

Supplementary Materials: Synthesis of a Half-Sandwich Hydroxidoiridium(III) Complex Bearing a Nonprotic *N*-Sulfonyldiamine Ligand and Its Transformations Triggered by the Brønsted Basicity

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Experimental Procedures

Synthesis of $\text{Cp}^*\text{IrCl}[\kappa^2(\text{N},\text{N})\text{-MsNCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]$ (1)

A solution of mesyl chloride (3.2 mL, 41.4 mmol) in CH_2Cl_2 (50 mL) was slowly added to a stirred solution of *N,N*-dimethylethylenediamine (4.5 mL, 41.3 mmol) in CH_2Cl_2 (180 mL) at 0 °C, and then stirred for 20 h at room temperature. After the addition of KO^tBu (9.3 g, 82.9 mmol), the reaction mixture was stirred for another 1 h. The resulting liquid phase was washed with 3 mL each of water and brine and dried over Na_2SO_4 . The solvent was removed in vacuo and subsequent purification by Kugelrohr distillation gave *N*-mesyl-*N',N'*-dimethylethylenediamine (2.18 g, 13.1 mmol). A mixture of $[\text{Cp}^*\text{IrCl}_2]_2$ (0.40 g, 0.51 mmol), *N*-mesyl-*N',N'*-dimethylethylenediamine (0.17 g, 1.04 mmol), and KO^tBu (0.12 g, 1.08 mmol) in CH_2Cl_2 (15 mL) was stirred at room temperature for 16 h. The resulting mixture was filtered through filter paper and the filtrate was evaporated to dryness. The residue was washed with diethyl ether and dried under vacuum. Orange crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into the solution in CH_2Cl_2 . Isolated yield: 49% (0.263 g, 0.50 mmol). ^1H NMR (300.4 MHz, $\text{CDCl}_3 + \text{CD}_2\text{Cl}_2$, −30 °C, δ/ppm): 1.50 (s, 15H; $\text{C}_5(\text{CH}_3)_5$), 2.99, 3.01, 3.08 (each s, 3H; $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$), 2.93–3.12 (each m, 1H; $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.6 MHz, $\text{CDCl}_3 + \text{CD}_2\text{Cl}_2$, rt, δ/ppm): 9.95 ($\text{C}_5(\text{CH}_3)_5$), 42.3 (SO_2CH_3), 49.6, 52.1, 56.0, 67.1 ($\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$), 86.7 ($\text{C}_5(\text{CH}_3)_5$). Anal. Calcd for $\text{C}_{15}\text{H}_{28}\text{N}_2\text{O}_2\text{S}\text{Cp}^*\text{Ir}$: C 34.11, H 5.34 N 5.30. Found: C 34.24, H 5.38, N 5.16.

Synthesis of $\text{Cp}^*\text{IrOH}[\kappa^2(\text{N},\text{N})\text{-MsNCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]$ (2)

A mixture of $\text{Cp}^*\text{IrCl}[\kappa^2(\text{N},\text{N})\text{-MsNCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]$ (0.226 g, 0.43 mmol) and KOH (0.10 g, 1.85 mmol) in THF (15 mL) containing H_2O (10 μL , 0.56 mmol) was stirred at room temperature for 5.5 h. The resulting mixture was filtered through filter paper and the filtrate was evaporated to dryness. The residue was washed with diethyl ether and dried under vacuum. Yellow crystals suitable for X-ray crystallography were obtained by THF. Isolated yield: 42% (0.092 g, 0.18 mmol). ^1H NMR (399.8 MHz, CD_2Cl_2 , −70 °C, δ/ppm): −0.79 (br, 1H; OH), 1.46 (s, 15H; $\text{C}_5(\text{CH}_3)_5$), 2.59, 2.83, 2.88 (each s, 3H; SO_2CH_3 , $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$), 2.61–3.15 (each m, 1H; $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$). $^{13}\text{C}\{^1\text{H}\}$ NMR (100.5 MHz, CD_2Cl_2 , −70 °C, δ/ppm): 9.58 ($\text{C}_5(\text{CH}_3)_5$), 42.9 (SO_2CH_3), 49.2, 49.4, 66.0, 83.1 ($\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$), 86.6 ($\text{C}_5(\text{CH}_3)_5$). Anal. Calcd for $\text{C}_{15}\text{H}_{29}\text{N}_2\text{O}_3\text{S}\text{Ir}$: C 35.34, H 5.73 N 5.50. Found: C 35.11, H 5.86, N 5.41.

