Mononuclear Complexes of a Tridentate Redox-Active Ligand with Sulfonamido Groups: Structure, Properties and Reactivity

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General Methods. The syntheses of metal complexes were completed under a nitrogen atmosphere in a VAC drybox. Solvents were sparged with argon and dried over columns containing Q-5 and molecular sieves. All reagents were purchased from commercial suppliers and used as received unless otherwise noted. Potassium hydride as a 30% suspension in mineral oil was filtered and washed five times each with Et₂O and pentane and dried under vacuum. Ferrocenium tetrafluoroborate (FcBF₄) was recrystallized before use. The ligand precursor HN(*o*-PhNH₂)₂,¹ the Ga starting material NMe₄[GaCl₄],² and the aryl azides 1-azido-2propylbenzene, 1-azido-2-phenethylbenzene, and 1-azido-4-methoxy-2-phenethylbenzene were prepared according to literature procedures.³

Physical Methods. Electronic absorption spectra were recorded in a 1-cm cuvette on an 8453 Agilent UV-Vis spectrometer equipped with a Unisoku Unispeks cryostat or in a 1 mm cuvette on a Cary 50 UV-Vis spectrometer. Negative-mode electrospray ionization mass spectra were collected using a Micromass MS Technologies LCT Premier mass spectrometer. Mössbauer spectra were recorded with a Janis Research Super-Varitemp dewar. Isomer shifts are reported relative to Fe metal at 298 K. Fourier transform infrared spectra were collected on a Varian 800 Scimitar Series FTIR spectrometer. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX500 spectrometer and referenced to the residual solvent peak. Elemental analyses were performed on a Perkin-Elmer 2400 CHNS analyzer. Product(s) were detected by gaschromatography mass spectrometry (GC-MS) in the Mass Spectrometry Facility at the University of California, Irvine. The GC-MS was a Trace MSplus from Thermo Fisher (San Jose,

CA) with a 30-m-long x 0.25 mm i.d. DB-5 column from Agilent JW Scientific (Santa Clara, CA). The mass spectrometer used electron ionization (70 eV) scanning (1/sec) from m/z = 50-650. An estimate of the product yield was determined using an HP-6890 gas chromatograph with a flame ionization detector (FID) and a 30 m × 0.32 mm (5% phenyl)-methylpolysiloxane (0.25 μ m coating) capillary column (J&W Scientific DB-5) and helium as the carrier gas. DLS measurements were recorded on a Malvern Zetasizer Nano DLS particle size analyzer and data were analyzed by Zetasizer software 7.11.

Electrochemical Measurements. Cyclic voltammetric experiments were conducted using a CHI600C electrochemical analyzer under an N₂ atmosphere with 0.1 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte. A 2.0-mm glassy carbon electrode was used as the working electrode with a silver wire reference electrode and a platinum wire counter electrode. A cobaltocenium/cobaltocene couple (-1.3 V vs. $[FeCp_2]^{1/0}$)⁴ was used as an internal reference to monitor the reference electrode (Ag⁺/Ag).

X-ray Crystallographic Methods. A Bruker SMART or Bruker Kappa APEX II CCD diffractometer was used to collect data. The APEX2⁵ program package was used to determine the unit-cell parameters and for data collection. The raw frame data were processed using SAINT⁶ and SADABS⁷ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁸ program. The analytical scattering factors⁹ for neutral atoms were used throughout the analysis. Hydrogen atoms were included using a riding model.

For **[Fe(ibaps)(DMA)**₂**] (DMA = dimethylacetamide).** The structure was solved by dual space methods and refined on F² by full-matrix least-squares techniques. There were 1.5 molecules of hexane solvent present per formula unit. One solvent molecule was located about

an inversion center. Several atoms, in particular those of the bound DMA molecules, were disordered and included using multiple components with partial site occupancy factors.

For **[Ga(ibaps)(DMA)**₂**].** The structure was solved by dual space methods and refined on F² by full-matrix least-squares techniques. Several atoms were disordered, in particular those of one of the bound DMA molecules and some of the isopropyl groups of the [ibaps]³⁻ ligand, and included using multiple components with partial site occupancy factors. Several high residuals were present in the final difference-Fourier map. It was not possible to determine the nature of the residuals, although it was probable that a toluene solvent molecule was present. The SQUEEZE¹⁰ routine in the PLATON¹¹ program package was used to account for the electrons in the solvent-accessible voids.

For **1-Co.** The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. Several atoms were disordered, in particular the isopropyl groups of the [ibaps]³⁻ ligand and the ethyl groups of the tetraehtylammonium ion, and included using multiple components with partial site occupancy factors. It was necessary to restrain the distances within the tetraethylammonium ion. There was one half-molecule of diethylether solvent present. The solvent was located about an inversion center and was disordered.

