SUPPLEMENTARY INFORMATION

Facile Bismuth Oxygen Bond Cleavage, C–H Activation, and Formation of a Monodentate Carbon-Bound Oxyaryl Dianion, $(C_6H_2{}^tBu_2\text{-}3,5\text{-}O\text{-}4)^{2-}$

Ian J. Casely, Joseph W. Ziller, Ming Fang, Filipp Furche, and William J. Evans*

Experimental Details

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. ^{1}H NMR spectra were recorded on Bruker DR400, GN500, or CRYO500 MHz spectrometers (^{13}C spectra on the 500 MHz spectrometer operating at 125 MHz) at 298 K unless otherwise stated, and referenced internally to residual protio-solvent resonances. UV-vis absorbance spectra (270-900 nm) were recorded on a Perkin-Elmer Lambda 800 double-beam spectrophotometer equipped with a PMT detector. EPR spectra were collected using a Brucker EMX spectrometer equipped with an ER041XG microwave bridge at ambient temperature. GC-MS spectra were collected on a ThermoTrace MS and GC-MS machine. Elemental analyses were conducted on a Perkin-Elmer 2400 Series II CHNS elemental analyzer. [2,6-$(Me_2NCH_2)_2C_6H_3$]$BiCl_2$, **1**, was synthesized according to literature procedures.[S1] $KOC_6H_3Me_2$-2,6, $KOC_6H_3{}^{i}Pr_2$-2,6, $KOC_6H_3{}^{t}Bu_2$-2,6, and $KOC_6H_2{}^{t}Bu_2$-2,6-Me-4 were synthesized via an adaptation of a literature procedure by treatment of the parent phenol with one equiv of $KN(SiMe_3)_2$ in toluene, followed by filtration of the resulting white solid and washing with hexanes.[S2] $KN(SiMe_3)_2$ was purchased from Aldrich, dissolved in toluene, and centrifuged to remove yellow insoluble material. Removal of solvent under reduced pressure afforded a white free-flowing solid. $[HNEt_3][BPh_4]$ was synthesized by treatment of $NEt_3{\cdot}HCl$ with

$NaBPh_4$ in water, followed by filtration and drying under high vacuum (10^{-5} Torr) for 48 h. $HOC_6H_3{}^iPr_2$-2,6 was degassed by three freeze-pump-thaw cycles and stored over molecular sieves prior to being filtered in the glovebox. All other phenol reagents were sublimed prior to use.

Ar'Bi($OC_6H_3Me_2$-2,6)$_2$, 2. A colorless THF (5 mL) solution of $KOC_6H_3Me_2$-2,6 (68 mg, 0.42 mmol) was added slowly to a stirred slurry of [2,6-$(Me_2NCH_2)_2C_6H_3$]$BiCl_2$, **1**, (100 mg, 0.21 mmol) in THF (5 mL) at room temperature. The solids dissolved and the yellow solution was stirred for 16 h. Following removal of the KCl byproduct by centrifugation and filtration, the solvent was removed from the yellow solution under reduced pressure to afford a yellow solid. This solid was dissolved in toluene (3 mL) and the yellow solution filtered to remove brown insoluble material. Following evaporation of the solvent, the resulting yellow solid was dissolved in hot MeCN (2 mL) and allowed to slowly cool to ambient temperature, from which X-ray quality single crystals formed. The mother liquor was decanted and the yellow crystalline solid washed with cold MeCN (2 mL) and dried under reduced pressure to afford **2** (87 mg, 64%). ^{1}H NMR (C_6D_6): δ 7.30 (d, 2H, $^3J_{H\text{-}H}$ = 7.5 Hz, *m*-Ar'-C*H*), 7.24 (t, 1H, $^3J_{H\text{-}H}$ = 7.4 Hz, *p*-Ar'-C*H*), 7.12 (d, 4H, $^3J_{H\text{-}H}$ = 7.3 Hz, *m*-OAr-C*H*), 6.69 (t, 2H, $^3J_{H\text{-}H}$ = 7.3 Hz, *p*-OAr-C*H*), 3.80 (bs $\nu_{1/2}$ = 43 Hz, 4H, NCH_2), 2.14 [s, 12H, OAr-$(CH_3)_2$], 2.03 [s, 12H, $N(CH_3)_2$]. ^{13}C (CD_3CN): δ The [Bi-*C*(Ar')] resonance could not be identified, 162.2 (q-Ar'-*C*), 151.5 and 126.3 (q-OAr-*C*), 128.4 (*m*-OAr-*C*H), 128.2 (*p*-Ar'-*C*H), 127.3 (*m*-Ar'-*C*H), 114.9 (*p*-OAr-*C*H), 66.8 (NCH_2), 45.1 [$N(CH_3)_2$], 18.7 [OAr-$(CH_3)_2$]. IR: 3056w, 3032w, 3002w, 2951w, 2921m, 2893m, 2838w, 2795w, 1587s, 1461s, 1417s, 1369m, 1268s, 1232s, 1174w, 1089s, 1030m, 1000m, 985w, 951w, 842s, 781m, 755s, 746s, 683m, 506m, 451 cm^{-1}.

