Supporting Information

for

A Bis(bismuth)toluene Inverted Sandwich Complex Supported by Amine Tris(phenoxide) Ligands

Luke E. Turner, Matthew G. Davidson,* Matthew D. Jones, Holger Ott,

Verena S. Schulz, and Paul J. Wilson*

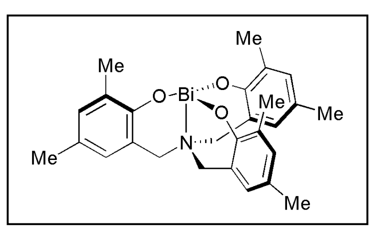
Department of Chemistry, University of Bath, Bath, BA2 7AY, United Kingdom.

E-mail: m.g.davidson@bath.ac.uk; p.j.wilson@bath.ac.uk

EXPERIMENTAL DETAILS

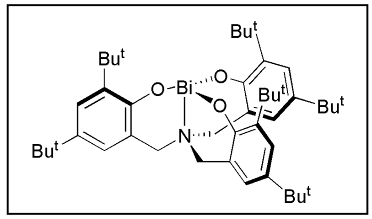
General Details. All operations were performed under dry nitrogen atmosphere using standard Schlenk techniques. Toluene was distilled from sodium/benzophenone[1] or purified by sequential elution over activated alumina and copper catalyst (R3-11) columns,[2] followed by storage under dry argon. Dichloromethane and acetonitrile were distilled from calcium hydride or eluted over activated alumina columns, and stored under dry argon. $[Bi(NMe_2)_3]$,[3] $[Bi(OBu^t)_3]$,[4] and $[Sb(NEt_2)_3]$[5] were prepared using previously reported procedures. Tris(phenol)amines **1** and **2** were synthesized from the established Mannich reaction of the corresponding phenol with *p*-formaldehyde and hexamethylenetetramine.[6,7] Chloroform-d_1 and dichloromethane-d_2 were purchased from Aldrich Chemical Co., Inc. (Gillingham, United Kingdom) and distilled from calcium hydride prior to use. The ^1H and ^{13}C NMR spectra were acquired using a Bruker Advance 300 spectrometer and referenced to the protio impurities of the solvents as internal standards. Elemental analysis and molecular structures were obtained through the University of Bath departmental facilities. We regret that accurate microanalysis for **4**, $(\mathbf{4})_2{\cdot}C_7H_8$, and **5** could not be obtained. Mass spectra of **4** and **5** were obtained to supplement the characterization of the complexes. Mass spectra were acquired from the EPSRC National Mass Spectrometry Service Center, Swansea, United Kingdom. Crystallography data were collected on a Nonius KappaCCD area detector diffractometer using Mo-Kα radiation (λ = 0.71073 Å), and all structures were solved by direct methods and refined on all F^2 data using the SHELXL-97 suite of programs hydrogen atoms, with the exception of those involved in hydrogen bonding, were included in idealized positions and refined using the riding model.[8]

Synthesis of $[Bi(OC_6H_2\text{-}\{CH_2\}\text{-}2\text{-}Me\text{-}3,5)_3N]$ (3)



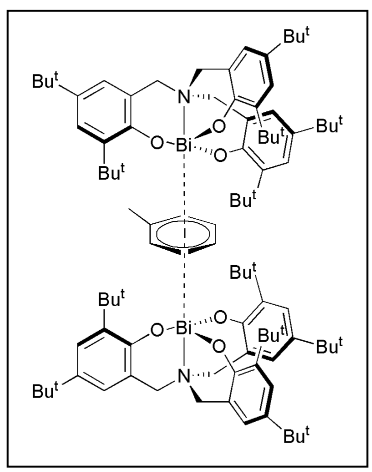
A solution of $[Bi(OBu^t)_3]$ (0.54 g, 1.3 mmol) in toluene was stirred as **1** (0.53 g, 1.3 mmol) in toluene was slowly added via cannula. The orange solution was stirred for 30 minutes and evacuated to dryness affording an orange powder that decomposes in solution (0.65 g, 82%) Anal. Calcd for $C_{27}H_{30}NO_3Bi$: C, 51.8; H, 4.83; N, 2.24. Found: C, 51.6; H, 4.89; N, 2.21. (HRMS): Calcd: 625.2024, Found: 625.2026. ^{1}H NMR (CD_2Cl_2, 25°C): δ 6.88, 6.53 (s, br., 6H, aromatics); 4.30 (s, br., 6H, CH_2); 2.21, 2.16 (s, br., 18H, CH_3). Attempts to obtain ^{13}C NMR were unsuccessful due to the instability of **3** in solution.

