

Silylenediamido $[(\text{CH}_3)_2\text{Si}(\text{NTs})_2]^{2-}$; Ts = *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2$] complexes of iridium: synthesis, structures and facile Si–N bond cleavage

Koji Ishiwata, Shigeki Kuwata* and Takao Ikariya*

Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan. Fax: +81 3 5734 2637; Tel: +81 3 5734 2150; E-mail: skuwata@apc.titech.ac.jp; tikariya@apc.titech.ac.jp

Experimental Details

All manipulations were performed under an atmosphere of argon using standard Schlenk technique unless otherwise specified. Solvents were dried by refluxing over sodium benzophenone ketyl (toluene, hexane, THF, diethyl ether), CaH_2 (CH_2Cl_2), Drierite (acetone) and distilled before use. Reagents were commercially obtained and used as received. ^1H (300.4 MHz), and $^{31}\text{P}\{^1\text{H}\}$ (121.6 MHz) NMR spectra were obtained on a JEOL JNM-LA300 spectrometer. ^1H NMR shifts are relative to the residual protiated solvent: CHCl_3 , δ 7.26; C_6D_6 , δ 7.15. ^{31}P NMR shifts are relative to an external 85% H_3PO_4 . Infrared spectra were recorded on a JASCO FT/IR-610 spectrometer. Elemental analyses were performed by the Analytical Facility at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology or on a Perkin-Elmer 2400II CHN analyzer.

Preparation of $(\text{CH}_3)_2\text{Si}(\text{NHTs})_2$ (1). To a solution of TsNH_2 (6.85 g, 40.0 mmol) in THF (100 mL) was added a hexane solution of *n*- $\text{C}_4\text{H}_9\text{Li}$ (1.59 M, 26 mL, 41.3 mmol) at 0 °C, and the mixture was slowly warmed to room temperature with stirring. After 1 h, dimethyldichlorosilane (2.4 mL, 20.1 mmol) was added to the resultant white suspension at 0 °C, and the mixture was slowly warmed to room temperature with stirring. After 1 h, the resultant colorless solution was dried up, washed with toluene (50 mL), and extracted with acetone (50 mL). Recrystallization from THF/hexane (20 mL/20 mL) afforded **1** as colorless crystals (4.61 g, 11.6 mmol, 58%). δ_{H} (300 MHz; CDCl_3) 7.75, 7.28 (d, 4H each, $^3J_{\text{HH}} = 8.4$ Hz, $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$), 4.98 (br, 2H, NH), 2.42 (s, 6H, $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$), 0.44 (s, 6H, $\text{Si}(\text{CH}_3)_2$). Satisfactory analytical data were not available for **1** due to its hygroscopic nature.

Preparation of $[\text{Cp}^*\text{Ir}(\text{NTs})_2\text{Si}(\text{CH}_3)_2]$ (2). To a suspension of $[\text{Cp}^*\text{IrCl}_2]_2$ (1.00 g, 1.26 mmol)¹ in toluene/ CH_2Cl_2 (80 mL/20 mL) was added triethylamine (1.40 mL, 10.04 mmol) and CaH_2 (1 g). After stirring for 3 h, **1** (1.21 g, 3.04 mmol) was added to the orange suspension and the suspension immediately turned into dark red. After stirring for 1 h, the resultant suspension was filtered and the filtrate was evacuated to dryness and washed with water (30 mL), diethyl ether (30 mL). Recrystallization from CH_2Cl_2 /hexane (5 mL/50 mL) afforded **2** as dark red crystals (1.28 g, 1.77 mmol, 73%). δ_{H} (300 MHz; C_6D_6) 7.98, 6.82 (d, 4H each, $^3J_{\text{HH}} = 8.1$ Hz, $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$), 1.95 (s, 6H, $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$), 1.25 (s, 15H, Cp*), 0.60 (s, 6H, $\text{Si}(\text{CH}_3)_2$). Anal. Calcd for $\text{C}_{26}\text{H}_{33}\text{IrN}_2\text{O}_4\text{S}_2\text{Si}$: C, 43.13; H, 4.87; N, 3.87. Found: C, 43.44; H, 4.96; N, 3.93.

Preparation of $[\text{Cp}^*\text{Ir}(\text{NTs})_2\text{Si}(\text{CH}_3)_2\{\text{P}(\text{C}_6\text{H}_5)_3\}]$ (3a). To a solution of **2** (100.3 mg, 0.14 mmol) in THF (2 mL) was added

$\text{P}(\text{C}_6\text{H}_5)_3$ (40.0 mg, 0.15 mmol). After stirring for 1 h, hexane (10 mL) was layered on the solution. The yellow crystals that formed were filtered off and dried in vacuo (129.1 mg, 0.131 mmol, 94%). δ_{H} (300 MHz; C_6D_6) 7.95–6.63 (m, 15H, aryl), 7.24, 6.59 (d, 4H each, $^3J_{\text{HH}} = 8.1$ Hz, $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$), 1.89 (s, 6H, $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$), 1.62 (d, 15H, $^4J_{\text{PH}} = 2.0$ Hz, Cp*), 0.95, –0.75 (s, 3H each, $\text{Si}(\text{CH}_3)_2$). δ_{P} (122 MHz; C_6D_6) 16.6 (s). Anal. Calcd for $\text{C}_{44}\text{H}_{50}\text{IrN}_2\text{O}_4\text{PSi}$: C, 53.58; H, 5.11; N, 2.84. Found: C, 53.53; H, 4.96; N, 2.84.

