar-*C*), 129.7 (*m*-Ar-*C*H), 127.9 (*p*-Ar-*C*H), 127.7 (*m*-OAr-*C*H), 113.7 (*p*-OAr-*C*H), 67.3 (N*C*H$_2$), 44.9 [N(*C*H$_3$)$_2$], 17.8 [OAr-(*C*H$_3$)$_2$]. Mp 97−99 °C. Anal. Calcd for $C_{32}H_{47}BiN_4O$: C, 53.92; H, 6.66; N, 7.86. Found: C, 53.31; H, 6.65; N, 7.49.

{[2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]$_2$Bi}[BPh$_4$], 5. Separate solutions of [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]$_2$BiCl (300 mg, 0.48 mmol) and NaBPh$_4$ (164 mg, 0.48 mmol) in THF (5 mL each) were cooled to −30 °C and the NaBPh$_4$ solution was added dropwise to the stirred bismuth solution. The reaction mixture was allowed to warm to room temperature, whereupon a pale yellow solution and fine white precipitate formed. After the mixture was stirred for 30 h, centrifuged, and filtered, the solvent was removed under reduced pressure to yield an off white foamy solid. Recrystallization from THF (2 mL) at −30 °C afforded colorless **5** (312 mg, 72%) as X-ray quality single crystals. ^{1}H NMR (CD$_3$CN): *δ* 7.61 (d, 4H, $^3J_{H-H}$ = 7.5 Hz, *m*−Ar-C*H*), 7.52 (t, 2H, $^3J_{H-H}$ = 7.5 Hz, *p*−Ar-C*H*), 7.27 (bm, 8H, *m*-BPh$_4$), 6.99 (t, 8H, $^3J_{H-H}$ = 7.4 Hz, *o*-BPh$_4$), 6.84 (t, 4H, $^3J_{H-H}$ = 7.4 Hz, *p*-BPh$_4$), 3.74 (s, 8H, NC*H*$_2$), 2.27 [s, 24H, N(C*H*$_3$)$_2$]. ^{13}C (CD$_3$CN): *δ* 189.5 (Bi-*C*), 165.0 (4-line multiplet, $^1J_{C-B}$ = 49.1 Hz, B-*C*), 151.3 (quaternary *o*-Ar-*C*), 137.0 (*m*-BPh$_4$), 131.4 (*m*-Ar-*C*H), 130.7 (*p*-Ar-*C*H), 126.9 (*o*-BPh$_4$), 123.0 (*p*-BPh$_4$), 69.0 (N*C*H$_2$), 47.0 [N(*C*H$_3$)$_2$]. Mp 154−156 °C. Anal. Calcd for $C_{48}H_{58}BBiN_4$: C, 63.29; H, 6.43; N, 6.15. Found: C, 63.10; H, 6.31; N, 6.07.

Compound **5** can also be synthesized by treatment of **2** with 1 equiv of [HNEt$_3$][BPh$_4$] in toluene. However, since the isolated product contained residual **2** that could not be removed, even with multiple washings, this method was not pursued further.

{[2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]$_2$Bi}[OC$_6$H$_3{}^t$Bu$_2$-2,6], 6. A solution of [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]$_2$BiCl (100 mg, 0.16 mmol) was added to a solution of KOC$_6$H$_3{}^t$Bu$_2$-2,6 (39 mg, 0.16 mmol) in THF (5 mL each) at room temperature. A dark yellow solution formed immediately, accompanied by a fine white precipitate. The mixture was stirred for 3 h, centrifuged, and filtered. The solvent was removed under reduced pressure yielding a yellow solid which was recrystallized from THF (2 mL) at −30 °C to afford yellow **6** (110 mg, 86%) as single crystals suitable for an X-ray diffraction study. ^{1}H NMR (CD$_3$CN): *δ* 7.60 (bs $\nu_{1/2}$ = 26 Hz, 4H, *m*−Ar-C*H*), 7.51 (bs, 2H, *p*−Ar-C*H*), 6.76 (d, 2H, $^3J_{H-H}$ = 7.6 Hz, *m*-OAr−C*H*), 5.81 (t, 1H, $^3J_{H-H}$ = 7.6 Hz, *p*-OAr−C*H*), 3.73 (bs $\nu_{1/2}$ = 25 Hz, 8H, NC*H*$_2$), 2.26 [bs $\nu_{1/2}$ = 26 Hz, 24H, N(C*H*$_3$)$_2$], 1.37 [s, 18H, OAr−C(C*H*$_3$)$_3$]. ^{13}C (CD$_3$CN): *δ* 188.2 (Bi-*C*), 169.1 and 136.2 (quaternary *i*/*o*-OAr-*C*), 149.8 (quaternary *o*-Ar-*C*), 130.1 ($\nu_{1/2}$ = 22 Hz, *m*-Ar-*C*H), 129.4 ($\nu_{1/2}$ = 18 Hz, *p*-Ar-*C*H), 123.2 (*m*-OAr-*C*H), 105.1 (*p*-OAr-*C*H), 67.6 (N*C*H$_2$), 45.7 [$\nu_{1/2}$ = 27 Hz, N(*C*H$_3$)$_2$], 34.5 [*C*(CH$_3$)$_3$], 29.5 [C(*C*H$_3$)$_3$]. ^{1}H NMR (C$_4$D$_8$O): *δ* 7.60 (d, 4H, $^3J_{H-H}$ = 7.4 Hz, *m*−Ar-C*H*), 7.44 (t, 2H, $^3J_{H-H}$ = 7.4 Hz, *p*−Ar-C*H*), 6.73 (d, 2H, $^3J_{H-H}$ = 7.5 Hz, *m*-OAr−C*H*), 5.84 (t, 1H, $^3J_{H-H}$ = 7.5 Hz, *p*-OAr−C*H*), 3.75 (s, 8H, NC*H*$_2$), 2.28 [s, 24H, N(C*H*$_3$)$_2$], 1.39 [s, 18H, OAr−C(C*H*$_3$)$_3$]. ^{13}C (C$_4$D$_8$O): *δ* 188.8 (Bi-*C*), 167.7 and 136.0 (quaternary *i*/*o*-OAr-*C*), 149.9 (quaternary *o*-Ar-*C*), 130.0 (*m*-Ar-*C*H), 128.9 (*p*-Ar-*C*H), 122.8 (*m*-OAr-*C*H), 106.4 (*p*-OAr-*C*H), 67.8 (N*C*H$_2$), 45.6 [N(*C*H$_3$)$_2$], 34.7 [*C*(CH$_3$)$_3$], 29.9 [C(*C*H$_3$)$_3$]. Mp 145−146 °C. Color changes observed at 85 °C (brown) and at 110 °C (purple). Anal. Calcd for $C_{38}H_{59}BiN_4O$: C, 57.26; H, 7.48; N, 7.03. Found: C, 57.06; H, 7.60; N, 6.85.