For **1**. The structure was solved by dual space methods and refined on F² by full-matrix least-squares techniques. Several atoms were disordered, in particular the atoms of the triisopropylphenyl groups of the [ibaps]³⁻ ligand and the ethyl groups of the tetraehtylammonium ion, and included using multiple components with partial site occupancy factors. Several high residuals were present in the final difference-Fourier map. It was not possible to determine the nature of the residuals, although it was probable that diethylether

solvent was present. The SQUEEZE¹⁰ routine in the PLATON¹¹ program package was used to account for the electrons in the solvent-accessible voids.

For **2-Co.** The structure was solved by direct methods and refined on F² by full-matrix least-squares techniques. There were two molecules of the formula unit and two molecules of tetrahydrofuran solvent present. Carbon atom C(86) of one of the isopropyl groups of the [ibaps]³-ligand was disordered and included using multiple components with partial site occupancy factors.

For **2**. Diffraction pointed to the crystal being cracked/twinned due to desolvation, so PLATON TWINROTMAT was used to deal with some minor, around 4%, contribution from 3 domains. Because of solvent disorder that could not be model, Platon SQUEEZE^{10,11} was used to remove the electron density from the lattice due to this solvent contribution. Solvent appeared to be a pentane molecule but was too diffuse to model. Two voids were found with approximately 59 electrons in one and 41 electrons in the other. One isopropyl group of the [ibaps]³⁻ ligand was modeled as a two-component disorder and the thermals parameters were restrained using RIGU to deal with thermal parameter issues.

Ligand Synthesis.

N,N'-(azanediylbis(2,1-phenylene))bis(2,4,6-triisopropylbenzenesulfonamide) (H₃ibaps). The triamine (1.28 g, 6.43 mmol) and pyridine (1.52 g, 19.2 mmol) were dissolved in 50 mL of MeCN in the glove box. Tri-isopropylbenzene sulfonyl chloride (4.08 g, 13.5 mmol) was dissolved in 20 mL of Et₂O and added dropwise to the acetonitrile solution over the course of ten minutes, causing a change from clear orange to heterogeneous dark orange to green. The reaction flask was sealed with a rubber septum, brought out of the glovebox, and fitted with a reflux condensor under a flow of N₂. The reaction was refluxed overnight under N₂ to give a dark red

solution. After checking the reaction for completion by ESI-MS, the mixture was concentrated to dryness under vacuum, redissolved in DCM, and washed with 1M HCl until the aqueous layer was no longer colored. The organic layer was further washed with H₂O and brine, dried over MgSO₄, filtered, and concentrated under vacuum to a foam. The ligand precursor was recrystallized from hot iso-octane as light pink crystals in 64% yield (3.0 g). ¹H NMR (500 MHz, d₆-DMSO, ppm): 9.24, (s, 2H, NH), 7.19 (s, 1H, NH), 7.09 (s, 4H), 6.94 (t, 2H), 6.84 (d, 2H), 6.74 (t, 2H), 6.59 (d, 2H), 3.86 (m, 4H), 2.85 (m, 2H), 1.15 (d, 12H), 1.00 (d, 24H). ¹³C NMR (125 MHz, d₆-DMSO, ppm): 152.0, 150.0, 140.6, 133.4, 128.2, 127.3, 126.0, 123.4, 121.0, 118.9, 33.2, 29.5, 24.6, 23.4. FTIR (Nujol, cm-1, selected bands): 3370 (NH), 3276 (NH), 3213 (NH), 1597 (m), 1314 (s), 1168 (s), 1040 (m), 881 (m), 759 (m). HRMS (ES+): Exact mass calcd (found) for [M + Na]: 754.3688 (754.3680).

Complex Syntheses.

NEt₄[Fe(ibaps)bpy]. A solution of H₃ibaps (0.10 g, 0.14 mmol) in 3 mL of DMA was treated with three equiv of solid KH (16 mg, 0.41 mmol). The reaction was stirred until gas evolution ceased, and then FeBr₂ was added. After 1 h, 2,2'-bipyridine and NEt₄Br were added to the reaction, which was stirred for an additional two hours before removing the solvent under vacuum. The crude product was redissolved in 8 mL of THF and filtered through a medium porosity frit to remove three equivalents (49 mg, 0.40 mmol) of insoluble KBr. The product was crystallized from Et₂O vapor diffusion into the THF filtrate to give 0.110 g (73%) of the product as dark green needle crystals. Elemental analysis calcd. (found) for NEt₄[Fe(ibaps)bpy] (C₆₀H₈₂N₆O₄S₂Fe): C, 67.27 (67.29); H, 7.72 (8.10); N, 7.84 (7.85) %. FTIR (Nujol, cm⁻¹, selected bands): 1564 (w), 1360 (m), 1231 (s), 1119 (s), 947 (m), 725 (m). λ_{max} , nm (THF, ε , M⁻¹cm⁻¹): 438 (sh).