Anal. Calcd for $C_{28}H_{37}BiN_2O_2$: C, 52.32; H, 5.81; N, 4.36. Found: C, 53.01; H, 5.70; N, 4.38.

Ar'Bi($OC_6H_3{}^iPr_2$-2,6)$_2$, 3. A THF (5 mL) solution of $KOC_6H_3{}^iPr_2$-2,6 (46 mg, 0.21 mmol) was added slowly to a stirred slurry of [2,6-$(Me_2NCH_2)_2C_6H_3$]$BiCl_2$, **1**, (50 mg, 0.11 mmol) in THF (5 mL) at room temperature. Following an analogous workup to that described for **2**, **3** was isolated as a yellow solid (75 mg, 94%). After warming an NMR sample of **3** to dissolve it in CD_3CN and cooling to ambient temperature, X-ray quality single crystals grew within 30 min. ^{1}H NMR (C_6D_6): δ 7.33 (d, 2H, $^3J_{H\text{-}H}$ = 7.4 Hz, *m*-Ar-C*H*), 7.22 (t, 1H, $^3J_{H\text{-}H}$ = 7.4 Hz, *p*-Ar-C*H*), 7.18 (d, 4H, $^3J_{H\text{-}H}$ = 7.5 Hz, *m*-OAr-C*H*), 6.85 (t, 2H, $^3J_{H\text{-}H}$ = 7.5 Hz, *p*-OAr-C*H*), 3.85 (s, 4H, NCH_2), 3.16 (bs $\nu_{1/2}$ = 144 Hz, 4H, [C*H*$(CH_3)_2$], 2.10 [s, 12H, N$(CH_3)_2$], 1.22 [bs $\nu_{1/2}$ = 35 Hz, 24H, CH(C$H_3)_2$]. ^{13}C (C_6D_6): δ 219.9 [Bi-*C*(Ar')], 159.0 (q-Ar'-*C*), 151.6 and 128.0 (q-OAr-*C*), 128.4 (*p*-Ar'-*C*H), 127.2 (*m*-Ar'-*C*H), 122.8 (*m*-OAr-*C*H), 115.5 (*p*-OAr-*C*H), 67.1 (NCH_2), 45.3 [N($CH_3)_2$], 23.6 [OAr-CH($CH_3)_2$]. The *iso*-propyl *C*H carbon could not be observed either in the ^{13}C or HMQC NMR experiments. The resonance for the proton attached to this carbon was very broad in the ^{1}H NMR spectrum, but coupling to the *iso*-propyl methyl groups was confirmed by a COSY experiment. IR: 3045w, 3011w, 2956s, 2865m, 2797w, 1585m, 1455m, 1420s, 1378w, 1355m, 1327s, 1255s, 1203m, 1173w, 1154w, 1138w, 1110w, 1094w, 1041w, 1028w, 999w, 950w, 932w, 883m, 839s, 769m, 754m, 679m, 530m, 446m cm^{-1}. Anal. Calcd for $C_{36}H_{53}BiN_2O_2$: C, 57.28; H, 7.08; N, 3.71. Found: C, 57.21; H, 7.27; N, 3.69.

Ar'Bi($C_6H_2{}^tBu_2$-3,5-O-4), 4. A colorless THF (5 mL) solution of $KOC_6H_3{}^tBu_2$-2,6 (156 mg, 0.64 mmol) was added in three portions to a stirred slurry of [2,6-

$(Me_2NCH_2)_2C_6H_3]BiCl_2$, **1**, (150 mg, 0.32 mmol) in THF (10 mL) at room temperature, resulting in dissolution of the solids and formation of an orange solution during the addition over one minute. A dark orange solution formed over the course of 1 h, after which it was centrifuged and filtered to remove the KCl byproduct. The isolated orange solution was concentrated to 3 mL and stored at −30 °C overnight. The mother liquor was decanted and the solids washed with cold THF (−30 °C) and dried under reduced pressure, yielding crystalline orange **4** (103 mg, 54%). X-ray quality single crystals were grown from a concentrated THF solution stored at −30 °C overnight. Subsequent recrystallization of a sample of this material from hot MeCN slowly cooled to ambient temperature also provided X-ray quality single crystals and led to collection of a better quality data set. ^{1}H NMR (CD_3CN): δ 7.55-7.49 (m, 5H, *m*- and *p*-Ar'-C*H* and OAr-C*H*, as confirmed by HMQC), 3.86 and 3.74 (d, 2H each, $^2J_{H\text{-}H}$ = 14.7 Hz, NCH_2), 2.67 and 2.26 [s, 6H each, N(CH_3)$_2$], 1.24 [s, 18H, C(CH_3)$_3$]. ^{13}C (CD_3CN): δ 182.7 [Bi-*C*(Ar')], 174.5 [Bi-*C*(OAr)], 159.0 and 139.6 (q-OAr-*C*), 149.7 (q-Ar'-*C*), 134.5, 129.0, and 127.7 (*m*- and *p*-Ar'-*C*H and OAr-*C*H), 67.2 (N*C*H$_2$), 46.5 and 46.4 [N(*C*H$_3$)$_2$], 34.9 [*C*(CH$_3$)$_3$], 29.1 [C(*C*H$_3$)$_3$]. IR: 3045w, 2991w, 2943m, 2894m, 2840w, 2797w, 1554s, 1477s, 1432s, 1374m, 1354m, 1333m, 1300w, 1254m, 1202w, 1173w, 1127w, 1091s, 1034w, 1005m, 885w, 840s, 803w, 775w, 709w, 530w, 444m cm^{-1}. Anal. Calcd for $C_{26}H_{39}N_2OBi$: C 51.64, H 6.51, N 4.63; Found: C 52.07, H 6.99, N 4.35. UV/vis (THF): λ_{max} (ε/L mol^{-1} cm^{-1}); 308 nm (6900), 467 nm (6900), and 395 nm (2800).