Results

Synthesis. The [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]$_2$BiX complexes (Ar′$_2$BiX), **2**−**6**, were prepared by reacting the previously reported bismuth chloride complex, Ar′$_2$BiCl, **1**,[28] with alkali and alkaline earth metal salts of allyl, alkoxide, aryloxide, and tetraphenylborate reagents as shown in Scheme 1. The bismuth products were isolated in good to excellent yields of 60−98% and were characterized using ^{1}H and ^{13}C NMR spectroscopy, elemental analysis, and X-ray diffraction. Structural and spectroscopic details are presented in the following sections.

Structure. X-ray crystallographic data on **2**−**6** are summarized in Tables 1 and 2 and compared below with the previously published structure of Ar′$_2$BiCl, **1**.[28] Complexes **1**−**6** are similar in that only three of the four amine donor arms of the two aryldiamine ligands coordinate to bismuth. Hence, one [2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$]$^-$ ligand functions as an (*N*,*C*,*N*) pincer ligand through binding of N1, C1, and N2, whereas the other coordinates in an (*N*,*C*) mode via binding of N4 and C13.

In complexes **1**, **2** (Figure 1), **3** (Figure 2), and **4** (Figure 3) of general formula Ar′$_2$BiX where X = Cl, CH$_2$CH=CH$_2$, O^{t}Bu, and OC$_6$H$_3$Me$_2$-2,6, respectively, the X ligand completes the coordination sphere such that six donor atoms surround the bismuth in a highly distorted octahedral geometry. The three nitrogen donor atoms are facial such that two are trans to the two aryl ligands and the third is trans to the X ligand. The distortion in the octahedral geometry can be seen in the deviation of the 137.93(6)−166.82(10)° N−Bi−C and N−Bi−X angles from 180° in a regular octahedron. The cis angles in these structures range from 59.95(6)−135.14(4)°, that is, significantly different from the octahedral 90°. In **2** the "cis" N−Bi−N angles are 94.03(5), 114.03(5), and 134.87(5)° compared to 65.61(7)−101.95(8)° for all the other cis angles in this complex. This means that looking down the pseudo 3-fold axis through Bi and perpendicular to the plane of N1, N2, and N4, the three nitrogen ligands are distorted away from octahedral more than the other three ligands C1, C13, and C25. Hence, the most likely place for lone pair electron density to be stereochemically active would be in the middle of the triangle defined by the three nitrogen atoms.

All eight Bi−C(aryl) distances in **1**−**4** fall in the narrow range 2.278(4)−2.310(2) Å. For **1**, **3**, and **4**, the Bi−N

Table 1. X-ray Data Collection Parameters for $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi(CH_2CH{=}CH_2)$, **2**, $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi(O^tBu)$, **3**, $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi(OC_6H_3Me_2\text{-}2,6)$, **4**, $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi\}[BPh_4]$, **5**, and $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi\}[OC_6H_3{}^tBu_2\text{-}2,6]$, **6**

	2	**3**	**4**	**5**	**6**
empirical formula	$C_{27}H_{43}BiN_4$	$C_{28}H_{47}BiN_4O$	$C_{32}H_{47}BiN_4O \bullet 1/2\ C_6H_{14}$	$C_{48}H_{58}BBiN_4$	$C_{38}H_{59}BiN_4O$
formula weight	632.63	664.68	755.80	910.77	796.87
temperature (K)	148(2)	93(2)	98(2)	148(2)	143(2)
crystal system	monoclinic	monoclinic	monoclinic	monoclinic	triclinic
space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	9.9777(5)	16.5591(9)	9.5132(5)	15.9493(9)	9.6863(6)
b (Å)	17.5299(9)	10.7987(6)	14.5142(8)	13.0162(7)	10.5364(6)
c (Å)	16.9668(8)	16.9911(9)	25.4014(13)	20.7895(11)	18.3169(11)
α (deg)	90	90	90	90	92.3499(7)
β (deg)	106.7253(5)	94.5780(7)	91.4692(6)	101.1256(7)	97.9458(7)
γ (deg)	90	90	90	90	99.2711(6)
volume (Å^3)	2842.1(2)	3028.6(3)	3506.2(3)	4234.8(4)	1823.43(19)
Z	4	4	4	4	2
ρ_{calcd} (Mg/m^3)	1.479	1.458	1.432	1.429	1.451
μ (mm^{-1})	6.223	5.846	5.059	4.201	4.868
R1 $[I > 2\sigma(I)]^a$	0.0182	0.0150	0.0183	0.0208	0.0289
wR2 (all data)^a	0.0445	0.0354	0.0446	0.0528	0.0706