NEt₄[Co(ibaps)bpy] · **Et₂O**. This complex was prepared according to the same procedure as that for NEt₄[Fe(ibaps)bpy] with H₃ibaps (0.10 g, 0.14 mmol), KH (16 mg, 0.41 mmol), CoBr₂ (30 mg, 0.14 mmol), 2,2'-bipyridine (21 mg, 0.14 mmol), and NEt₄Br (29 mg, 0.14 mmol) in 3 mL of DMA. The crude product was redissolved in 6 mL of MeCN and filtered through a medium porosity frit to remove three equivalents (49 mg, 0.40 mmol) of insoluble KBr. The product was crystallized from Et₂O vapor diffusion into the MeCN filtrate to give 0.130 g (86%) of the product as green needle crystals. Elemental analysis calcd. (found) for NEt₄[Co(ibaps)bpy] (C₆₄H₉₂N₆O₅S₂Co): C, 66.93 (66.53); H, 8.07 (7.97); N, 7.32 (7.72) %. FTIR (Nujol, cm⁻¹, selected bands): 1597 (m), 1562 (m), 1228 (s), 1118 (s), 1060 (m), 1037 (m), 944 (s), 791 (m), 726 (s).

[Fe^{III}(ibaps)(DMA)₂**].** To a vial containing a DMA solution of H₃ibaps (0.300 g, 0.411 mmol, 1 equiv) was added solid KH (0.048 g, 1.2 mmol, 3 equiv), and the reaction was allowed to continue for 1 h, after which bubbling ceased and a yellow solution formed. To this solution of the triply deprotonated ligand was added solid Fe^{III}Br₃ (0.120, 0.411 mmol, 1 equiv), forming a dark purple solution. After 2 h, the DMA solvent was removed under reduced pressure, and the crude solid was triturated with Et₂O. The compound was extracted from the KBr byproduct with 10 mL of Et₂O and filtered through a medium porosity fritted filter. The filtrate was dried and recrystallized via vapor diffusion of pentane (10 mL) into a toluene (2 mL) solution, which formed large purple X-ray quality crystals after 2 d. Yield: 0.20 g (51%). Anal. Calcd. for Fe(ibaps)(DMA)₂, C₅₀H₇₂N₅O₆S₂Fe: C, 62.61; H, 7.57; N, 7.30. Found: C, 62.03; H, 7.51; N, 7.10.

[Ga^{III}(ibaps)(DMA)₂]. To a solution of the triply deprotonated ligand prepared as above was added solid NMe₄[GaCl₄] (0.114 g, 0.411 mmol, 1 equiv), forming a light pink solution. After 3 h, solid KBF₄ (0.051, 0.440, 1 equiv) was added to the reaction mixture, which was stirred for an additional 2 h. The DMA solvent was removed under reduced pressure, and the crude off-white solid was triturated with Et₂O. The compound was extracted from the KCl and NMe₄BF₄

byproducts with 15 mL of Et₂O and filtered through a medium porosity fritted filter. The filtrate was dried and recrystallized via vapor diffusion of pentane (15 mL) into a toluene (3 mL) solution, which formed large colorless X-ray quality crystals after 2 d. Yield: 0.17 g (43%). Anal. Calcd. for Ga(ibaps)(DMA)₂•0.5tol, $C_{53.5}H_{76}N_5O_6S_2Ga$: C, 63.06; H, 7.52; N, 6.87. Found: C, 63.09; H, 7.66; N, 6.47. ¹H NMR (500 MHz, CDCl₃, ppm): 7.61 (d, J = 7.75 Hz, 2H), 7.08 (s, 4H), 6.74–6.70 (m, 4H), 6.41 (t, J = 7.45 Hz, 2H), 4.61 (sep, J = 6.80 Hz, 4H), 3.23 (br s, 6H), 3.17 (br s, 6H), 2.85 (sep, J = 6.90 Hz, 2H), 2.26 (br s, 6H), 1.22 (d, J = 6.9 Hz, 12H) 1.14 (d, 6.80 Hz, 24H).