Identification of HOC$_6$H$_3$^{t}Bu$_2$-2,6 byproduct. Removal of the solvent from the mother liquor from the crystallization of Ar'Bi(C_6H_2^{t}Bu$_2$-3,5-O-4), **4**, yielded an orange/ yellow solid. Hexane (5 mL) was added and the suspension stirred for 1 h, after which

the solution was decanted, filtered, and solvent removed under reduced pressure to afford a pale yellow solid (33 mg). ^{1}H NMR (CD_3CN): δ 7.14 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, *m*-HOAr-C*H*), 6.75 (t, 1H, $^3J_{H-H}$ = 7.8 Hz, *p*-HOAr-C*H*), 5.38 (bs, 1H, *H*OAr), 1.40 [s, 18H, $C(CH_3)_3$]. GC/MS (EI): Retention Time 11.31 min: *m/z*(%) 206.3(23) $[M]^+$, 191.3(100) $[M-Me]^+$. The ^{1}H NMR spectrum and GC/MS data were identical to that of an authentic sample of $HOC_6H_3{}^tBu_2$-2,6.

[Ar'Bi($C_6H_2{}^tBu_2$-3,5-OH-4)][BPh_4], 5. A THF (5 mL) solution of [$HNEt_3$][BPh_4] (55.7 mg, 0.13 mmol) was added dropwise to a stirred dark orange solution of **4** (80.0 mg, 0.13 mmol) in THF (10 mL). As the addition proceeded, the reaction mixture became yellow and finally colorless, whereupon it was stirred for 1 h. Subsequent filtration and removal of volatiles from the filtrate afforded an off white solid (120 mg) which was dissolved in MeCN and allowed to slowly evaporate to dryness overnight, forming large colorless crystals and a small amount of yellow solid. MeCN (1 mL) was added and mixed to dissolve the yellow material. Following storage at –30 °C overnight, the product was isolated from the pale yellow mother liquor and dried under reduced pressure to afford colorless **5** (95 mg, 78%). X-ray quality single crystals were grown by the slow evaporation of a concentrated MeCN solution at ambient temperature. ^{1}H NMR (CD_3CN): δ 7.84 (s, 2H, OAr-C*H*), 7.62 (s, 3H, *m*- and *p*-Ar'-C*H* as confirmed by HMQC), 7.27 (bm, 8H, *m*-BPh), 6.99 (t, 8H, $^3J_{H-H}$ = 7.4 Hz, *o*-BPh), 6.84 (t, 4H, $^3J_{H-H}$ = 7.4 Hz, *p*-BPh), 5.75 (bs, 1H, OH), 4.01 and 3.75 (d, 2H each, $^2J_{H-H}$ = 15.0 Hz, NCH_2), 2.72 and 2.23 [s, 6H each, $N(CH_3)_2$], 1.31 [s, 18H, $C(CH_3)_3$]. ^{13}C (CD_3CN): δ 184.9 [Bi-*C*(Ar')], 171.9 [Bi-*C*(OAr)], 163.8 (4-line multiplet, $^1J_{C-B}$ = 49.1 Hz, B-*C*), 155.3 and 140.1 (q-OAr-*C*), 150.4 (q-Ar'-*C*), 135.8 (*m*-BPh), 135.1 (OAr-*C*H), 129.8 (*p*-Ar'-*C*H),

128.1 (*m*-Ar'-*C*H), 125.7 (m, $^2J_{C\text{-}B}$ = 25.2 Hz , *o*-BPh), 121.8 (*p*-BPh), 67.5 (N*C*H_2), 47.0 [N(*C*H_3)$_2$], 34.6 [*C*(CH_3)$_3$], 29.4 [C(*C*H_3)$_3$]. IR: 3608m, 3054m, 3038m, 2998m, 2966m, 2910m, 2974m, 2844w, 2811w, 1945w, 1881w, 1820w, 1763w, 1580m, 1561w, 1479m, 1453m, 1426s, 1403m, 1360w, 1311w, 1240m, 1203m, 1174m, 1149m, 1116m, 1064w, 1030w, 999w, 985m, 950w, 913w, 882w, 842s, 808w, 781m, 750m, 736s, 706s, 612m, 574w, 453m cm^{-1}. Anal. Calcd for $C_{50}H_{60}BBiN_2O$: C, 64.92; H, 6.55; N, 3.03. Found: C, 65.15; H, 6.69; N, 3.02.