^{a} Definitions: $R1 = \sum||F_o| - |F_c||/\sum|F_o|, wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

Table 2. Metrical Data for $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi(CH_2CH{=}CH_2)$, **2**, $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi(O^tBu)$, **3**, $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi(OC_6H_3Me_2\text{-}2,6)$, **4**, $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi\}[BPh_4]$, **5**, and $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi\}[OC_6H_3{}^tBu_2\text{-}2,6]$, **6**

	2	**3**	**4**	**5**	**6**
	X = C25	X = O1	X = O1		X = O1
Bi−C1/−C13	2.304(2)/ 2.310(2)	2.283(2)/ 2.314(2)	2.309(2)/ 2.308(2)	2.210(2)/ 2.283(2)	2.210(3)/ 2.311(3)
Bi1−X	2.331(2)	2.151(1)	2.228(1)		3.455(2)
Bi1−N1	3.102(2)	2.916(2)	2.708(2)	2.509(2)	2.579(3)
Bi1−N2	3.064(2)	3.064(2)	3.552(2)	2.552(2)	2.494(3)
Bi1−N3	4.998	5.015	5.043	4.329	4.218
Bi1−N4	3.176(2)	3.321(2)	3.052(2)	3.003(2)	3.025(3)
O1−C25		1.426(2)	1.337(3)		1.293(4)
C25−C26	1.453(4)				
(C26−C27)	1.282(5)				
C1−Bi1−C13	96.70(8)	97.58(6)	97.88(7)	106.83(8)	102.07(12)
N1−Bi1−C1	66.48(7)	67.57(5)	70.50(6)	73.71(7)	71.23(11)
N1−Bi1−C13	74.83(7)	77.45(5)	85.50(6)	95.34(7)	90.90(10)
N1−Bi1−N2	114.03(5)	110.64(4)	114.74(5)	146.12(6)	144.97(9)
N1−Bi1−N4	94.30(5)	95.54(4)	105.79(5)	82.61(5)	132.96(8)
N2−Bi1−C1	65.61(7)	64.56(5)	59.95(6)	72.42(7)	74.27(11)
N2−Bi1−C13	151.41(7)	152.99(5)	137.93(6)	93.54(7)	102.11(10)
N2−Bi1−N4	134.87(5)	135.14(4)	131.80(5)	130.97(5)	81.85(8)
N4−Bi1−C1	158.27(7)	159.41(5)	165.41(6)	155.73(7)	151.38(10)
N4−Bi1−C13	67.24(7)	66.15(5)	67.57(6)	69.64(7)	67.49(10)
X−Bi1−C1	101.95(8)	92.99(5)	95.91(6)		93.21(9)
X−Bi1−C13	87.97(8)	91.22(5)	87.38(6)		164.27(9)
X−Bi1−N1	157.39(7)	155.52(5)	163.57(5)		97.61(8)
X−Bi1−N2	74.95(7)	70.84(5)	62.66(5)		78.28(7)
X−Bi1−N4	92.36(7)	99.62(4)	85.02(5)		97.21(7)
Bi1−X−C25		123.79(10)	126.12(14)		149.8(2)

bonds trans to aryl ligands are in the range 3.052(2)−3.552(2) Å, but the Bi1−N1 bonds trans to the Cl, O^{t}Bu, and $OC_6H_3Me_2$-2,6 ligands are significantly shorter, 2.699(3), 2.916(2), and 2.708(2) Å, respectively. For **2**, however, the 3.102(2) Å Bi1−N1 bond trans to the allyl ligand is not the shortest Bi−N distance since the Bi1−N2 distance trans to an aryl ligand is 3.064(2) Å. This is consistent with the fact that the allyl carbon donor atom would be more similar to the aryl carbon in its effect on the trans nitrogen ligand. The 2.331(2) Å Bi−C(allyl) distance is similar to the 2.304(2) and 2.310(2) Å Bi−C(aryl) distances of the Ar′ ligands in **2**.

$[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi(CH_2CH{=}CH_2)$, 2. Only two other bismuth allyl compounds have been reported in the literature to compare with **2**: $Bi(C_3H_5)_3$, a liquid at room temperature,[34] and $[C(SiMe_3)_2C_5H_4N\text{-}2]BiCl[CH_2CH{=}C(SiMe_3)C_5H_4N\text{-}2]$,[35] which was isolated as a decomposition product from the reaction of $BiCl_3$ and 2 equiv of $Li[C(SiMe_3)_2C_5H_4N\text{-}2]$ in THF. The Bi−C(allyl) bond length in the latter compound was measured as 2.23(2) Å.

$[2,6\text{-}(Me_2NCH_2)_2C_6H_3]_2Bi(O^tBu)$, 3. The 2.151(1) Å Bi1−O1(O^{t}Bu) bond length in **3** is similar to the 2.117(4) and 2.159(5) Å analogs in $\{(C_5H_4Me)_2Mo[Bi(O^tBu)_2]_2\}$,[37] and is within the broad range of distances found for these

---

(34) Hyeon, J.-Y.; Lisker, M.; Silinskas, M.; Burte, E.; Edelmann, F. T. *Chem. Vap. Deposition* **2005**, *11*, 213.