Synthesis of [Bi(OC$_6$H$_2$-{CH$_2$}-2-Bu^t-3,5)$_3$N] (4)



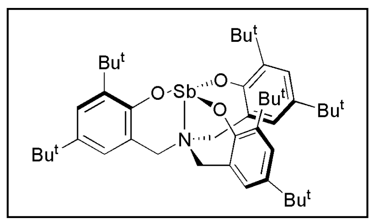
A sample of [Bi(OBu^t)$_3$] (0.65 g, 1.5 mmol) was dissolved in dichloromethane (10 mL). This solution was stirred as a solution of **2** (1.02 g, 1.5 mmol) in dichloromethane (10 mL) was slowly added via cannula. The orange solution was stirred for 8 hours and evacuated to dryness affording an orange powder that was pure by ^{1}H NMR analysis (1.22 g, 92%). (HRMS): Calcd: 877.4841, Found: 877.4836. ^{1}H NMR ($CDCl_3$, 25°C): δ 7.51, 6.67 (d, 6H, 2.5 Hz, aromatics); 4.34 (s, br., 6H, CH_2); 1.42, 1.28 (s, 54H, CMe_3). ^{13}C NMR ($CDCl_3$, 25°C): δ 154.4 (Bi-O-C); 140.6, 139.8, 125.2, 125.0, 122.3 (aromatics); 60.0 (CH$_2$); 34.7, 34.0 (CMe$_3$); 31.9, 30.1 (CMe_3).

Synthesis of [Bi(OC$_6$H$_2$-{CH$_2$}-2-Bu^t-3,5)$_3$N]$_2$·[C$_7$H$_8$] (4)$_2$·(C$_7$H$_8$)



A sample of [Bi(NMe$_2$)$_3$] (0.49 g, 1.4 mmol in toluene (10 mL) was stirred as a solution of **2** (0.96 g, 1.4 mmol) in toluene (10 mL) was added via cannula. The orange solution was stirred for 8 hours and evacuated to dryness affording an orange powder. Recrystallization of the crude material from dichloromethane/acetonitrile produced orange crystals of **4** suitable for X-ray analysis (0.65 g, 52%). ^{1}H NMR ($CDCl_3$, 25°C): δ 7.45, (d, 6H, 2.5 Hz, aromatics); 7.30-7.25, 7.20-7.14, (m, 5H toluene); 6.96, (d, 6H, 2.5 Hz, aromatics); 4.34 (s, br., 12H, CH_2); 2.37 (s, 3H, toluene); 1.42, 1.28 (s, 54H, C*Me*$_3$). ^{13}C NMR ($CDCl_3$, 25°C): δ 154.4 (Bi-O-*C*); 140.6, 139.8, 125.2, 125.0, 122.3 (aromatics); 60.0 (*C*H_2); 34.7, 34.0 (*C*Me_3); 31.9, 30.1 (C*Me*$_3$). Crystal data for [(**4**)$_2$·(C_7H_8)] ($C_{97}H_{140}Bi_2N_2O_6$): M = 1848.07, 0.25 x 0.20 x 0.15 mm^3, monoclinic, space group C2/c (No. 15), a = 20.5340(2), b = 11.1350(1), c = 40.2690(4) Å, β = 90.3940(1)°, V = 9207.13(15) Å^3, Z = 4, D_c = 1.333 g/cm^3, F_{000} = 3800, MoKα radiation, λ = 0.71073 Å, T = 150(2)K, $2\Theta_{max}$ = 55.1°, 48999 reflections collected, 10382 unique (R_{int} = 0.0552). Final GooF = 1.093, R1 = 0.0373, wR2 = 0.0875, R indices based on 9027 reflections with I >2sigma(I) (refinement on F^2), 702 parameters, 0 restraints, μ = 3.868 mm^{-1}. Absorption correction applied. CCDC 295729.