Ar'Bi($C_6H_2{}^tBu_2$-2,6-Me-4)$_2$, 6. A colorless THF (5 mL) solution of $KOC_6H_2{}^tBu_2$-2,6-Me-4 (110 mg, 0.42 mmol) was added slowly to a stirred slurry of [2,6-(Me_2NCH_2)$_2C_6H_3$]$BiCl_2$, **1**, (100 mg, 0.21 mmol) in THF (10 mL) at room temperature. The solids dissolved and the orange solution was stirred for 1 h. The solvent was removed under reduced pressure to afford a pale orange solid, which was stirred in toluene (10 mL) for 30 min. Insoluble material was removed by centrifugation and filtration and the resulting orange solution was dried under reduced pressure and the residue stirred in hexane (10 mL) for 1 h. After subsequent filtration, the remaining orange solid was dried under reduced pressure (129 mg). X-ray quality single crystals were grown by slow cooling of a hot toluene/hexane mixture (1:1, 5 mL total) to ambient temperature overnight. The mother liquor was decanted from the orange crystals, which were washed with cold hexane (5 mL) and dried under reduced pressure to afford **6** (82 mg, 47%). ^{1}H NMR (C_4D_8O): δ 7.75 (d, 2H, $^3J_{H\text{-}H}$ = 7.4 Hz, *m*-Ar'-C*H*), 7.51 (t, 1H, *p*-Ar'-C*H*), 6.82 and 6.64 (s, 2H each, *m*-OAr-C*H*), 4.46 (s, 4H, NCH_2), 2.49 [s, 12H, N(CH_3)$_2$], 2.10 (s, 6H, *p*-OAr-CH_3), 1.59 and 0.89 [s, 18H each, C(CH_3)$_3$]. ^{13}C (C_4D_8O): δ 226.6 [Bi-*C*(Ar')], 164.1 (q-Ar'-*C*), 156.2, 141.1, 138.3, and 121.6 (q-OAr-*C*), 131.7 (*p*-

Ar'-*C*H), 129.9 (*m*-Ar'-*C*H), 127.1 and 126.4 (OAr-*C*H), 71.4 (N*C*H_2), 48.0 [N(*C*H_3)$_2$], 37.0 and 36.1 [*C*(CH_3)$_3$], 34.2 and 31.9 [C(*C*H_3)$_3$], 22.1 (OAr-*C*H_3). IR: 3052w, 3002m, 2951m, 2912m, 2868m, 2798w, 2724w, 1601w, 1583w, 1545w, 1456m, 1404s, 1380m, 1372m, 1354m, 1257m, 1230s, 1216s, 1196m, 1148w, 1116m, 1024m, 1013m, 1001m, 984w, 924w, 885w, 858w, 842m, 813m, 789s, 766m, 704w, 618w, 575w, 545w, 489m, 463m, 452m, 430w cm^{-1}. Anal. Calcd for $C_{42}H_{65}BiN_2O_2$: C, 60.12; H, 7.82; N, 3.34. Found: C, 60.66; H, 7.72; N, 3.34.

Crystallographic Details

Table S1. X-ray Data Collection Parameters for $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(OC_6H_3Me_2\text{-}2,6)_2$, **2**, $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(OC_6H_3{}^iPr_2\text{-}2,6)_2$, **3**, $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(C_6H_2{}^tBu_2\text{-}3,5\text{-}O\text{-}4)$, **4** (with lattice MeCN) and **4'** (with lattice benzene), $\{[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(C_6H_2{}^tBu_2\text{-}3,5\text{-}OH\text{-}4)\}[BPh_4]$, **5**, and $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)_2$, **6**.