(35) Jones, C.; Engelhardt, L. M.; Junk, P. C.; Hutchings, D. S.; Patalinghug, W. C.; Raston, C. L.; White, A. H. *J. Chem. Soc., Chem. Commun.* **1991**, 1560.

(36) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.

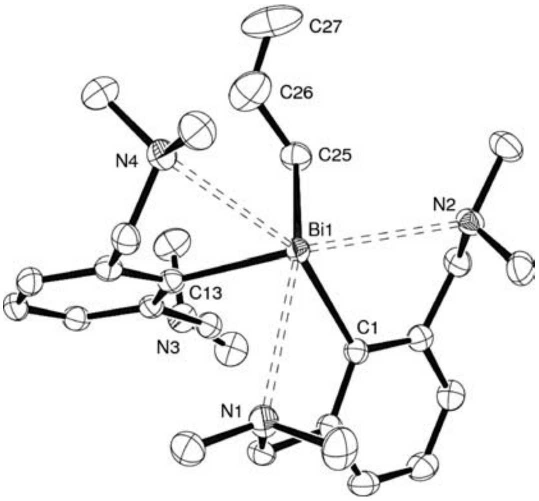


Figure 1. ORTEP[36] representation of [2,6-(Me_2NCH_2)$_2C_6H_3$]$_2$Bi(CH_2-$CH{=}CH_2$), **2**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

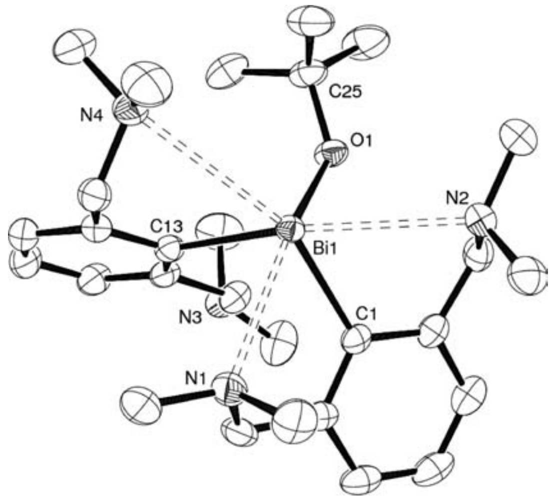


Figure 2. ORTEP representation of [2,6-(Me_2NCH_2)$_2C_6H_3$]$_2$Bi-(O^tBu), **3**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

bonds, for example, 2.215(5) Å in {(C_5H_4Me)$_2$Mo[μ-Bi-(O^tBu)]}$_2$,[37] and 2.061(3) Å in (calix[4]arene)BiO^tBu.[38] The 123.79(10)° Bi1−O1−C25 angle in **3** is in the range of values found for the examples above, 128.3(4)°, 121.9(4)°, 118.5(5)°, and 121.4(2)°, respectively.

[2,6-(Me_2NCH_2)$_2C_6H_3$]$_2$Bi($OC_6H_3Me_2$-2,6), 4. The 2.228(1) Å Bi1−O1(OAr) bond length in the aryloxide complex **4** is longer than that observed in **3**, in Bi-($OC_6H_3Me_2$-2,6)$_3$ [2.085(11)−2.097(9) Å],[39] and in the repeat unit of polymeric {Bi[OC_6H_3-2-OMe-4-($CH_2CH{=}CH_2$)]$_3$}$_n$ [2.135(3)−2.201(3) Å].[40] The Bi−O−C angles in these complexes are 126.12(14)°, 123(4)° (average), and 122.8(3)−127.5(2)°, respectively.

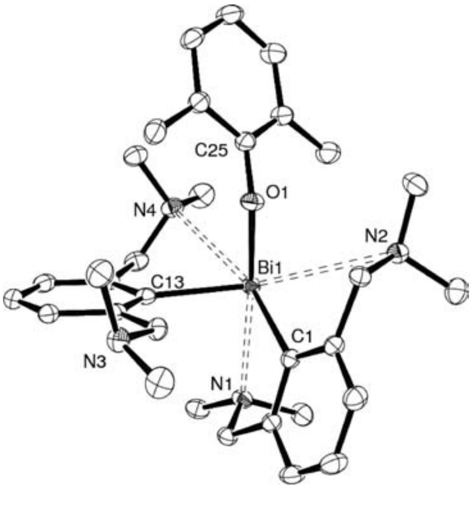


Figure 3. ORTEP representation of [2,6-(Me_2NCH_2)$_2C_6H_3$]$_2$Bi(OC_6-H_3Me_2-2,6), **4**, drawn at the 50% probability level. Hydrogen atoms and solvent are omitted for clarity.

