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Investigating the Reactions of $BiCl_3$, a Diiminopyridine Ligand, and Trimethylsilyl Trifluoromethanesulfonate

John R. Tidwell and Caleb D. Martin*

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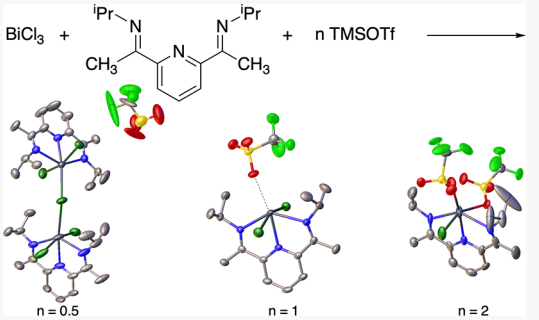
ABSTRACT: The reactions of bismuth(III) chloride, a diiminopyridine ligand, and various stoichiometries of trimethylsilyl trifluoromethanesulfonate (TMSOTf) generated the first bismuth complexes with this ubiquitous ligand. The reaction with 0.5 equivalents of TMSOTf furnished a chloride bridged $Bi_2Cl_5^+$ complex, with each bismuth center complexed by a ligand; 1 equivalent yielded a $BiCl_2^+$ chelated species; and 2 equivalents provided a ligated $BiCl^{2+}$ cation.



INTRODUCTION

Bismuth has a rich chemistry with coordination numbers ranging from 2 to 10 and can be in oxidation states ranging from −3 to +5.[1] Recent studies have demonstrated bismuth complexes with rigid nitrogen-containing pincer ligands to have unusual properties and promote catalytic transformations (e.g., **A** and **B**, Figure 1).[2] Cornella and co-workers have prepared a series of bismuth(I) complexes with an NCN ligand scaffold (**A**) that can catalyze transfer hydrogenation to unsaturated bonds and the deoxygenation of nitrous oxide as well as the hydrodefluorination of fluoroarenes.[2d,g,j,l] Other tridentate chelates, including OCO and OCN, have been reported by the Dostál and Evans groups to stabilize both neutral and cationic bismuth complexes.[2a,3] The NCN scaffold not only stabilizes low oxidation states of bismuth but also affords interesting reactivity, including C−H activation, oxygen bond cleavage, and insertion of small molecules.[4] Chitnis and co-workers prepared a bismuth complex with a tethered triamide ligand (**B**) that, based on reactivity and calculations, exhibits characteristics of both Bi(I) and Bi(III).[2e,f,h,k] Moreover, the bismuth center is ambiphilic with the ability to act as a Lewis acid or a Lewis base. These exemplify how rigid pincer ligands can impart interesting properties and reactivity on bismuth centers.

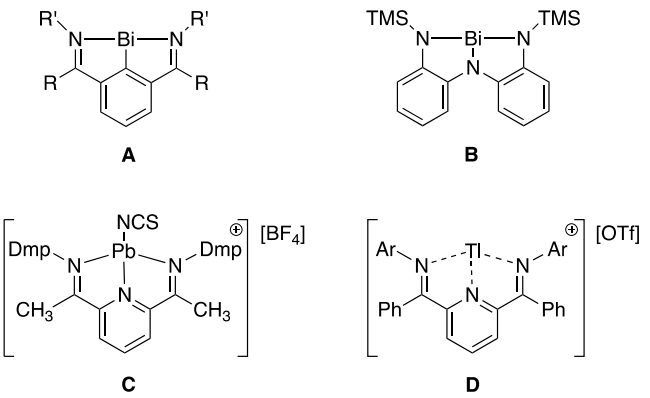


Figure 1. Bismuth pincer complexes with NCN (**A**) and NNN (**B**) ligands. Known row 6 p-block diiminopyridine complexes **C** and **D** (Dmp = 2,6-$(CH_3)_2C_6H_3$, Ar = 2,5-$tBu_2C_6H_3$).