Synthesis of $\text{Cp}^*\text{Ir}(\text{NHCOC}_6\text{H}_5)[\kappa^2(\text{N},\text{N})\text{-MsNCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]$ (3)

A mixture of $\text{Cp}^*\text{IrOH}[\kappa^2(\text{N},\text{N})\text{-MsNCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2]$ (0.118 g, 0.23 mmol) and benzamide (0.31 mg, 0.26 mmol) in THF (5 mL) was stirred at room temperature for 1.5 h. The resulting mixture was filtered through filter paper and the filtrate was evaporated to dryness. The residue was washed with diethyl ether and dried under vacuum. Yellow crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into the solution in CH_2Cl_2 . Isolated yield: 36% (0.050 g, 0.082 mmol). ^1H NMR (399.8 MHz, CD_2Cl_2 , rt, δ/ppm): 1.57 (s, 15H; $\text{C}_5(\text{CH}_3)_5$), 2.26, 2.87, 3.26 (each s, 3H; SO_2CH_3 , $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$), 2.89–3.44 (each m, 1H; $\text{NCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$), 6.22 (br, 1H;

NHCOC₆H₅), 7.31–7.35 (each m, 1H; NHCOC₆H₅), 7.72–7.74 (each m, 1H; NHCOC₆H₅). ¹³C{¹H} NMR (100.5 MHz, CDCl₃, rt, δ/ppm): 9.41 (C₅(CH₃)₅), 40.5 (SO₂CH₃), 47.4, 49.1 (NCH₂CH₂N(CH₃)₂), 55.4, 69.0 (NCH₂CH₂N(CH₃)₂), 86.0 (C₅(CH₃)₅), 126.9, 127.9, 128.9, 140.9 (NHCOC₆H₅), 171.6 (NHCOC₆H₅). Anal. Calcd for C₂₂H₃₄N₃O₃Si: C 43.12, H 5.59 N 6.86. Found: C 42.94, H 5.58, N 6.74.

Synthesis of Cp*Ir(CH₂CN)[κ²(N,N)-MsNCH₂CH₂N(CH₃)₂] (4)

A mixture of Cp*IrOH[κ²(N,N)-MsNCH₂CH₂N(CH₃)₂] (0.204 g, 0.41 mmol) in CH₃CN (3 mL) was stirred at room temperature for 3.5 h. The resulting mixture was filtered through filter paper and the filtrate was evaporated to dryness. The residue was washed with diethyl ether and dried under vacuum. Yellow crystals were obtained by slow diffusion of diethyl ether into the solution in CH₂Cl₂. Isolated yield: 70% (0.152 g, 0.29 mmol). ¹H NMR (399.8 MHz, CD₂Cl₂, rt, δ/ppm): 1.57 (s, 15H; C₅(CH₃)₅), 2.14 (d, ²J_{HH} = 64 Hz, 1H; CH₂CN), 2.14 (d, ²J_{HH} = 33 Hz, 1H; CH₂CN) 2.50–3.30 (each m, 1H; NCH₂CH₂N(CH₃)₂). ¹³C{¹H} NMR (100.5 MHz, CDCl₃, rt, δ/ppm): −18.8(CH₂CN), 9.10 (C₅(CH₃)₅), 41.4 (SO₂CH₃), 49.2, 51.6, 57.4, 69.6 (NCH₂CH₂N(CH₃)₂), 87.0 (C₅(CH₃)₅), 129.7 (CH₂CN). IR (cm^{−1}, KBr): 2187 (s), 1636 (w), 1458 (m), 1382 (s), 1316 (s), 1267(s), 1167 (w), 1115 (s), 1011 (w), 969 (w), 933 (w), 880 (w), 797 (w), 746 (w). Anal. Calcd for C₁₇H₃₀N₃O₂Si: C 38.33, H 5.68 N 7.89. Found: C 37.99, H 5.70, N 7.57.