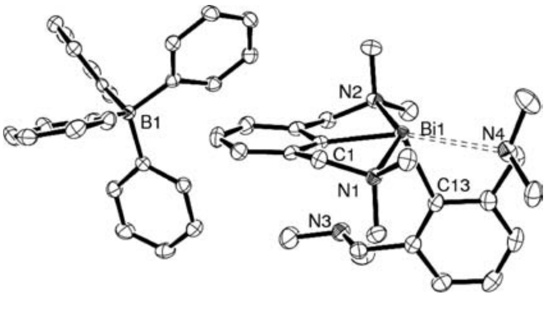


Figure 4. ORTEP representation of {[2,6-(Me_2NCH_2)$_2C_6H_3$]$_2$Bi}-[BPh_4], **5**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

{[2,6-(Me_2NCH_2)$_2C_6H_3$]$_2$Bi}[BPh_4], 5, and {[2,6-(Me_2-NCH_2)$_2C_6H_3$]$_2$Bi}[$OC_6H_3{}^tBu_2$-2,6], 6. The [Ar′$_2$Bi][X] complexes **5** (Figure 4) and **6** (Figure 5) differ from the Ar′$_2$BiX compounds, **1**−**4**, in that the X ligands are outer sphere anions. As a consequence, there are only five donor atoms around bismuth. Since the largest ligand−Bi−ligand angles in **5** and **6** are the 155.73(7)° and 151.4(1)° C1−Bi−N4 angles, respectively, and since C1, N1, and N2 are nearly coplanar with bismuth in a plane that contains the C1···N4 vector, there is no regular five coordinate geometry that closely matches the ligand arrangement in these complexes. A distorted octahedral geometry with a vacant vertex (Ψ-octahedral) may be the best description of these complexes.[41] The structure of the cation in [Ar′$_2$Bi][W(CO)$_5$Cl], which was reported online while this paper was under review,[42] is similar to the cation in **5**.

In contrast to **1**−**4**, there are two types of Bi−C distances: the 2.283(2) and 2.311(3) Å Bi−C13 distances in **5** and **6**, respectively, are similar to those in **1**−**4**, whereas the 2.210(2) and 2.210(3) Å Bi−C1 distances, respectively, are shorter.

---

(37) Roggan, S.; Limberg, C.; Ziemer, B.; Brandt, M. *Angew. Chem., Int. Ed.* **2004**, *43*, 2846.

(38) Liu, L.; Zakharov, L. N.; Golen, J. A.; Rheingold, A. L.; Hanna, T. A. *Inorg. Chem.* **2008**, *47*, 11143.

(39) Evans, W. J.; Hain, J. H.; Ziller, J. W. *J. Chem. Soc., Chem. Commun.* **1989**, 1628.

(40) Kou, X.; Wang, X.; Mendoza-Espinosa, D.; Zakharov, L. N.; Rheingold, A. L.; Watson, W. H.; Brien, K. A.; Jayarathna, L. K.; Hanna, T. A. *Inorg. Chem.* **2009**, *48*, 11002.

(41) Davidovich, R. L.; Stavila, V.; Marinin, D. V.; Voit, E. I.; Whitmire, K. H. *Coord. Chem. Rev.* **2009**, *253*, 1316.

(42) Breunig, H. J.; Nema, M. G.; Silvestru, C.; Soran, A. P.; Varga, R. A. *Dalton Trans.* **2010**, *39*, 11277.

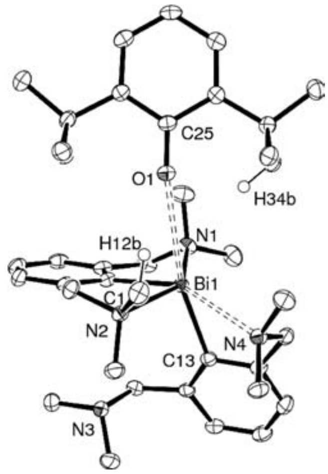


Figure 5. ORTEP representation of {[2,6-$(Me_2NCH_2)_2C_6H_3]_2Bi$}[$OC_6H_3{}^tBu_2$-2,6], **6**, drawn at the 50% probability level. Hydrogen atoms are omitted for clarity, except H34b and H12b.

Similarly, the 3.003(2) and 3.025(3) Å Bi−N4 distances in **5** and **6**, respectively, for the amine trans to C1 are similar to those in **1**−**4**, but the Bi−N1 and Bi−N2 distances are much shorter, 2.494(3)−2.579(3) Å. Hence, both lower coordinate complexes have some closer metal ligand contacts.

In complexes **5** and **6**, neither N1 nor N2 has a ligand directly trans: the N1−Bi1−N2 angles are 146.12(6)° and 144.97(9)°, respectively. These angles are similar to the analogous 144.18(11)° angle in $Ar'BiCl_2$.[28] Further similarities are seen with five-coordinate $Ar'BiCl_2$ in that it has 2.561(3) and 2.570(4) Å Bi−N(amine) distances and a 2.224(4) Å Bi−C(aryl) bond length.[28]

The $(BPh_4)^-$ anion in **5** acts as an outer sphere anion and has no close interactions with the bismuth center. A similar outer sphere unsolvated complex was previously structurally characterized with an unsymmetrically substituted 1,4,7-triazacyclononane ligand, [{*cyclo*[$N(CH_2)_2]_3$-1-(CH_2COO)-4,7-[2-$CH_2(MeNCHCHN)]_2$}BiCl][BPh_4].[43] However, most of the other bismuth cations reported in the literature have some interaction of either solvent or the counteranion with the metal center. For example, in {[2-$(Me_2CH_2)C_6H_4]_2Bi$}{PF_6},[44] there is a short Bi···F contact to one of the fluorine atoms in the $(PF_6)^-$ counterion. Similarly, in [$^tBuN(CH_2C_6H_4)_2Bi$][$B(C_6F_5)_4$] a vacant site at bismuth is filled by one of the fluorine atoms of the anion.[45] The Bi···F lengths in these complexes are 3.49 and 2.971(2) Å, respectively, within the sum of the van der Waals radii (3.75 Å) and much longer than the range of reported covalent Bi−F bond distances (2.088(8)−2.59(1) Å).[45] Upon addition of neutral donor solvents, this interaction is displaced and a range of solvated cations, [$^tBuN(CH_2C_6H_4)_2BiL$][$B(C_6F_5)_4$] (L = MeCHO, MeOH, MeCN, and CH_2Cl_2), were isolated and structurally characterized.[45] Cationic bismuth complexes of formula [$Ph_2Bi(Donor)_2$][X] [Donor = $OP(NMe_2)_3$, $OPPh_3$, and X = BF_4, PF_6;[46,47] Donor = PPh_3 and X = PF_6[48]] are also known and have been structurally characterized.