Diiminopyridine (DIMPY) ligands offer a rigid pincer framework capable of stabilizing reactive metal centers competent in activating bonds that have been applied in the catalytic polymerization of olefins as well as promoting cycloaddition and borylation reactions.[5] Almost all of the heavy group 13−16 elements have been reported, but for row 6, complexes exist only for Tl and Pb.[6] The cationic lead complex (**C**) bears an isothiocyanate ligand with an unusual geometry at lead as the ligand retains planarity with the isothiocyanate perpendicular to the PbN_3 plane rationalized by the Pb(II) center having a stereochemically active lone pair.[6a] The thallium(I) complex (**D**) could be crystallized as a dimer through Tl-arene interactions with the ligand of another molecule or could be co-crystallized with benzene or toluene to form Tl-η^6 arene complexes, with the arene bridging two

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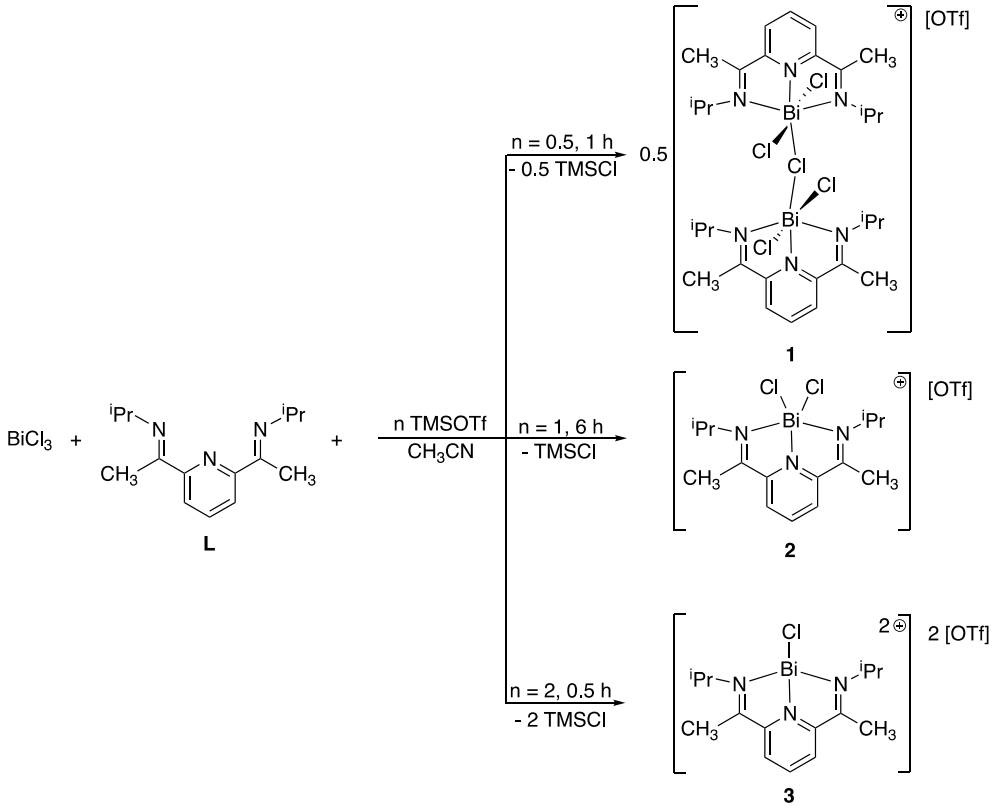
Scheme 1. Reactions of L with $BiCl_3$ and TMSOTf in Varying Stoichiometries; the Products Are Depicted as Their Structures in Solution as 2 and 3 Exhibit Weak Interactions between the Triflate(s) and Bismuth in the Solid State