	2	**3**	**4**	**4'**	**5**	**6**
Empirical formula	$C_{28}H_{37}BiN_2O_2$	$C_{36}H_{53}BiN_2O_2$	$C_{26}H_{39}BiN_2O$ •½(CH_3CN)	$C_{26}H_{39}BiN_2O$ •C_6H_6	$C_{50}H_{60}$ $BBiN_2O$	$C_{42}H_{65}BiN_2O_2$
Formula weight	642.58	754.78	625.10	682.68	924.79	838.94
Temperature (K)	143(2)	143(2)	143(2)	143(2)	138(2)	143(2)
Crystal system	orthorhombic	monoclinic	triclinic	orthorhombic	triclinic	monoclinic
Space group	$P2_12_12_1$	$C2/c$	$P\bar{1}$	$Pca2_{(1)}$	$P\bar{1}$	$P2_1/n$
a (Å)	13.2256(7)	53.677(3)	10.1403(6)	18.0313(14)	10.8059(7)	11.3693(7)
b (Å)	13.4893(7)	10.8825(6)	14.3990(8)	10.0840(8)	13.1895(9)	29.7135(19)
c (Å)	15.2210(8)	39.936(3)	18.6374(10)	16.5021(13)	17.5277(17)	13.0038(8)
α (deg)	90	90	98.9882(6)	90	98.2130(10)	90
β (deg)	90	130.6780(10)	96.4784(6)	90	92.6680(10)	114.7896(7)
γ (deg)	90	90	90.1828(6)	90	113.5650(10)	90
Volume ($Å^3$)	2715.5(2)	17692(2)	2670.1(3)	3000.5(4)	2251.5(3)	3988.2(4)
Z	4	20	4	4	2	4
ρ_{calcd} (Mg/m^3)	1.572	1.417	1.555	1.511	1.364	1.397
μ (mm^{-1})	6.518	5.014	6.624	5.901	3.952	4.456
R1 [I > 2σ(I)][a]	0.0146	0.0226	0.0165	0.0199	0.0235	0.0373
wR2 (all data)[a]	0.0358	0.0507	0.0399	0.0460	0.0596	0.0855

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

Table S2. Selected Bond Distances (Å) and Angles (deg) for [2,6-$(Me_2NCH_2)_2C_6H_3$] $Bi(OC_6H_3Me_2$-2,6$)_2$, **2**, [2,6-$(Me_2NCH_2)_2C_6H_3$]$Bi(OC_6H_3{}^iPr_2$-2,6$)_2$, **3**, and [2,6-$(Me_2NCH_2)_2C_6H_3$]$Bi(OC_6H_2{}^tBu_2$-2,6-Me-4$)_2$, **6**.

2		**3**				**6**	
Bi1–C1	2.183(2)	Bi1–C1	2.197(2)	Bi2–C37	2.183(3)	Bi1–C1	2.194(4)
Bi1–N1	2.5178(18)	Bi1–N1	2.555(2)	Bi2–N3	2.488(2)	Bi1–N1	2.557(3)
Bi1–N2	2.522(2)	Bi1–N2	2.553(2)	Bi2–N4	2.577(2)	Bi1–N2	2.531(4)
Bi1–O1	2.2972(17)	Bi1–O1	2.2969(16)	Bi2–O3	2.2732(18)	Bi1–O1	2.350(3)
Bi1–O2	2.3068(17)	Bi1–O2	2.3000(16)	Bi2–O4	2.3031(17)	Bi1–O2	2.321(3)
O1–C13	1.321(3)	O1–C13	1.333(3)	O3–C49	1.327(3)	O1–C13	1.337(5)
O2–C20	1.323(2)	O2–C25	1.334(3)	O4–C61	1.330(3)	O2–C28	1.346(5)
N1–Bi1–N2	146.02(6)	N1–Bi1–N2	144.62(7)	N3–Bi2–N4	145.47(7)	N1–Bi1–N2	146.10(13)
O1–Bi1–O2	167.06(6)	O1–Bi1–O2	174.98(6)	O3–Bi2–O4	164.71(7)	O1–Bi1–O2	171.87(11)
N1–Bi1–O1	79.09(7)	N1–Bi1–O1	78.50(6)	N3–Bi2–O3	88.11(7)	N1–Bi1–O1	91.83(11)
N1–Bi1–O2	92.19(6)	N1–Bi1–O2	102.37(6)	N3–Bi2–O4	79.15(7)	N1–Bi1–O2	96.24(11)
N1–Bi1–C1	73.20(7)	N1–Bi1–C1	71.83(8)	N3–Bi2–C37	72.98(8)	N1–Bi1–C1	72.97(14)
N2–Bi1–O1	96.25(7)	N2–Bi1–O1	97.50(6)	N4–Bi2–O3	85.94(7)	N2–Bi1–O1	90.69(12)
N2–Bi1–O2	85.61(7)	N2–Bi1–O2	78.89(6)	N4–Bi2–O4	99.75(7)	N2–Bi1–O2	81.87(11)
N2–Bi1–C1	72.97(7)	N2–Bi1–C1	72.81(8)	N4–Bi2–C37	72.55(9)	N2–Bi1–C1	73.23(14)
C1–Bi1–O1	87.34(7)	C1–Bi1–O1	85.08(7)	C37–Bi2–O3	83.42(8)	C1–Bi1–O1	90.14(13)
C1–Bi1–O2	80.95(7)	C1–Bi1–O2	90.49(7)	C37–Bi2–O4	84.79(8)	C1–Bi1–O2	90.94(13)

Table S3. Selected experimental and calculated bond distances (Å) and angles (deg) for [2,6-$(Me_2NCH_2)_2C_6H_3$]Bi($C_6H_2{}^tBu_2$-3,5-O-4), **4** (with lattice MeCN) and **4'** (with lattice benzene). Both molecules display similar metrical parameters.