[Fe(ibaps)bpy]. *Method A.* To a THF solution of [NEt₄][Fe(ibaps)bpy] (0.10 g, 0.093 mmol, 1 equiv) was added an MeCN solution of FcBF₄ (0.025 g, 0.093 mmol, 1 equiv), and the reaction was stirred at room temperature for 2 h. The volatiles were removed under reduced pressure, and the crude solid was washed with pentane. [Fe(ibaps)bpy] was extracted using THF, filtered through a medium porosity fritted filter, and recrystallized via diffusion of pentane into the THF filtrate. Yield: 0.056 g (64%). *Method B.* To a toluene solution of [Fe(ibaps)(DMA)₂] (0.096, 0.10 mmol, 1 equiv) was added a toluene solution of 2,2'-bipyridine (0.016 g, 0.10 mmol, 1 equiv), and the solution was allowed to sit at room temperature for 2 h. The microcrystalline solid that precipitated was collected on a medium porosity fritted filter and dried under reduced pressure. Yield: 0.086 g (91%). Anal. Calcd. for Fe(ibaps)bpy•DMA, C₅₆H₇₁N₆O₅S₂Fe: C, 65.42; H, 6.96; N, 8.17. Found: C, 64.93; H, 6.91; N, 7.82. λmax, nm (THF, ε, M⁻¹cm⁻¹): 378 (9676), 415 (sh), 550 (sh), 640 (5646), 1025 (4082).

[Ga(ibaps)bpy]. This complex was prepared according to *Method B* for Fe(ibaps)bpy but with [Ga(ibaps)(DMA)₂]. Yield: 0.073 g (77%). Anal. Calcd. for Ga(ibaps)bpy •DMA, C₅₆H₇₁N₆O₅S₂Ga: C, 64.55; H, 6.87; N, 8.06. Found: C, 64.82; H, 6.84; N, 7.86. ¹H NMR (500 MHz, CDCl₃, ppm): 9.04 (d, J = 5.00 Hz, 2H), 8.29 (d, J = 8.50 Hz, 2H), 7.99 (t, J = 7.50, 2H), 7.64–7.60 (m, 4H), 6.95 (s, 4H), 6.80 (t, J = 8.00 Hz, 2H), 6.76 (d, J = 7.50 Hz, 2H), 6.41 (t, J = 7.50 Hz, 2H), 4.18 (sep, J = 7.00

Hz, 4H), 2.78 (sep, J = 7.00 Hz, 2H), 1.16 (d, J = 7.00 Hz, 12H), 0.94 (d, J = 7.00 Hz, 24H). ¹³C NMR (125.8 MHz, 298K, CDCl₃, ppm): 151.1, 149.6, 148.6, 147.4, 142.4, 138.8, 136.5, 134.6, 126.5, 123.4, 122.0, 120.6, 117.4, 117.1, 112.7, 34.0, 28.9, 24.7, 23.7.

[**Co(ibaps)bpy].** This complex was prepared according to *Method A* for [Fe(ibaps)bpy] but with [NEt₄][Co(ibaps)bpy]. Yield: 0.052 g (60%). Anal. Calcd. for Co(ibaps)(bpy)•0.5THF, C₅₄H₆₆N₅O_{4.5}S₂Co: C, 66.17; H, 6.79; N, 7.14. Found: C, 65.64; H, 6.73; N, 6.94.

[Fe(ibaps)bpy]BF₄. To a THF solution of NEt₄[Fe(ibaps)bpy] (0.30 g, 0.279 mmol, 1 equiv) precooled to $-35 \,^{\circ}$ C for 1 h was added an MeCN solution of FcBF₄ that was precooled to $-35 \,^{\circ}$ C for 1h (0.153 g, 0.561, 2 equiv), and the reaction was stirred for 5 min every 15 min over the course of 2 h while the temperature was maintained at $-35 \,^{\circ}$ C. The solution was filtered through a precooled medium porosity fritted filter. The filtrate was layered with Et₂O and allowed to sit at $-35 \,^{\circ}$ C for 4 days, after which X-ray quality crystals precipitated. These crystals were collected and dried. Yield: 0.273 g (95%). λ_{max} , nm (THF, ε , M⁻¹cm⁻¹): = 425 (7340), 550 (6910), 700 (sh), 757 (14,570), 1000 (1070).

Procedure for the C-H Bond Amination of Aryl Azides. To a DMF solution of **1** (0.0102 g, 0.0095 mmol, 0.10 equiv) was added a DMF solution of aryl azide (0.095 mmol, 1 equiv), and the mixture was diluted to 3 mL with DMF. From this stock mixture, 1 mL was removed and added to a pressure tube equipped with a stir bar and molecular sieves. The pressure tube was sealed, heated to 115 °C, and allowed to react for 24 h, after which the reaction mixture was removed from the heat. For GC analysis, the reaction mixture was analyzed directly by diluting an aliquot with DCM. For ¹H NMR analysis, 100 μ L of a 100 mM DCM stock solution of 1,3,5-trimethoxybenzene was added to the reaction as an internal standard before removing the volatiles under reduced pressure. The products were redissolved in ~600 μ L of CDCl₃ and

filtered. The conversions to indoline were determined by comparing the integration of the singlet for the aryl protons of 1,3,5-trimethoxybenzene at 6.09 ppm to that of the triplet resonance of the indoline product at ~5.0 ppm.