Synthesis of Cp*IrH[κ²(N,N)-MsNCH₂CH₂N(CH₃)₂] (5)

A mixture of Cp*IrOH[κ²(N,N)-MsNCH₂CH₂N(CH₃)₂] (0.092 g, 0.18 mmol) in 2-propanol (4 mL) was stirred at room temperature for 12 h. The resulting mixture was evaporated to dryness. The residue was washed with diethyl ether and dried under vacuum. Isolated yield: 99% (0.088 g, 0.18 mmol). ¹H NMR (399.8 MHz, CD₂Cl₂, rt, δ/ppm): −11.56 (s, 1H; H), 1.72 (s, 15H; C₅(CH₃)₅), 2.60, 2.97, 3.07 (each s, 3H; SO₂CH₃, NCH₂CH₂N(CH₃)₂), 2.40–3.14 (each m, 1H; NCH₂CH₂N(CH₃)₂). ¹³C{¹H} NMR (100.5 MHz, CD₂Cl₂, rt, δ/ppm): 10.3 (C₅(CH₃)₅), 35.0, 51.9, 56.5, 61.6, 71.5 (SO₂CH₃, NCH₂CH₂N(CH₃)₂), 86.8 (C₅(CH₃)₅). IR (cm^{−1}, KBr): 2060 (s), 1455 (m), 1377 (w), 1327 (w), 1303 (w), 1277 (s), 1256 (m), 1183 (w), 1171 (w), 1122 (s), 1084 (w), 1017 (w), 1001 (s), 979 (s), 944 (m), 834 (m), 774 (m), 738 (m). Anal. Calcd for C₁₅H₂₉N₂O₂Si: C 36.50, H 5.92 N 5.67. Found: C 36.55, H 5.99, N 5.68.

Synthesis of Cp*IrCN[κ²(N,N)-MsNCH₂CH₂N(CH₃)₂] (6)

A mixture of Cp*Ir(OH)[κ²(N,N)-MsNCH₂CH₂N(CH₃)₂] (0.112 g, 0.22 mmol) and acetone cyanohydrin (19.9 μL, 0.22 mmol) in CH₂Cl₂ (5 mL) was stirred at room temperature for 30 min. The resulting mixture was filtered through filter paper and the filtrate was evaporated to dryness. The residue was washed with diethyl ether and dried under vacuum. Yellow crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into the solution in CH₂Cl₂. Isolated yield: 100% (0.111 g, 0.22 mmol). ¹H NMR (399.8 MHz, CD₂Cl₂, rt, δ/ppm): 1.68 (s, 15H; C₅(CH₃)₅), 2.88, 3.00, 3.11 (each s, 3H; SO₂CH₃, NCH₂CH₂(CH₃)₂), 2.95–3.14 (each m, 1H; NCH₂CH₂(CH₃)₂). ¹³C{¹H} NMR (100.5 MHz, CD₂Cl₂, rt, δ/ppm): 9.69 (C₅(CH₃)₅), 38.5 (SO₂CH₃), 50.5, 56.2 (NCH₂CH₂N(CH₃)₂), 70.4, 91.5 (NCH₂CH₂N(CH₃)₂), 121.3 (CN). IR (cm^{−1}, KBr): 2103 (s), 1269 (m), 1381 (w), 1320 (w), 1287 (s), 1256 (m), 1173 (m), 1130 (s), 1081 (m), 1034 (w), 986 (s), 959 (w), 935 (w), 855 (s), 780 (m), 739 (m), 581 (w), 561 (w). Anal. Calcd for C₁₆H₂₈N₃O₂Si: C 37.05, H 5.43 N 8.10. Found: C 36.79, H 5.32, N 8.06.