The structure of **6** differs from that of **5** in that the oxygen of the counteranion points toward a vacant site on bismuth. The 3.455(2) Å Bi1···O1 distance is much longer than the 2.151(1) and 2.228(1) Å Bi−O distances in **3** and **4**, respectively, although it is still within the sum of the van der Waals radii for bismuth and oxygen (3.80 Å),[29,30] a similar situation to that observed for the cationic complexes containing Bi···F interactions. For comparison, another bismuth complex with 2,6-di-*tert*-butyl aryloxide ligands, Bi[$OC_6H_2{}^tBu_3$-2,4,6]$_2$Cl,[40] has an average Bi−O bond length of 2.093(3) Å, well within the sum of *covalent* radii for bismuth and oxygen (2.18 Å).[30]

The 1.293(4) Å C25−O1 bond length in **6** is shorter than the 1.337(3) Å distance observed in **4** and the 1.345(6) Å value in [$LiOAr^{tBu,Me}(OEt_2)]_2$,[49] but it is similar to values found in complexes containing aryloxide anions not attached to metal ions such as 1.302(3) Å in {$(C_5Me_5)_2$-[$^iPrNC(Me)N^iPr$]U}($Ar^{tBu,Me}O\cdots HOAr^{tBu,Me}$)[50] and 1.306(2) Å in [$HC(MesNCH)_2$][$OAr^{tBu,Me}$],[51] both of which are stabilized by hydrogen bonding. There may be a long-range contact in **6** between Bi1···H34b (3.1822 Å) and a weak C−H12b···O1 hydrogen bond of 2.476 Å, which is longer than OH···O and NH···O hydrogen bonds, but typical for weaker CH···O interactions.[52] The Bi1−H34b−C34 and O1−H12b−C12 angles are 160.25 and 156.73°, respectively.

NMR Studies. NMR data on **2**−**6** are shown in Table 3. The resonances of the Ar′ ligand in each complex are similar. One resonance that differentiates the Ar'_2BiX complexes **2**, **3**, and **4** from the [Ar'_2Bi][X] complexes **5** and **6** is the *p*-Ar′-CH resonances which are within the range 7.15−7.36 ppm for the former complexes and 7.51−7.52 ppm for the latter.

In **2**, the methylene groups of the ligand arms are split into two doublets at 3.33 and 3.14 ppm ($^2J_{H-H}$ = 13.2 Hz). A variable temperature NMR study on **2** in MeCN-d_3 up to 80 °C elicited no change in the ^1H NMR spectrum. In contrast, for **3** in benzene-d_6, the methylene groups appear as two broad resonances, one of which manifests as a doublet ($^2J_{H-H}$ = 12.3 Hz). Unfortunately, this complex decomposes upon heating and is insoluble in MeCN-d_3, so direct comparison was not possible. The broadening seen in benzene-d_6 may result from exchange of the three coordinated amines with the amine that is not oriented toward bismuth. However, in **4**, only a single resonance for the methylene groups is observed at 3.60 ppm. Single methylene resonances are also found for **5** and **6**, but the amine arms in these compounds are all oriented toward bismuth in the solid state structures. In the case of **6**, the Ar′ ligand resonances are substantially broadened in MeCN-d_3. Heating the sample to 80 °C elicited no change, but changing

---

(43) Di Vaira, M.; Mani, F.; Stoppioni, P. *Eur. J. Inorg. Chem.* **1999**, 833.

(44) Carmalt, C. J.; Walsh, D.; Cowley, A. H.; Norman, N. C. *Organometallics* **1997**, *16*, 3597.

(45) Bao, M.; Hayashi, T.; Shimada, S. *Organometallics* **2007**, *26*, 1816.

(46) Carmalt, C. J.; Farrugia, L. J.; Norman, N. C. *J. Chem. Soc., Dalton Trans.* **1996**, 443.

(47) Carmalt, C. J.; Norman, N. C.; Orpen, A. G.; Stratford, S. E. *J. Organomet. Chem.* **1993**, *460*, C22.

(48) Kilah, N. L.; Petrie, S.; Stranger, R.; Wielandt, J. W.; Willis, A. C.; Wild, S. B. *Organometallics* **2007**, *26*, 6106.

(49) Cetinkaya, B.; Gumrukcu, I.; Lappert, M. F.; Atwood, J. L.; Shakir, R. *J. Am. Chem. Soc.* **1980**, *102*, 2086.

(50) Evans, W. J.; Walensky, J. R.; Ziller, J. W. *Chem. Commun.* **2009**, 7342.

(51) Cowan, J. A.; Clyburne, J. A. C.; Davidson, M. G.; Harris, R. L. W.; Howard, J. A. K.; Kupper, P.; Leech, M. A.; Richards, S. P. *Angew. Chem., Int. Ed.* **2002**, *41*, 1432.