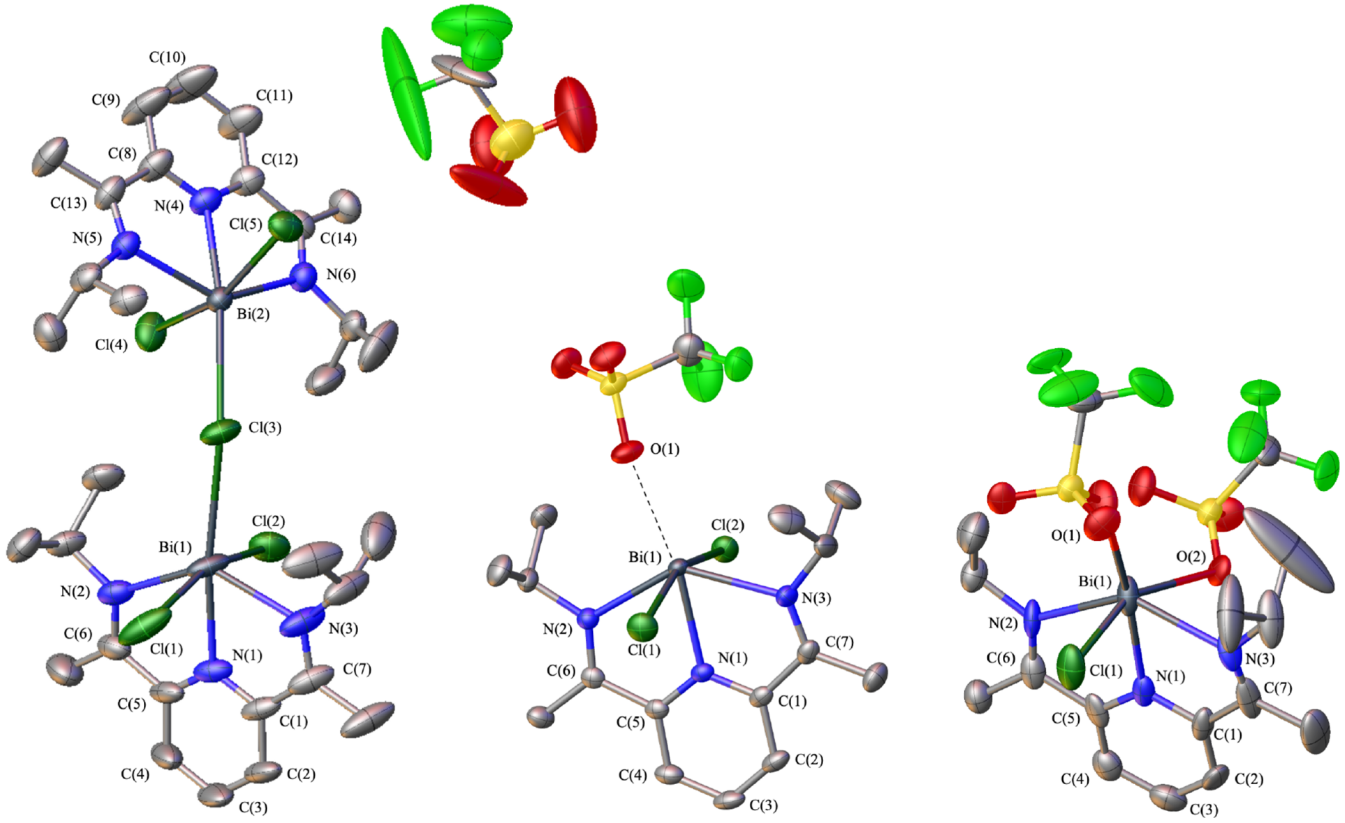


Figure 2. Solid-state structures of **1**−**3** (left to right). Thermal ellipsoids are drawn at the 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity. In species with disorder, only the major component is shown.

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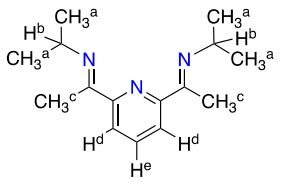
thallium centers.[6m] Thallium complex **D** has notably long Tl−N bonds that are classified as weak interactions and the ligand binds lead more tightly in **C** [Tl−N range = 2.739(2)−2.795(2) c.f. Pb−N range = 2.456(6)−2.577(6) Å]. These unusual structures motivated us to target bismuth diiminopyridine complexes.