4 exp				**4 calc**	**4' exp**	
Bi1–C1	2.207(2)	Bi2–C27	2.1987(19)	2.227	Bi1–C1	2.208(3)
Bi1–N1	2.5161(17)	Bi2–N3	2.5159(17)	2.574	Bi1–N1	2.568(3)
Bi1–N2	2.5774(17)	Bi2–N4	2.5837(17)	2.604	Bi1–N2	2.517(3)
Bi1–C13	2.188(2)	Bi2–C39	2.182(2)	2.196	Bi1–C13	2.190(3)
O1–C16	1.278(2)	O2–C42	1.275(2)	1.280	O1–C16	1.278(3)
C13–C14	1.398(3)	C39–C40	1.407(3)	1.402	C13–C14	1.397(4)
C14–C15	1.383(3)	C40–C41	1.383(3)	1.386	C14–C15	1.381(4)
C15–C16	1.458(3)	C41–C42	1.459(3)	1.456	C15–C16	1.451(4)
C16–C17	1.453(3)	C42–C43	1.458(3)	1.454	C16–C17	1.459(4)
C17–C18	1.384(3)	C43–C44	1.382(3)	1.387	C17–C18	1.377(4)
C18–C13	1.406(3)	C44–C39	1.403(3)	1.404	C18–C13	1.393(4)
N1–Bi1–N2	143.91(5)	N3–Bi2–N4	143.78(5)	143.28	N1–Bi1–N2	144.07(9)
N1–Bi1–C1	72.17(6)	N3–Bi2–C27	72.25(6)	71.74	N1–Bi1–C1	71.91(10)
N1–Bi1–C13	89.99(6)	N3–Bi2–C39	89.65(7)	91.45	N1–Bi1–C13	93.26(10)
N2–Bi1–C1	71.74(6)	N4–Bi2–C27	71.54(6)	70.59	N2–Bi1–C1	72.18(10)
N2–Bi1–C13	93.43(6)	N4–Bi2–C39	93.05(6)	95.69	N2–Bi1–C13	89.70(9)
C1–Bi1–C13	95.11(7)	C27–Bi2–C39	94.71(7)	98.59	C1–Bi1–C13	96.91(10)
Bi1–C13–C14	122.84(14)	Bi2–C39–C40	123.59(14)	125.22	Bi1–C13–C14	119.1(2)
C13–C14–C15	122.99(18)	C39–C40–C41	122.62(18)	122.40	C13–C14–C15	122.1(3)
C14–C15–C16	119.43(17)	C40–C41–C42	119.58(17)	119.77	C14–C15–C16	120.3(3)
C15–C16–C17	116.45(17)	C41–C42–C43	116.96(17)	117.47	C15–C16–C17	116.8(2)
C15–C16–O1	121.54(18)	C41–C42–O2	121.61(18)	121.23	C15–C16–O1	122.0(3)
O1–C16–C17	122.01(17)	O2–C42–C43	121.44(18)	121.30	O1–C16–C17	121.2(3)
C16–C17–C18	120.00(17)	C42–C43–C44	119.52(17)	119.51	C16–C17–C18	119.4(2)
C17–C18–C13	122.24(18)	C43–C44–C39	122.83(18)	122.64	C17–C18–C13	123.1(3)
C18–C13–Bi1	119.41(14)	C44–C39–Bi2	118.57(14)	116.54	C18–C13–Bi1	122.4(2)

Table S4. Selected experimental and calculated bond distances (Å) and angles (deg) for {[2,6-$(Me_2NCH_2)_2C_6H_3$]Bi($C_6H_2{}^tBu_2$-3,5-OH-4)}[BPh_4], **5**.

5 exp		**5 calc**	**5 exp**		**5 calc**
Bi1–C1	2.202(3)	2.218	N1–Bi1–C13	87.04(8)	90.73
Bi1–N1	2.512(2)	2.538	N2–Bi1–C1	72.89(8)	72.26
Bi1–N2	2.547(2)	2.569	N2–Bi1–C13	93.74(8)	94.15
Bi1–C13	2.221(3)	2.242	C1–Bi1–C13	93.34(9)	97.24
O1–C16	1.376(3)	1.367	Bi1–C13–C14	122.43(19)	124.35
C13–C14	1.389(4)	1.394	C13–C14–C15	122.1(3)	122.12
C14–C15	1.393(4)	1.395	C14–C15–C16	116.5(3)	116.99
C15–C16	1.398(4)	1.414	C15–C16–C17	123.6(2)	122.84
C16–C17	1.415(4)	1.412	C15–C16–O1	115.3(3)	116.01
C17–C18	1.399(4)	1.397	O1–C16–C17	121.2(3)	121.14
C18–C13	1.384(4)	1.393	C16–C17–C18	116.5(3)	116.85
N1–Bi1–N2	145.42(7)	144.52	C17–C18–C13	121.7(3)	122.19
N1–Bi1–C1	72.55(9)	72.26			