(52) Steiner, T. *Chem. Commun.* **1997**, 727.

Table 3. Selected ^{1}H and ^{13}C NMR Chemical Shift (ppm), *J* Coupling Constant, and Peak Width (Hz) Data for Complexes **2**−**6** in CD_3CN

complex	*m*-Ar-C*H*	*p*-Ar-C*H*	NCH_2	N(CH_3)$_2$	Bi-*C*(Ar)
2	7.25, d, $^3J = 7.4$	7.15, t, $^3J = 7.4$	3.33, d, $^2J = 13.2$ 3.14, d, $^2J = 13.2$	1.97	167.7
3[a]	7.43, bd	7.21, t, $^3J = 7.4$	3.75, bs 3.39, bs, $^2J = 12.3$	2.06	185.4
4	7.53, d, $^3J = 7.5$	7.36, t, $^3J = 7.5$	3.60	2.03	192.0
5	7.61, d, $^3J = 7.5$	7.52, t, $^3J = 7.5$	3.74	2.27	189.5
6	7.60, bs $\nu_{1/2} = 26$	7.51	3.73, bs $\nu_{1/2} = 25$	2.26, bs $\nu_{1/2} = 26$	188.2

[a] **3** run in C_6D_6.

the solvent to THF-d_8 produces a much more resolved spectrum.

The ^{1}H and ^{13}C NMR spectra of **2** indicate that the allyl ligand binds in an η^1-mode in solution as was found in the solid state. The splittings and couplings are characteristic of η^1-allyl ligands.[53] The NMR data of the other X ligands in compounds **2**−**6** are unexceptional.

Discussion

The syntheses shown in Scheme 1 have similarities between bismuth and lanthanides in that they involve ionic metathesis between metal chlorides and alkali and alkaline earth metal reagents. An important difference is that the bismuth starting material, Ar'_2BiCl, **1**, is a monomer with only three amines coordinated (like **2**, **3**, and **4**), whereas the analogous bis(pentamethylcyclopentadienyl) lanthanide chloride exists as a Lewis acid base adduct with KCl, $(C_5Me_5)_2LnCl_2K(THF)_2$.[54,55] Although $[(C_5Me_5)_2LnCl]_x$ complexes are known, they are not easy to generate and are generally at least dimeric.[56,57] In contrast to Ar'_2BiCl, the $(C_5Me_5)_2LnCl$ unit typically either adds a ligand such as a solvent like THF or binds a residual alkali metal halide, that is, it is a much stronger Lewis acid. As described in the following sections, this difference between bismuth and the lanthanides became established as a trend in this study.

Although the allyl complex **2** is synthesized in the same manner as $(C_5Me_5)_2Ln(\eta^3\text{-}C_3H_5)$ complexes,[58−63] its η^1-structure is quite different. Structural and NMR studies of the eight $(C_5Me_5)_2Ln(\eta^3\text{-}C_3H_5)$ complexes in the literature indicate that all have the allyl ligand bound in an η^3-manner. Since allyl is a rather small chelating ligand, it should be sterically possible for it to bind η^3 to bismuth. However, this is not observed.

To the best of our knowledge, there are no examples of structurally characterized $(C_5Me_5)_2Ln(O^tBu)$ complexes, although examples of $[(C_5Me_5)Ln(O^tBu)(\mu\text{-}O^tBu)]_2$ (Ln = Ce[64] and Eu[65]) are known. The Ln−O−C angles for the terminal alkoxide ligands in these cyclopentadienyl complexes are 176.9(7)° and 174.5°, respectively, considerably more linear than the corresponding 123.79(10)° angle observed in **3**. These angles would allow the oxygen atom to donate more electron density to the more Lewis acidic lanthanide metal centers. The closest $(C_5Me_5)_2Ln(OAr^R)$ complexes to **4** are the samarium complexes $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$[66] and $(C_5Me_5)_2Sm(OC_6H_2{}^tBu_3\text{-}2,4,6)$.[67] The latter complexes have 172.3(13)° and 165.8(5)° Sm−O−C angles, respectively, that again are larger than the analogous angle in the bismuth aryloxide, **4**, of 126.12(14)°.

Complex **5** differs from $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ complexes in both synthesis and structure. $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ complexes are not known to form by ionic metathesis between $NaBPh_4$ and chloride precursors. Instead, they are typically generated from $[HNEt_3][BPh_4]$ and $(C_5Me_5)_2Ln(C_3H_5)$ complexes in a halide free environment.[58,62] An analogous bismuth reaction occurs in the conversion of **2** to **5**.

The structural difference between $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ and **5** is that some of the C−H bonds of the phenyl groups of the $(BPh_4)^-$ anion are oriented toward the Lewis acidic lanthanide centers at distances within 0.12 Å of a typical $Ln{-}C(C_5Me_5)$ bond distance. In contrast, the $(BPh_4)^-$ ligand in **5** is neither close nor oriented toward the bismuth center. A further difference in the lanthanide cations is that addition of any coordinating solvent, L, to $[(C_5Me_5)_2Ln][(\mu\text{-}Ph)_2BPh_2]$ immediately displaces the $(BPh_4)^-$ anion and forms a solvated complex with an outer sphere anion, $[(C_5Me_5)_2Ln(L)_2][BPh_4]$. In contrast, **5** is crystallized from THF, and no THF adduct forms.