RESULTS AND DISCUSSION

The reactions of trimethylsilyl trifluoromethanesulfonate (TMSOTf) and bismuth(III) trichloride with a diiminopyridine ligand featuring isopropyl groups on nitrogen and methyl substituents on the α-carbon (**L**) in 0.5:1:1, 1:1:1, and 2:1:1 stoichiometries in CD_3CN at room temperature were monitored by in situ ^1H and ^{19}F NMR spectroscopy (Scheme 1). Full conversion to single products was achieved at 1 h (0.5 equivalents of TMSOTf, **1**), 6 h (1 equivalent of TMSOTf, **2**), and 0.5 h (2 equivalents of TMSOTf, **3**). Upon conducting reactions on scale to isolate materials, the trimethylsilyl chloride (TMSCl) byproduct and solvent were removed in vacuo and all three reaction products were isolated in quantitative yield as yellow (**1**), pistachio green (**2**), and off-white (**3**) solids. Single-crystal X-ray diffraction studies on the grown crystals revealed their identities as κ^3-*N*,*N*′,*N*″-chelated bismuth(III) diimino-pyridine cations, with the reaction of 0.5 equivalents furnishing a chloride bridged $Bi_2Cl_5^+$ complex, with each bismuth center complexed by **L** (**1**, Figure 2); 1 equivalent yielding a $BiCl_2^+$ chelated complex (**2**), and 2 equivalents providing a $BiCl^{2+}$ complex (**3**).[7]

The ^1H NMR spectra of **1**−**3** revealed protons on the complexed ligand shifted downfield from **L** (Table 1). The largest shifts were observed for the methine septets from the N-bound isopropyl groups to the products (**1**: 5.22, **2**: 5.37, and **3**: 5.44 ppm c.f. **L**: 3.96 ppm) with all other peaks shifted between 0.49 and 0.95 ppm from **L**. The magnitude of the shifts of the methine and pyridine protons are directly correlated to the charge of the complex (**3** > **2** > **1**). The ^{19}F NMR spectra of all three products display resonances at −79.2 ppm, which correspond to ionic triflate in solution (−78.3 to −79.2 ppm ionic triflate versus covalent triflate CH_3OTf = −76.3 ppm).[6t,8] The supported ionic nature in the solution is consistent with other known bismuth, antimony, and arsenic ionic complexes, with triflates bearing similar ^{19}F NMR shifts (−78.3 to −79.1 ppm) and weak interactions in the solid state attributed to electrostatic interactions.[9] Attempts to access a tris(triflato) complex by adding 3 equivalents resulted in the formation of **3** by ^1H NMR spectroscopy with unreacted TMSOTf (Figures S26−S28). Reaction of **3** with silver trifluoromethanesulfonate resulted in no reaction by ^1H NMR spectroscopy (Figures S29−S31). Stoichiometric amounts of acetonitrile were added to CD_2Cl_2 solutions of **1**−**3**. By ^1H NMR spectroscopy, no change in the resonance from free acetonitrile was observed (resonance at 1.97 ppm).[10] The ^{19}F NMR spectra display single peaks corresponding to the triflate(s) for **1**−**3** ranging from −79.3 to −79.5 ppm, which lie in the reported range of ionic triflates (Figures S32−S40), disproving the possibility of acetonitrile displacing triflate in CD_3CN and indicating that the triflates are not bound to bismuth.

Table 1. ^1H and ^{19}F NMR Resonances for L and 1−3



	L	1	2	3
H^a	1.18	1.69	1.67	1.67
H^b	3.96	5.22	5.37	5.44
H^c	2.39	2.71	2.73	2.73
H^d	7.77	8.60	8.69	8.72
H^e	8.05	8.86	8.96	9.00
F (triflate)		−79.2	−79.2	−79.2