Synthesis of [Sb(OC_6H_2-{CH_2}-2-Bu^t-3,5)$_3$N] (5)



A sample of [Sb(NEt_2)$_3$] (1.54 g, 4.55 mmol) was dissolved in toluene (20 mL). This solution was stirred as a solution of **2** (3.06 g, 4.55 mmol) in toluene (20 mL) was slowly added via cannula. The yellow-green solution was stirred for 8 hours and evacuated to dryness affording a white powder that was pure by ^{1}H NMR analysis (3.34 g, 92.8%). A portion of the product was recrystallized from dichloromethane/acetonitrile affording colorless crystals of **5** suitable for X-ray analysis. MALDI (*m/z*): 791 ($M^{\bullet+}$). ^{1}H NMR (C_6D_6, 25°C): δ 7.51, 6.67 (d, 2.5 Hz, 6H, aromatics); 3.49 (s, br., 6H, C*H*$_2$) (s); 1.57 (s), 1.35 (s, 54H, C*Me*$_3$). ^{13}C NMR (C_6D_6, 25°C): δ 156.0 (Sb-O-*C*); 140.6, 139.6, 125.3, 125.0, 122.1 (aromatics); 61.1 (*C*H_2); 35.2, 34.3 (*C*Me_3); 32.0, 30.3 (C*Me*$_3$). Crystal data for **5** ($C_{45}H_{66}NO_3Sb$): M = 790.74, 0.25 x 0.17 x 0.15 mm^3, triclinic, space group P-1 (No. 2), a = 10.0320(1), b = 12.5450(1), c = 17.9630(2) Å, α = 88.1860(1), β = 83.7930(1), γ = 73.0340(1)°, V = 2149.61(4) Å^3, Z = 2, D_c = 1.222 g/cm^3, F_{000} = 836, MoKα radiation, λ = 0.71073 Å, T = 150(2)K, $2\theta_{max}$ = 60.1°, 53041 reflections collected, 12476 unique (R_{int} = 0.0288). Final GooF = 1.040, R1 = 0.0238, wR2 = 0.0576, R indices based on 11790 reflections with I >2sigma(I) (refinement on F^2), 496 parameters, 0 restraints, μ = 0.679 mm^{-1}. Absorption correction applied. CCDC 608946.

DETAILS OF DFT CALCULATIONS

Molecular and electronic structure calculations on C_6H_6, **6**, [**6**·C_6H_6], and [(**6**)$_2$·C_6H_6] under D_{6h}, C_3, C_3, and D_3 symmetries, respectively, were performed using density functional theory with the Gaussian 03 program.[9] Geometry optimizations were performed using the B3LYP functional[10] along with the 6-31G* basis set for C, N, O and H[11] and the SDD energy-consistent pseudopotential basis set for Bi.[12] Electronic structures and single-point energies were determined for the optimised geometries at the B3LYP level along with the 6-31++G** basis set for C, N, O and H and the SDD energy-consistent pseudopotential basis set for Bi.

[1] *Caution!* Sodium is pyrophoric and should be disposed of with extreme care. For a convenient procedure on the safe quenching and disposal of alkali metal waste see Roesky, H. W. *Inorg. Chem.* **2001**, *40*, 6855-6856.

[2] Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

[3] Clegg, W.; Compton, N. A.; Errington, R. J.; Fisher, G. A.; Green, M. E.; Hockless, D. C. R.; Norman, N. C. *Inorg. Chem.* **1991**, *30*, 4680.

[4] Evans, W. J.; Hain, J. H.; Ziller, J. W. *J. Chem. Soc., Chem. Commun.* **1989**, 1628.

[5] Kiennemann, A.; Levy, G.; Schué, F.; Taniélian, C.; *J. Organomet. Chem.* **1972**, *35*, 143-148.

[6] Kol, M.; Shamis, M.; Goldberg, I.; Goldschmidt, Z.; Alfri, S.; Hayut-Salant, E. *Inorg. Chem. Commun.* **2001**, *4*, 177.

[7] Ugrinova, V.; Ellis, G. A.; Brown, S. N. *Chem. Commun.* **2004**, 468.

[8] Sheldrick, SHELXL-97, University of Gottingen, Germany, 1997.

[9] Gaussian 03, Revision B.05, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A. Gaussian, Inc., Wallingford CT, 2004.

[10] Lee, C. T.; Yang, W. T.; Parr, R. G. *Phys. Rev. B,* **1988**, *37*, 785; Stephens, P. J.; Devlin, F. J.;Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.*, **1994**, *98*, 11623. Johnson, B. G.; Gill, P. M. W.; Pople, J. A. *J. Chem. Phys.*, **1993**, *98*, 5612. Becke, A. D. *J. Chem. Phys.*, **1993**, *98*, 5648.

[11] Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory;* John Wiley & Sons, 1986.

[12] Dolg, M.; Kuchle, W.; Stoll, H.; Preuss, H.; Schwerdtfeger, P. *Mol. Phys.*, **1991**, *74*, 1265.