There is no analogue to the structure of **6** in lanthanide chemistry. The closest example is found with uranium in $\{(C_5Me_5)_2U[^iPrNC(Me)N^iPr\text{-}\kappa N,N']\}(4\text{-}Me\text{-}2,6\text{-}^tBu_2C_6H_2O\cdots HOC_6H_2\text{-}2,6\text{-}^tBu_2\text{-}4\text{-}Me)$ where steric crowding unexpectedly prevented the aryloxide ligand from binding.[50] Since the aryloxide in **4** is inner sphere and the larger aryloxide in **6** is outer sphere, steric factors again may be the reason for the difference in structure. However, in both $(C_5Me_5)_2Sm(OC_6HMe_4\text{-}2,3,5,6)$[66] and $(C_5Me_5)_2Sm(OC_6H_2\text{-}^tBu_3\text{-}2,4,6)$,[67] the aryloxide ligands bind inner sphere. All of these results show clear differences between Ar'_2BiX and

---

(53) Casely, I. J.; Suh, Y. S.; Ziller, J. W.; Evans, W. J. *Organometallics* **2010**, *29*, 5209.

(54) Evans, W. J.; Keyer, R. A.; Ziller, J. W. *Organometallics* **1993**, *12*, 2618.

(55) Evans, W. J.; Boyle, T. J.; Ziller, J. W. *Inorg. Chem.* **1992**, *31*, 1120.

(56) Evans, W. J.; Olofson, J. M.; Zhang, H.; Atwood, D. A. *Organometallics* **1988**, *7*, 629.

(57) Evans, W. J.; Broomhall-Dillard, R. N. R.; Foster, S. E.; Ziller, J. W. *J. Coord. Chem.* **1999**, *46*, 565.

(58) Evans, W. J.; Siebel, C. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1998**, *120*, 6745.

(59) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 2314.

(60) Evans, W. J.; Kozimor, S. A.; Brady, J. C.; Davis, B. L.; Nyce, G. W.; Siebel, C. A.; Ziller, J. W.; Doedens, R. J. *Organometallics* **2005**, *24*, 2269.

(61) Evans, W. J.; Davis, B. L.; Champagne, T. M.; Ziller, J. W. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103*, 12678.

(62) Evans, W. J.; Perotti, J. M.; Kozimor, S. A.; Champagne, T. M.; Davis, B. L.; Nyce, G. W.; Fujimoto, C. H.; Clark, R. D.; Johnston, M. A.; Ziller, J. W. *Organometallics* **2005**, *24*, 3916.

(63) Windisch, H.; Scholz, J.; Taube, R.; Wrackmeyer, B. *J. Organomet. Chem.* **1996**, *520*, 23.

(64) Heeres, H. J.; Teuben, J. H.; Rogers, R. D. *J. Organomet. Chem.* **1989**, *364*, 87.

(65) Evans, W. J.; Shreeve, J. L.; Ziller, J. W. *Organometallics* **1994**, *13*, 731.

(66) Evans, W. J.; Hanusa, T. P.; Levan, K. R. *Inorg. Chim. Acta* **1985**, *110*, 191.

(67) Hou, Z.; Zhang, H.; Yoshimura, T.; Wakatsuki, Y. *Organometallics* **1997**, *16*, 2963.

$(C_5Me_5)_2LnX$ complexes. Since the supporting ligands in these two sets of complexes are different, the ligand to metal electron density donation and steric effects are not identical. However, the differences in both of these categories should make the lanthanides less likely to bind X, a result that is not observed. Specifically, since the cyclopentadienyl ligands in the $(C_5Me_5)_2LnX$ complexes are always bound in a pentahapto mode, they could provide more electron density to the lanthanide than the pincer ligands provide to bismuth when some of the nitrogen donor arms are not directed toward the bismuth. This should reduce the Lewis acidity of the lanthanides. Likewise, the fully coordinated cyclopentadienyl ligands provide less room around the metal than the partially bound pincer ligands. This should decrease the tendency for the X ligands to coordinate, but the opposite trend is observed.

Conclusion

Despite identical charge and similar ionic radii, Bi^{3+} and Ln^{3+} ions display significantly different chemistry in their interactions with X ligands in Ar'_2BiX and $(C_5Me_5)_2LnX$ complexes. When X = allyl, bismuth adopts η^1 binding despite room to form the η^3-mode always found with the lanthanides. When X = BPh_4, there is no interaction between the $[Ar'_2Bi]^+$ cation and the outer sphere $(BPh_4)^-$ ion, whereas the lanthanide cations, $[(C_5Me_5)_2Ln]^+$, orient to interact with two of the phenyl rings of the tetraphenylborate. Similarly, the $[Ar'_2Bi]^+$ cation does not bind THF, whereas the lanthanide cation readily forms $[(C_5Me_5)_2Ln(THF)_x]^+$ species. Evidently, the charge-to-radius ratio is not the dominating feature in this chemistry. The markedly different chemistry can be understood in terms of the differences in electronegativity and the presence of an inert pair of electrons on bismuth. The Bi^{3+} ion in Ar'_2BiX complexes is much less Lewis acidic than Ln^{3+} ions in $(C_5Me_5)_2LnX$ species, and this significantly affects both reactivity and structure.

Acknowledgment. For support, we thank the Idaho National Laboratory and the Chemical Sciences, Geosciences, and Biosciences Division of the Office of Basic Energy Sciences of the Department of Energy. We also thank Dr. Michael K. Takase for assistance with X-ray crystallography.

Supporting Information Available: CIF files giving crystallographic data for all complexes. This material is available free of charge via the Internet at http://pubs.acs.org.