Preparation of $[\text{Cp}^*\text{Ir}(\text{NTs})_2\text{Si}(\text{CH}_3)_2\{\text{P}(\text{OC}_2\text{H}_5)_3\}]$ (3b). To a solution of **2** (100.3 mg, 0.14 mmol) in THF (2 mL) was added $\text{P}(\text{OC}_2\text{H}_5)_3$ (25 μL , 0.14 mmol). After stirring for 1 h, hexane (10 mL) was layered on the solution. The yellow crystals that formed were filtered off and dried in vacuo (113.1 mg, 0.127 mmol, 92%). δ_{H} (300 MHz; C_6D_6) 8.02, 6.84 (d, 4H each, $^3J_{\text{HH}} = 8.1$ Hz, $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$), 3.82 (dq, 6H, $^3J_{\text{PH}} = ^3J_{\text{HH}} = 7.1$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_3$), 1.96 (s, 6H, $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$), 1.77 (d, 15H, $^4J_{\text{PH}} = 3.4$ Hz, Cp*), 1.04 (t, 9H, $^3J_{\text{HH}} = 7.1$ Hz, $\text{P}(\text{OCH}_2\text{CH}_3)_3$), 0.52, 0.42 (s, 3H each, $\text{Si}(\text{CH}_3)_2$). δ_{P} (122 MHz; C_6D_6) 79.2 (s). Anal. Calcd for $\text{C}_{32}\text{H}_{50}\text{IrN}_2\text{O}_7\text{PSi}$: C, 43.18; H, 5.66; N, 3.15. Found: C, 42.80; H, 5.68; N, 3.11.

Preparation of $[\text{Cp}^*\text{Ir}(\text{NTs})_2\text{Si}(\text{CH}_3)_2(\text{CO})]\cdot\text{CH}_2\text{Cl}_2$ (3c· CH_2Cl_2). A solution of **2** (33.5 mg, 0.05 mmol) in CH_2Cl_2 (3 mL) was stirred for 1 h under CO atmosphere. Hexane (10 mL) was layered on the concentrated solution (*ca.* 1 mL) under CO atmosphere. The yellow crystals of **3c**· CH_2Cl_2 were filtered off and dried in vacuo (34.0 mg, 0.04 mmol, 88%). δ_{H} (300 MHz; C_6D_6) 7.88, 6.81 (d, 4H each, $^3J_{\text{HH}} = 8.1$ Hz, $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$), 1.86 (s, 6H, $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$), 1.57 (s, 15H, Cp*), 0.77, 0.58 (s, 3H each, $\text{Si}(\text{CH}_3)_2$). $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 2036 (CO). Anal. Calcd for $\text{C}_{28}\text{H}_{37}\text{Cl}_2\text{IrN}_2\text{O}_5\text{S}_2\text{Si}$: C, 40.18; H, 4.46; N, 3.35. Found: C, 40.31; H, 4.24; N, 3.40.

Preparation of $[\text{Cp}^*\text{Ir}(\text{NHTs})_2\{\text{P}(\text{C}_6\text{H}_5)_3\}]$ (5). To a solution of **3a** (37.5 mg, 0.04 mmol) in CH_2Cl_2 (5 mL) was added water (10.0 μL , 0.55 mmol) and the mixture was stirred for 20 h. Addition of hexane (10 mL) to the concentrated solution (*ca.* 1 mL) afforded **5** as yellow solid (26.8 mg, 0.03 mmol, 76%) along with small amount of yellow crystals of **5**· CH_2Cl_2 . δ_{H} (300 MHz; C_6D_6) 7.52, 6.99 (br, 15H, aryl), 7.44, 6.65 (d, 4H each, $^3J_{\text{HH}} = 8.1$ Hz, $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$), 2.65 (d, 2H, $^3J_{\text{PH}} = 3.4$ Hz, NH), 1.97 (s, 6H, $\text{SO}_2\text{C}_6\text{H}_4\text{CH}_3$), 1.56 (d, 15H, $^4J_{\text{PH}} = 2.4$ Hz, Cp*). δ_{P} (122 MHz; C_6D_6) 7.3 (s). $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3346, 3281 (NH). Anal. Calcd for $\text{C}_{42}\text{H}_{46}\text{IrN}_2\text{O}_4\text{PSi}$: C, 54.23; H, 4.98; N, 3.01. Found: C, 54.09; H, 4.93; N, 2.92.