Reaction Procedures for Transfer Hydrocyanation of Benzaldehyde with Acetone Cyanohydrin Catalyzed by 6

Under an argon atmosphere, acetone cyanohydrin (450 μL, 4.9 mmol) was added to a dioxane solution (1.0 mL) of benzaldehyde (0.052 g, 0.49 mmol) containing 6 (0.026 g, 0.05 mmol) and then stirred for 12 h at 30 °C. The reaction mixture was filtered through a pad of Florisil (100–200 mesh, Nacalai Tesque Inc.). The Florisil was washed with Et₂O and the combined organic solution was evaporated. The mixture was dissolved in CDCl₃ and the yield was determined by ¹H NMR using 1,2,4,5-tetramethylbenzene (10.8 mg, 0.08 mmol) as an internal standard.

X-Ray Crystallographic Data for 1, 2, 3, and 6

Table S1. Crystallographic data for 1 and 2.

	1	2
Empirical Formula	C ₁₅ H ₂₈ ClIrN ₂ O ₂ S	C ₁₅ H ₂₉ IrN ₂ O ₃ S
Formula Weight	528.13	509.69
Crystal Color, Habit	orange, block	yellow, prism
Crystal System	orthorhombic	monoclinic
Space Group	P2 ₁ 2 ₁ 2 ₁ (#19)	P2 ₁ /n (#14)
Lattice Parameters	<i>a</i> = 8.8643(9) Å	<i>a</i> = 8.776(3) Å
	<i>b</i> = 13.6959(15) Å	<i>b</i> = 15.179(6) Å
	<i>c</i> = 14.0454(12) Å	<i>c</i> = 13.383(5) Å
	<i>V</i> = 1814.4(3) Å ³	<i>V</i> = 1782.1(11) Å ³
Z value	4	4
<i>D</i> _{calc}	1.933 g/cm ³	1.900 g/cm ³
<i>F</i> ₀₀₀	1032.00	1000.00
(MoKα)	76.488 cm ^{−1}	76.430 cm ^{−1}
Exposure Rate	4.0 sec./°	10.0 sec./°
No. of Reflections Measured	13342	13621
No. of Unique Reflections	3967	4043
No. Variables	199	203
<i>R</i> 1 (<i>I</i> > 2.00σ(<i>I</i>))	0.0160	0.0384
<i>wR</i> 2 (All Reflections)	0.0394	0.0790
GOF on <i>F</i> ²	0.864	1.158
Flack Parameter	−0.005(4)	

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

Table S2. Crystallographic data for 3 and 6.

	3	6
Empirical Formula	C ₂₂ H ₃₄ IrN ₃ O ₃ S	C ₁₆ H ₂₈ IrN ₃ O ₂ S
Formula Weight	612.81	518.70
Crystal Color, Habit	yellow, prism	yellow, platelet
Crystal System	orthorhombic	monoclinic
Space Group	P2 ₁ 2 ₁ 2 ₁ (#19)	C2 (#5)
Lattice Parameters	<i>a</i> = 8.5166(8) Å	<i>a</i> = 15.158(5) Å
	<i>b</i> = 15.794(2) Å	<i>b</i> = 8.800(3) Å
	<i>c</i> = 17.528(2) Å	<i>c</i> = 14.210(5) Å
	<i>V</i> = 2357.7(5) Å ³	<i>V</i> = 6470.7(12) Å ³
Z value	4	4
<i>D</i> _{calc}	1.726 g/cm ³	1.858 g/cm ³
<i>F</i> ₀₀₀	1216.00	1016.00
(MoKα)	57.948 cm ^{−1}	73.450 cm ^{−1}
Exposure Rate	4.0 sec./°	20.0 sec./°
No. of Reflections Measured	18008	7193
No. of Unique Reflections	5296	4151
No. Variables	271	208
<i>R</i> 1 (<i>I</i> > 2.00σ(<i>I</i>))	0.0297	0.0333
<i>wR</i> 2 (All Reflections)	0.0730	0.0762
GOF on <i>F</i> ²	1.010	0.973
Flack Parameter	−0.009(10)	0.010(15)

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

^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR Spectra