Examining the solid-state structures of **1**−**3**, each of the bismuth centers are in octahedral environments with meridional coordination of the tridentate ligand (Figure 2, see Table 2 for representative bond lengths). In **1**, the octahedron is completed with two terminal chlorides trans to each other and the bridging chlorine trans to the pyridine nitrogen, with no interaction between bismuth and the triflate counter anion. This chloride bridged feature is similar to that of other pnictogen analogues with NCN- and OCO-based pincer ligands.[11] In **2**, the two terminal chlorides are trans to each other, with a weak interaction to a triflate oxygen [**2**: Bi−O 2.906(3) Å c.f. covalent Bi−O 2.14 Å and sum of van der Waals radii = 3.59 Å][12] occupying the position trans to the pyridine nitrogen. In the solid-state structure of **3**, a triflate bridges to another bismuth atom that forms a coordination polymer (Figures S47−S48).[11b,13] In **3**, one of the chlorides in **2** is replaced by a triflate, with the Bi−O contacts being closer but still far beyond a covalent interaction, with the Bi−O bond of the triflate trans to the strongly donating pyridine being slightly longer [**3**: Bi−O 2.643(19) and 2.764(34) Å]. These weak interactions are not detected in CD_3CN solution as the ^{19}F NMR resonances are consistent with the ionic triflate. In all three complexes, the "lone pair" is not stereochemically active, which is attributed to the inert s-pair effect.[14] The Bi−Cl bond lengths of the trans chlorides in **1** and **2** [2.678(3) and 2.583(2) Å] are virtually identical, while the bridging chloride bonds in **1** are the longest [3.109(2) Å] and the Bi−Cl bond in **3** is the shortest (2.471(4) Å].

Table 2. Salient Bond Lengths (in Å) for 1−3[a]

	1	2	3
Bi(1)−N(1)	2.339(6)	2.319(2)	2.290(13)
Bi(1)−N(2)	2.453(8)	2.423(3)	2.412(13)
Bi(1)−N(3)	2.446(8)	2.399(3)	2.428(11)
Bi(1)−Cl(1)	2.678(3)	2.5885(8)	2.471(4)
Bi(1)−Cl(2)	2.583(2)	2.6548(8)	
Bi(1)−Cl(3)	3.109(2)		
Bi(1)−O(1)		2.906(3)	2.643(19)
Bi(1)−O(2)			2.764(34)

[a]For **2** and **3**, the bond lengths are similar for both bismuth centers, and accordingly, only values for one are listed

The Lewis acidity of the bismuth cations was evaluated by the Gutmann−Beckett method, with triethylphosphine oxide based on the equation: acceptor number = 2.21 × (δ_{SAMPLE} − 41.0 ppm).[15] The acceptor number values for **1**−**3** obtained in CD_3CN are 27, 27, and 45, respectively, and acceptor numbers in CD_2Cl_2 are 29, 32, and 25. In comparison to the literature values of the bismuth trihalides in CD_2Cl_2, they are stronger Lewis acids than BiI_3 (AN = 22), comparable to $BiBr_3$ (AN = 30), and weaker than $BiCl_3$ (AN = 49).[16]

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CONCLUSIONS

Treatment of a diiminopyridine ligand with bismuth(III) chloride and trimethylsilyl trifluoromethanesulfonate yielded the first examples of bismuth diiminopyridine complexes. The reaction stoichiometry of TMSOTf dictated the product with a chlorine bridged Bi_2Cl_5 cation obtained with 0.5 equivalents, a ligated $BiCl_2$ cation from 1 equivalent, and a ligated BiCl dication from 1 equivalent. The X-ray diffraction structures revealed octahedral geometries at bismuth for all species with stereochemically inactive lone pairs.