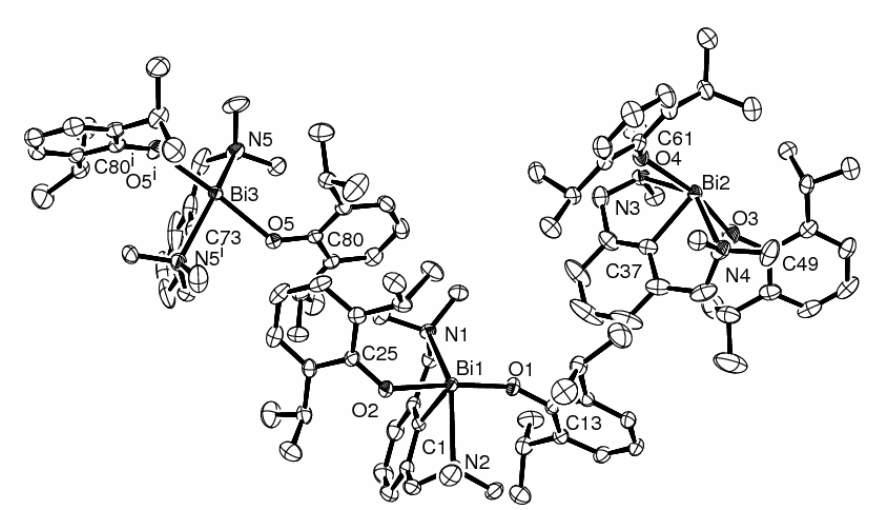

Figure S1. ORTEP drawing of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(OC_6H_3{}^iPr_2\text{-}2,6)_2$, **3**, with ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity. All molecules of **3** present in the asymmetric unit are shown. Only one component of disorder is shown for the molecule containing Bi3.

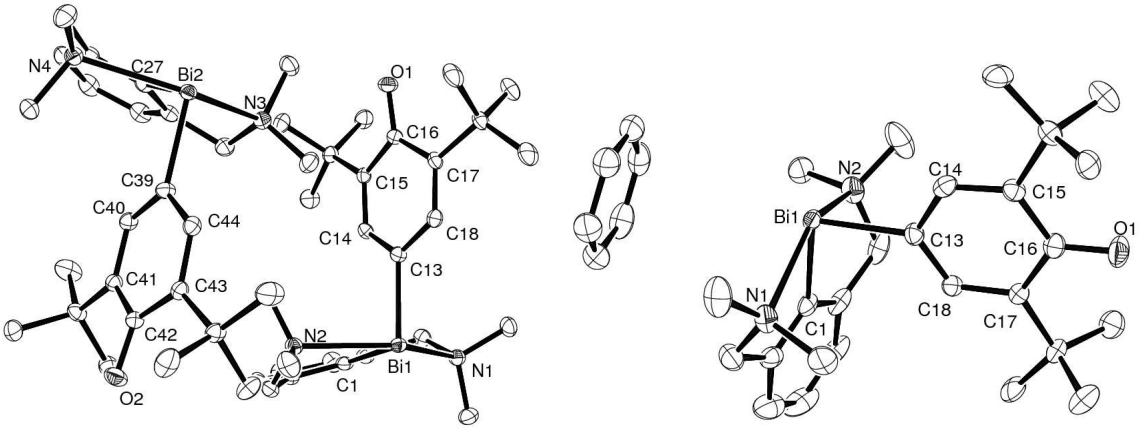

Figure S2. ORTEP drawing of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(C_6H_2{}^tBu_2\text{-}3,5\text{-}O\text{-}4)$: left, **4**, (with lattice MeCN, not shown) and right, **4'**, (with lattice benzene). Ellipsoids are drawn at the 50% probability level and hydrogen atoms are omitted for clarity. Both molecules of **4** present in the asymmetric unit are shown.