For the reaction of **1** with 1-azido-2-phenethylbenzene: the organic products were isolated using preparative TLC methods with 10% ethyl acetate/hexanes as eluent. The spot corresponding to product ($R_f = 0.59$) was scraped off and added to a glass funnel plugged with glass wool and washed with DCM. Volatiles were removed under reduced pressure leading to a 41% isolated yield of indoline product.

For the reaction of **1** with 1-azido-4-methoxy-2-phenethylbenzene: the organic products were isolated using preparative TLC methods with 20% ethyl acetate/hexanes as eluent. The spot corresponding to product ($R_f = 0.49$) was scraped off and added to a glass funnel plugged with glass wool and washed with DCM. Volatiles were removed under reduced pressure leading to a 55% isolated yield of a mixture of indoline and indole products, which could not be further resolved.

Sample Preparation

For Titration Experiments of 1 with [FeCp₂]BF₄. A 10 mM stock solution of 57-Fe enriched 1 was prepared in THF and 1 mL was added to each of 5 vials and cooled to -35 °C. A 200 mM stock solution of [FeCp₂]BF₄ was prepared in MeCN and cooled to -35 °C. To each vial containing 1 mL of the 10 mM stock solution of 57-Fe enriched 1 was added varying amounts of the [FeCp₂]BF₄ stock solution (0 µL for 0 equiv; 25 µL for 0.5 equiv; 50 µL for 1 equiv; 75 µL for 1.5 equiv, 100 µL for 2 equiv) and cold MeCN (100 µL for 0 equiv; 75 µL for 0.5 equiv; 50 µL for 0.5 equiv; 50 µL for 1 equiv; 25 µL for 1.5 equiv; 0 µL for 2 equiv) and the vials were allowed to sit at -35 °C for 2 h. Each were filtered while cold into precooled vials. For Mössbauer, 500 µL of each sample was

diluted with 500 μ L of precooled Et₂O and added to a solution Mössbauer cup and frozen in liquid nitrogen. For EPR, 100 μ L of each sample was diluted with precooled mixtures of 400 μ L THF/500 μ L of Et₂O. ~300 μ L of each diluted sample was added to an EPR tube and frozen in liquid nitrogen.

For solid-state Mössbauer Studies. A powder of the compound to be analyzed was added to a solid-state Mössbauer cup such that the mass of naturally-abundant ⁵⁷Fe (2.119%) amounted to \sim 2 mg. The sample was either capped with a screw-on lid or covered with \sim 3 drops of Nujol to create a Nujol mull and frozen in liquid N₂ for transportation.

For Dynamic Light Scattering (DLS) Experiments. In a drybox (Ar), (NEt₄)[Fe(II)ibaps(bpy)] (3.4 mg, 0.00317 mmol, 0.1 equiv.) and 1 mL of dry DMF were added into a pressure tube. 1-azido-2-propylbenzene (1 equiv) was added to the solution, and the tube was sealed and taken out of the box. The reaction was stirred at 115-120 °C for 24 h and then allowed to cool to rt. The tube was opened in a drybox, and the reaction mixture was diluted with an additional 2 mL of DMF and transferred to an air-tight 1 cm quartz cuvette and sealed. The sealed cuvette was taken out of the drybox for measurements.



Figure S1. Thermal ellipsoid diagram of [Fe(ibaps)(DMA)₂]. The ellipsoids are drawn at the 30% probability level, and interstitial solvent molecules and hydrogen atoms are omitted for clarity.



Figure S2. Thermal ellipsoid diagram of [Ga(ibaps)(DMA)₂]. The ellipsoids are drawn at the 30% probability level, and hydrogen atoms are omitted for clarity.



Figure S3. ¹H NMR spectrum of [Ga(ibaps)(DMA)₂] in CDCl₃.



Figure S4. ¹H NMR spectrum of [Ga(ibaps)(bpy)] in CDCl₃.



Figure S5. ¹³C NMR spectrum of [Ga(ibaps)(bpy)] in CDCl₃.



Figure S6. Cyclic voltammogram (small scan window) of 1 at room temperature in THF.



Figure S7. Cyclic voltammogram (small scan window) of 1 at room temperature in DMF.



Figure S8. Cyclic voltammogram (full scan window) of 1 at room temperature in THF.



Figure S9. Cyclic voltammogram (full scan window) of 1 at room temperature in DMF.



Figure S10. Thermal ellipsoid diagram of **1**. The ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.



Figure S11. Overlay of the thermal ellipsoid diagrams of **1** (red) and **1**-Co (blue). The ellipsoids are drawn at the 30% probability level, and interstitial solvents, tetraethylammonium cations, and hydrogen atoms are omitted for clarity.



Figure S12. Thermal ellipsoid diagram of **2**-Co. The ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.



Figure S13. Thermal ellipsoid diagram of **2**. The ellipsoids are drawn at the 50% probability level, and hydrogen atoms are omitted for clarity.