Experimental Section. General considerations: all manipulations were performed under an inert atmosphere in a nitrogen-filled MBraun Unilab glovebox or using standard Schlenk techniques. Acetonitrile-d^3 for NMR spectroscopy was purchased from Cambridge Isotope Laboratories, Inc., dried by stirring for 5 days over CaH_2, distilled, and stored over 4 Å molecular sieves. Dichloromethane-d^2 for NMR spectroscopy was purchased from Aldrich Chemical and used directly from ampules. All other solvents were purchased from commercial sources as anhydrous grade, dried further using a JC Meyer Solvent System with dual columns packed with solvent-appropriate drying agents, and stored over 3 or 4 Å molecular sieves. Isopropylamine (Aldrich Chemical, 99.5%), 2,6-diacetylpyridine (Chem-Impex International, 99.83%), *p*-toluenesulfonic acid monohydrate (Alfa Aesar, 97%), bismuth trichloride (Strem Chemicals, 99.9%), trimethylsilyl trifluoromethanesulfonate (Alfa Aesar, 99%), silver trifluoromethanesulfonate (Alfa Aesar, 98%), and triethylphosphine oxide (Alfa Aesar, 99.3%) were purchased from the indicated commercial sources and were used as received. Multinuclear NMR spectra (^{1}H, ^{13}C{^{1}H}, ^{19}F) were recorded on a Bruker AVANCE III HD 400 MHz or 600 MHz instrument. ^{19}F NMR spectra were referenced to an internal standard, fluorobenzene. High-resolution mass spectra (HRMS) were obtained in the Baylor University Mass Spectrometry Center on a Thermo Scientific LTQ Orbitrap Discovery spectrometer using + ESI. Melting points were measured with a Thomas Hoover Uni-melt capillary melting point apparatus and are uncorrected. FTIR spectra were recorded on a Bruker Alpha ATR FTIR spectrometer on solid samples. Single-crystal X-ray diffraction data were collected on a Bruker Apex III-CCD detector using Mo-Kα radiation (λ = 0.71073 Å). Crystals were selected under paratone oil, mounted on MiTeGen micromounts, and immediately placed in a cold stream of N_2. Structures were solved and refined using SHELXTL,[17] and figures were produced using OLEX2.[18] Elemental analysis samples were sent to Atlantic Microlab and were evaluated with a Carlo Erba 1108 Analyzer. The purity of new complexes was established by multinuclear NMR (^{1}H, ^{13}C{^{1}H}, and ^{19}F); the spectra are available in the Supporting Information.

L: This compound was synthesized by the literature procedure reported by Chirik and co-workers;[19] the NMR data is reported in acetonitrile to enable comparison with **1**−**3**. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.05 (d, J = 7.8 Hz, 2H), 7.77 (t, J = 8.0 Hz, 1H), 3.96 (sept, J = 6.2 Hz, 2H), 2.39 (s, 6H), 1.18 (d, J = 6.0 Hz, 12H). ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ (ppm) 164.14, 157.59, 137.46, 121.56, 52.28, 23.78, 13.36.

1: Bismuth trichloride (136.8 mg, 0.4338 mmol) was dissolved in 2 mL acetonitrile, and neat trimethylsilyl trifluoromethanesulfonate (39.5 μL, 0.2183 mmol) was added. An acetonitrile solution (4 mL) of **L** (106.9 mg, 0.4357 mmol) was added to the bismuth trichloride/trimethylsilyl trifluoromethanesulfonate mixture dropwise at room temperature and stirred for 1 h. All volatiles were removed in vacuo, yielding a yellow solid. Yield: quantitative (267.9 mg). Single crystals for X-ray diffraction studies were grown via vapor diffusion of a dichloromethane solution of **1** into toluene. d.p. 130−135 °C. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.86 (t, J = 8.0 Hz, 1H), 8.60 (d, J = 8.0 Hz, 2H), 5.22 (sept, J = 6.4 Hz, 2H), 2.71 (s, 6H), 1.69 (d, J = 6.4 Hz, 12H); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ (ppm) 168.94, 155.78, 146.24, 132.02 56.43, 23.54, 18.72; ^{19}F NMR (376 MHz, CD_3CN): δ (ppm) −79.2; FT-IR [cm^{-1} (ranked intensity)]: 1683(9), 1584(12), 1457(8), 1373(13), 1256(2), 1209(10), 1156(5), 1066(15), 1026(3), 954(14), 814(4), 731(11), 637(1), 572(7), 517(6); High-resolution mass spectrometry electrospray ionization (HRMS-ESI) for $C_{30}H_{46}N_6Bi_2Cl_5^+$ [M]$^+$ calcd 1083.1834 m/z; found, 1083.1794 m/z.