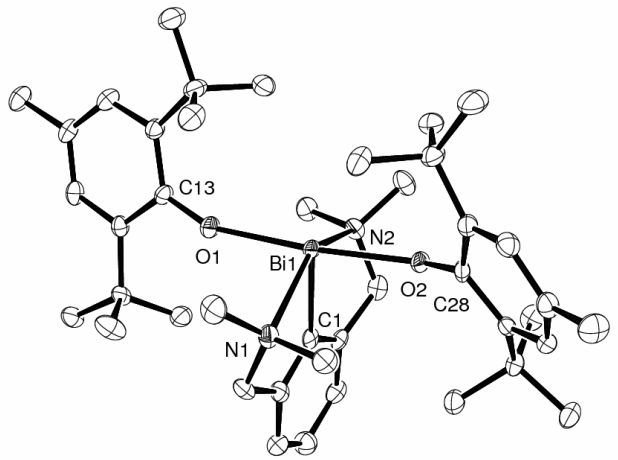

Figure S3. ORTEP drawing of $[2,6\text{-}(Me_2NCH_2)_2C_6H_3]Bi(OC_6H_2{}^tBu_2\text{-}2,6\text{-}Me\text{-}4)_2$, **6**, with ellipsoids drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Computational Details. The structures of **4** and **5** were initially optimized using the TPSSh[S3] hybrid meta-GGA functional and split valence basis sets with polarization functions on non-hydrogen atoms (SV(P)).[S4] The TPSSh functional contains only one empirical parameter and is uniformly accurate for a wide range of organometallic compounds.[S5,S6] Relativistic small-core pseudopotentials[S7] were employed for Bi. Fine quadrature grids (size m4)[S8] were used throughout except for the final TZVP optimization. Vibrational frequencies were computed at the TPSSh/SV(P)[S9] level and scaled by a factor of 0.95 to account for anharmonicity and basis set incompleteness. All structures were found to be minima. Natural population analyses[S10] was also obtained at the TPSSh/SV(P) level. The structural parameters reported in the text are the result of re-optimization using larger triple-zeta valence basis sets with two sets of polarization functions (def2-TZVP).[S11] For **4** and **5**, the "Conductor-like Screening Model" (COSMO)[S12] with complete screening ($\varepsilon = \infty$) was used in the final geometry

optimization to simulate the large charge screening effect in the solid state and approximately account for packing effects. The differences between the SV(P) and the TZVP structures were found to be small, typically amounting to 0.01 Å in bond lengths or less. The electronic stability of the ground state was tested by performing open-shell calculations. No spin symmetry breaking was found. All computations were performed using the TURBOMOLE program package.[S13]

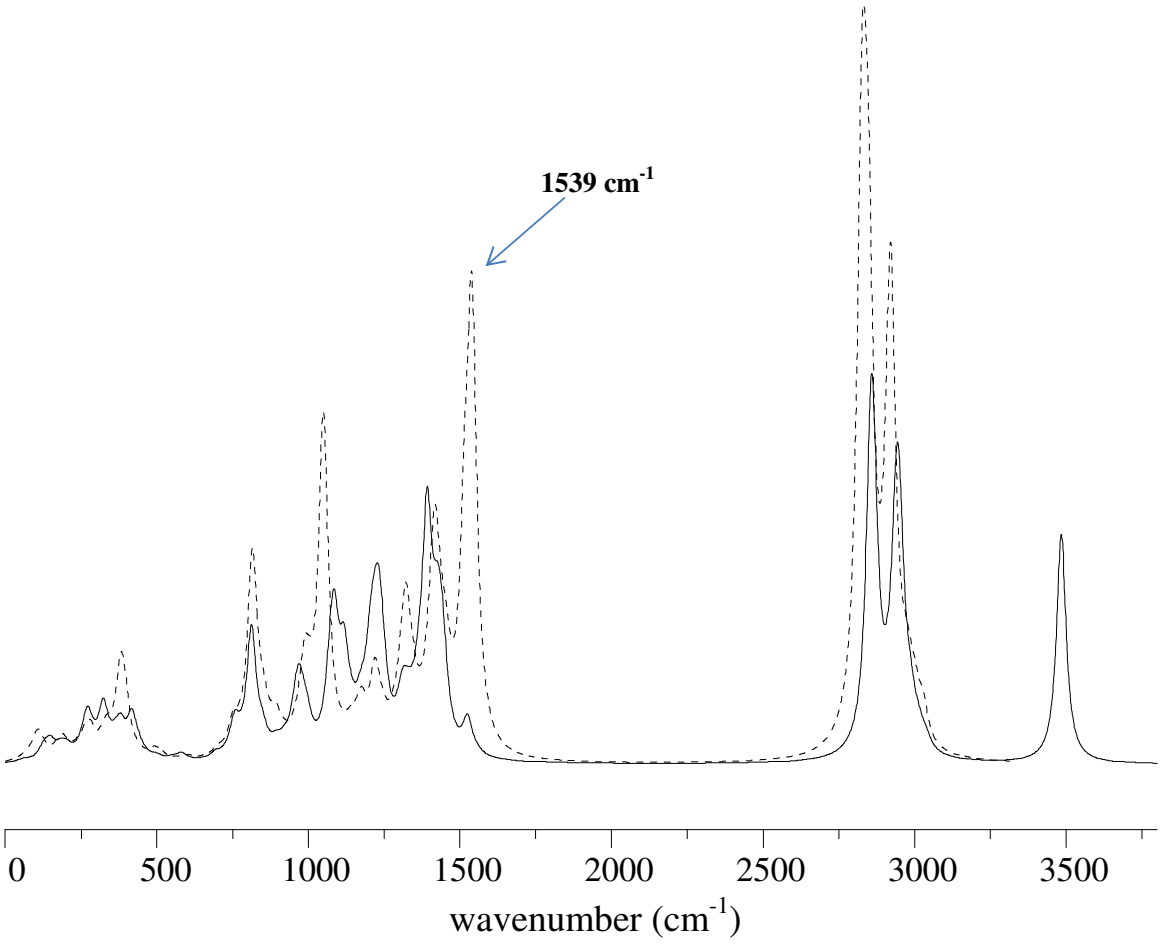

Figure S4. Computed infrared spectra of **4** (dashed) and **5** (solid).

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