Figure S14. Electronic absorbance spectra of 1-3 recorded at room temperature in THF.



Figure S15. Size distribution by volume of the particles suspended in the reaction solutions was determined by three combined measurements composed of multiple scans, each of which were determined by backscattering method (DMF as solvent, 25 °C). The studies were done on mixtures of 1-azido-2-propylbenzene and **1** in the absence of molecular sieves that were allowed to react for 24 h at 115 °C in DMF. Experiments and measurements were conducted under Ar with no exposure to air. Average size distribution = 5.3 nm ± 2.2 nm (99.7%)

Salt	[Fe(ibaps)(DMA) ₂]•1.5Hexane	[Ga(ibaps)(DMA)2]
CCDC#	1813040	1813043
Empirical Formula	$C_{59}H_{93}FeN_5O_6S_2$	$C_{50}H_{72}GaN_5O_6S_2$
fw	1088.35	972.96
Т (К)	88(2)	133(2)
space group	Р	$P2_{1}/c$
a (Å)	9.4615(9)	16.1329(11)
b (Å)	18.3994(18)	27.6083(19)
<i>c</i> (Å)	18.7650(19)	13.2048(9)
α (deg)	107.6055(12)	90
β (deg)	100.0237(12)	105.6127(8)
γ (deg)	93.8094(12)	90
Z	2	4
V (Å ³)	3041.4(5)	5664.4(7)
δ_{calcd} (Mg/m ³)	1.188	1.141
R1	0.0785	0.0624
wR2	0.2149	0.1769
GOF	1.032	1.051

Table S1. Crystallographic data for [Fe(ibaps)(DMA)₂] and [Ga(ibaps)(DMA)₂]

 $wR2 = \left[\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\right]^{1/2}; R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; Goof = S = \left[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\right]^{1/2} where n is the number of reflections and p is the total number of parameters refined.$

Distances (Å) or angles (deg)	[Fe(ibaps)(DMA) ₂]	[Ga(ibaps)(DMA)2]
M1-N1	1.947(3)	1.881(2)
M1-N2	2.110(3)	2.068(2)
M1-N3	2.101(3)	2.048(3)
M1–O5	1.901(10)	1.899(2)
M1-O6	2.001(4)	1.889(3)
N1-C1	1.384(4)	1.387(4)
C1-C2	1.406(5)	1.395(4)
C2-C3	1.394(5)	1.375(5)
C3-C4	1.383(5)	1.368(5)
C4-C5	1.389(6)	1.391(5)
C5-C6	1.399(5)	1.375(5)
C1-C6	1.430(4)	1.422(4)
N3-C6	1.400(5)	1.417(4)
N1-C7	1.390(4)	1.394(4)
C7-C8	1.406(4)	1.395(4)
C8-C9	1.395(5)	1.390(5)
C9-C10	1.384(5)	1.374(6)
C10-C11	1.394(5)	1.386(5)
C11-C12	1.399(4)	1.388(4)
C7-C12	1.416(4)	1.412(5)
N2-C12	1.413(4)	1.421(4)
O5-M1-N1	125.7(3)	125.17(13)
O5-M1-O6	113.5(3)	100.23(18)
N1-M1-O6	120.79(18)	134.59(18)
O5-M1-N3	98.9(3)	96.39(10)
N1-M1-N3	78.22(11)	82.49(10)
O6-M1-N3	91.13(14)	94.30(12)
O5-M1-N2	94.4(3)	95.03(11)
N1-M1-N2	77.87(11)	81.96(11)
O6-M1-N2	101.72(14)	94.44(13)
N3-M1-N2	156.08(11)	164.16(10)
φ	36.79	28.09
$ au_5$	0.59	0.49

Table S2. Selected bond distances and angles for the [M(ibaps)(DMA)₂] complexes

The dihedral angle, ϕ , is defined as the angle between the two planes formed by the two aryl rings of the [ibaps] backbone.

Salt	1-Co•0.5Et ₂ O	2-Co•THF	1	2
CCDC#	1813044	1813041	1813042	1813039
Empirical	$C_{62}H_{87}CoN_6O_{4.5}S_2$	$C_{56}H_{70}CoN_5O_5S_2$	$C_{60}H_{82}FeN_6O_4S_2$	$C_{52}H_{62}FeN_5O_4S_2$
Formula				
fw	1111.42	1016.22	1071.28	941.03
Т (К)	88(2)	88(2)	88(2)	100.0
space group	$P2_{1}/n$	Р	Р	Р
a (Å)	17.4061(12)	18.006(2)	10.6709(11)	10.175(2)
b (Å)	10.7648(8)	18.271(2)	17.4933(18)	16.218(3)
c (Å)	31.052(2)	18.568(2)	17.8715(18)	16.588(3)
α (deg)	90	110.9719(12)	113.4776(12)	84.402(6)
β (deg)	91.3044(9)	109.6022(13)	98.8759(12)	81.108(7)
γ (deg)	90	95.4770(13)	91.3574(13)	76.300(7)
Ζ	4	4	2	2
V (Å3)	5816.7(7)	5209.7(11)	3009.9(5)	2622.3(10)
δ_{calcd}	1.269	1.296	1.182	1.192
(Mg/m³)				
R1	0.0718	0.0790	0.0895	0.0961
wR2	0.1912	0.2105	0.2428	0.2401
GOF	1.046	1.009	1.036	1.041