2: Bismuth trichloride (264.1 mg, 1.076 mmol) was dissolved in 6 mL acetonitrile, and neat trimethylsilyl trifluoromethanesulfonate (194.5 μL, 1.075 mmol) was added. The mixture was added dropwise to an acetonitrile solution (6 mL) of **L** (341.0 mg, 1.081 mmol) at room temperature and stirred for 6 h. All volatiles were removed in vacuo, yielding a pistachio green solid. Yield: quantitative (724.8 mg). Single crystals for X-ray diffraction studies were grown via slow evaporation of an acetonitrile solution of **2**. d.p. 116−120 °C. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 8.96 (t, J = 8.0 Hz, 1H), 8.69 (d, J = 8.0 Hz, 2H), 5.37 (sept, J = 6.4 Hz, 2H), 2.73 (s, 6H), 1.67 (d, J = 6.4 Hz, 12H); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ (ppm) 169.30, 155.37, 146.98, 132.59, 56.41, 23.27, 18.79; ^{19}F NMR (376 MHz, CD_3CN): δ (ppm) −79.2; FT-IR [cm^{-1} (ranked intensity)]: 2967 (11), 1642 (13), 1587 (9), 1462 (10), 1376(12), 1257 (15), 1209 (3), 1158 (6), 1021 (1), 812(4), 758 (14), 733 (8), 634 (2), 572 (7), 515 (5); high-resolution mass spectrometry electrospray ionization (HRMS-ESI) for $C_{15}H_{23}N_3BiCl_2^+$ [M]$^+$ calcd 524.1073 m/z; found, 524.1078 m/z; Anal. calcd (found) (%): C 28.50 (28.40); H 3.44 (3.54); N 6.23 (6.14).

3: Bismuth trichloride (295.1 mg, 1.203 mmol) was dissolved in 14 mL acetonitrile, and neat trimethylsilyl trifluoromethanesulfonate (435.5 μL, 2.407 mmol) was added. The mixture was then added dropwise to an acetonitrile solution (2 mL) of **L** (379.9 mg, 1.205 mmol) at room temperature and stirred for 0.5 h. All volatiles were removed in vacuo, yielding an off-white solid. Yield: quantitative (947.6 mg). Single crystals for X-ray diffraction studies were grown via vapor diffusion of a dichloromethane solution of **3** into benzene. d.p. 98−101 °C. ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) 9.00 (t, J = 8.0 Hz, 1H), 8.72 (d, J = 8.0 Hz, 2H), 5.44 (sept, J = 6.4 Hz, 2H), 2.73 (s, 6H), 1.67 (d, J = 6.4 Hz, 12H); ^{13}C{^{1}H} NMR (101 MHz, CD_3CN): δ (ppm) 170.97, 156.62, 147.90, 132.63. 56.28, 22.91, 18.96; ^{19}F NMR (376 MHz, CD_3CN): δ (ppm) −79.2; FT-IR [cm^{-1} (ranked intensity)]: 2981 (13), 1643 (12), 1589 (9), 1463 (10), 1376 (11), 1282 (15), 1205 (3), 1157 (6), 1014 (2), 813 (5), 759 (14), 733 (8), 633 (1), 572 (7), 515 (4); High-resolution mass spectrometry electrospray ionization (HRMS-ESI) for $C_{16}H_{23}N_3BiClO_3S_1F_3^+$ [M]$^+$ calcd 638.0905 m/z; found, 638.0911 m/z.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.2c00093.

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Experimental details, NMR spectra, Gutmann−Beckett studies, FTIR spectra, and crystallographic information (PDF)

Accession Codes

CCDC 2152623−2152625 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

Caleb D. Martin − *Department of Chemistry and Biochemistry, Baylor University, Waco, Texas 76798, United States;* orcid.org/0000-0001-9681-0160; Email: caleb_d_martin@baylor.edu

Author

John R. Tidwell − *Department of Chemistry and Biochemistry, Baylor University, Waco, Texas 76798, United States;* orcid.org/0000-0001-9216-7913

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.2c00093

Notes

The authors declare no competing financial interest.

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