 $wR2 = \left[\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\right]^{1/2}; R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|; Goof = S = \left[\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)\right]^{1/2} where n is the number of reflections and p is the total number of parameters refined.$

Distances (Å) or angles (deg)	1-Co	2-Co	1	2
M1-N1	1.970(3)	1.841(3)	2.032(3)	1.992(5)
M1-N2	2.113(3)	1.974(3)	2.166(3)	2.066(6)
M1-N3	2.159(3)	1.989(3)	2.150(3)	2.064(6)
M1-N4	2.132(3)	1.942(3)	2.197(3)	2.157(5)
M1-N5	2.077(3)	1.977(3)	2.143(3)	2.132(5)
N1-C1	1.389(4)	1.393(5)	1.390(5)	1.377(8)
C1-C2	1.404(4)	1.397(5)	1.407(5)	1.393(9)
C2-C3	1.394(5)	1.392(5)	1.387(6)	1.371(10)
C3-C4	1.383(5)	1.376(5)	1.374(7)	1.404(11)
C4-C5	1.395(5)	1.384(5)	1.394(6)	1.357(10)
C5-C6	1.394(5)	1.406(5)	1.388(6)	1.399(10)
C1-C6	1.429(4)	1.430(5)	1.419(6)	1.404(9)
N3-C6	1.426(4)	1.395(5)	1.430(4)	1.408(9)
N1-C7	1.372(4)	1.393(5)	1.373(5)	1.399(8)
C7-C8	1.409(4)	1.404(5)	1.409(5)	1.384(9)
C8-C9	1.395(5)	1.383(5)	1.384(7)	1.386(10)
C9-C10	1.382(5)	1.387(6)	1.382(8)	1.394(11)
C10-C11	1.393(5)	1.392(6)	1.394(6)	1.389(10)
C11-C12	1.398(5)	1.406(5)	1.394(6)	1.367(10)
C7-C12	1.439(4)	1.413(5)	1.433(5)	1.434(10)
N2-C12	1.421(4)	1.409(5)	1.418(5)	1.433(8)
N1-M1-N5	106.09(11)	111.02(13)	103.34(12)	92.9(2)
N1-M1-N3	78.92(11)	81.72(13)	77.76(12)	78.2(2)
N5-M1-N3	102.02(11)	89.39(12)	107.37(12)	107.4(2)
N1-M1-N2	79.23(11)	82.10(13)	76.15(12)	78.3(2)
N5-M1-N2	108.20(11)	108.01(13)	101.10(12)	104.5(2)
N3-M1-N2	146.54(11)	159.60(13)	144.98(12)	140.9(2)
N1-M1-N4	177.15(12)	167.45(13)	178.72(12)	166.8(2)
N5-M1-N4	76.49(12)	81.50(13)	75.38(12)	76.0(2)
N3-M1-N4	99.44(11)	97.99(13)	102.69(11)	111.7(2)
N2-M1-N4	101.22(11)	95.12(13)	103.91(11)	97.4(2)
φ	33.75	28.45	33.28	27.29
$ au_5$	0.51	0.13	0.56	0.43

Table S4. Selected bond distances and angles for the [M(ibaps)bpy]ⁿ complexes

Distances (Å) or angles (deg)	2-Co
Co2-N6	1.835(3)
Co2–N7	1.995(3)
Co2–N8	1.980(3)
Co2–N9	1.971(3)
Co2-N10	1.999(3)
N6-C53	1.396(5)
C53-C54	1.404(5)
C54–C55	1.389(5)
C55-C56	1.391(6)
C56-C57	1.374(6)
C57-C58	1.422(5)
C53–C58	1.420(5)
N8-C58	1.387(5)
N6-C59	1.405(5)
C59-C60	1.405(5)
C60-C61	1.391(6)
C61-C62	1.384(6)
C62-C63	1.381(6)
C63-C64	1.411(5)
C59-C64	1.410(5)
N7-C64	1.410(5)
N6-Co2-N10	126.69(14)
N6-Co2-N8	81.41(13)
N8-Co2-N10	89.39(13)
N6-Co2-N7	82.05(13)
N7-Co2-N10	104.49(12)
N8-Co2-N7	162.74(13)
N6-Co2-N9	153.33(13)
N9-Co2-N10	79.98(13)
N9-Co2-N8	100.35(13)
N9-C02-N/	92.25(12)
φ	28.44
τ ₅	0.16

Table S5. Selected bond distances and angles for the second molecule of 2-Co

The dihedral angle, ϕ , is defined as the angle between the planes formed by the two aryl rings of the [ibaps] backbone.



Entry	Catalyst	mol %	Solvent	Т (°С)	Yield Indoline [%]
1	1	10	Toluene:DMF 4:1	115	25
2	1	20	Toluene:DMF 4:1	115	33
3	1	50	Toluene:DMF 4:1	115	52
4	1	10	Toluene:DMF 4:1	rt	No reaction
5	1	10	Toluene:DMF 4:1	80	12
6	1	10	Toluene	115	34
7	1	10	DMF	115	57
8	1	10	DMA	115	27
9	1	10	CF ₃ -Toluene	115	17
10	Fe(OAc)/Bp y	10	DMF	115	No reaction
11	H₃ibaps	10	DMF	115	No reaction
12			DMF	115	No reaction

Table S6: Optimization and screening conditions for aliphatic C-H amination with 1.

Reaction conditions: Drybox (Ar); in a pressure tube: catalyst (10 mol %), solvent (1 mL), 4Å MS, azide (1 equiv.), sealed tube taken out of the box and placed in a hot oil bath at a set temperature for heating, 24 h; analysis by GC-MS for product assignment, and GC-FID for yields. *^a* mixture of 1:1 mol of Fe(OAc)₂ and bpy.



Figure S16. ¹H NMR spectrum of the product mixture from the reaction of 1-azido-2-phenethylbenzene with **1**.



Figure S17. ¹H NMR spectrum of the isolated indoline product from the reaction of 1-azido-2-phenethylbenzene with **1**.



Figure S18. ¹³C NMR spectrum of the isolated indoline product from the reaction of 1-azido-2-phenethylbenzene with 1.



Figure S19. ¹H NMR spectrum of the product mixture from the reaction of 1-azido-4-methoxy-2-phenethylbenzene with **1**.



Figure S20. ¹H NMR spectrum of the isolated indoline and indole products from the reaction of 1-azido-4-methoxy-2-phenethylbenzene with **1**.



Figure S21. ¹³C NMR spectrum of the isolated indoline and indole products from the reaction of 1-azido-4-methoxy-2-phenethylbenzene with **1**.

References.

- (1) Sharma, S. K.; May, P. S.; Jones, M. B.; Lense, S.; Hardcastle, K. I.; MacBeth, C. E. Catalytic Dioxygen Activation by Co(ii) Complexes Employing a Coordinatively Versatile Ligand Scaffold. *Chem. Commun.* 47 (6), 1827–1829.
- (2) Wilson, R. J.; Jones, J. R.; Bennett, M. V. Unprecedented Gallium-Nitrogen Anions: Synthesis and Characterization of [(Cl3Ga)3N]3- and [(Cl3Ga)2NSnMe3]2-. *Chem. Commun.* **2013**, *49* (44), 5049–5051.
- (3) Sun, K.; Sachwani, R.; Richert, K. J.; Driver, T. G. Intramolecular Ir(I)-Catalyzed Benzylic C-H Bond Amination of Ortho-Substituted Aryl Azides. *Org. Lett.* **2009**, *11* (Copyright (C) 2011 American Chemical Society (ACS). All Rights Reserved.), 3598– 3601.
- (4) Connelly, N. G.; Geiger, W. E. Chemical Redox Agents for Organometallic Chemistry. Chem. Rev. 1996, 96 (2), 877–910.
- (5) Bruker AXS Inc, APEX2 Version 2014.11-0. Madison, WI 2014.
- (6) Bruker AXS Inc, SAINT Version 8.34a. Madison, WI 2013.
- (7) Sheldrick, G. M. SADABS. Bruker AXS, Inc: Madison 2014.
- (8) Sheldrick, G. M. SHELXTL. Bruker AXS, Inc: Madison 2014.
- (9) Wilson, A. J. C.; Geist, V. International Tables for Crystallography. Volume C: Mathematical, Physical and Chemical Tables. Kluwer Academic Publishers, Dordrecht/Boston/London 1992 (Published for the International Union of Crystallography), 883 Seiten, ISBN 0-792-3-16-38X. *Cryst. Res. Technol.* **1993**, *28* (1), 110–110.
- (10) Spek, A. L. PLATON SQUEEZE: A Tool for the Calculation of the Disordered Solvent Contribution to the Calculated Structure Factors. *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71* (1), 9–18.
- (11) Spek, A. L. Structure Validation in Chemical Crystallography. Acta Crystallogr. Sect. D Biol. Crystallogr. 2009, 65 (2), 148–155.