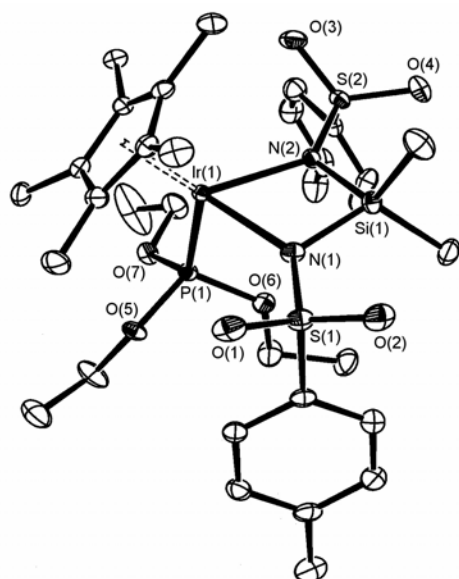
X-ray Diffraction Studies. Diffraction experiments were performed on a Rigaku Saturn CCD area detector with graphite monochromated Mo-K α radiation ($\lambda = 0.71070 \text{ \AA}$). Single crystals suitable for X-ray analyses were mounted on glass fibers. Intensity data were corrected for Lorentz-polarization effects and for absorption. Details of crystal and data collection parameters are summarized in Table S1.

Structure solution and refinements were carried out by using the CrystalStructure program package.² The heavy-atom positions were determined by a direct methods program (SIR92³ for **3a**, **3b** and **3c**:CH₂Cl₂, SIR2002⁴ for **2** and **5**:CH₂Cl₂) and remaining non-hydrogen atoms were found by subsequent Fourier syntheses. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares techniques based on F^2 . All hydrogen atoms except for the amide hydrogens in **5** were placed at calculated positions; these hydrogen atoms were included in the final stages of the refinements. The atomic scattering factors were taken from ref 5, and anomalous dispersion effects were included; the values of $\Delta f'$ and $\Delta f''$ were taken from ref 6.

References

- 1 C. White, A. Yates and P. M. Maitlis, *Inorg. Synth.*, 1992, **29**, 230.
- 2 *CrystalStructure 3.8: Crystal Structure Analysis Package*, Rigaku and Rigaku/MSK, The Woodlands TX 77381 USA, 2000–2006.
- 3 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori and M. Camalli, *J. Appl. Cryst.*, 1994, **27**, 435.
- 4 M. C. Burla, M. Camalli, B. Carrozzini, G. L. Cascarano, C. Giacovazzo, G. Polidori and R. Spagna, *J. Appl. Cryst.*, 2003, **36**, 1103.
- 5 *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.
- 6 *International Tables for X-ray Crystallography*; Kluwer Academic Publishers: Boston, MA, 1992; Vol. C.

(3b)



(3c)

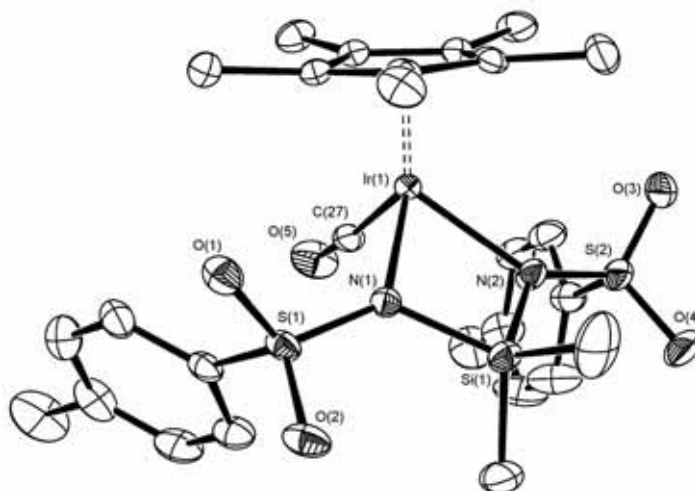


Fig. S1 Crystal Structures of **3b** and **3c·CH₂Cl₂**. Hydrogen atoms and the solvating CH₂Cl₂ in **3c·CH₂Cl₂** are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability.

Table S1 Crystallographic Data for **2**, **3a**, **3b**, **3c·CH₂Cl₂** and **5·CH₂Cl₂**

	2	3a	3b	3c·CH₂Cl₂	5·CH₂Cl₂
Formula	C ₂₆ H ₃₅ IrN ₂ O ₄ S ₂ Si	C ₄₄ H ₅₀ IrN ₂ O ₄ PS ₂ Si	C ₃₂ H ₅₀ IrN ₂ O ₇ PS ₂ Si	C ₂₈ H ₃₇ Cl ₂ IrN ₂ O ₅ S ₂ Si	C ₄₃ H ₄₈ Cl ₂ IrN ₂ O ₄ PS ₂
molecular wt	724.00	986.29	890.16	836.94	1015.08
color	dark red	yellow	yellow	yellow	yellow
crystal dimens, mm	0.20 × 0.20 × 0.20	0.50 × 0.20 × 0.20	1.00 × 0.80 × 0.50	0.70 × 0.40 × 0.30	0.50 × 0.30 × 0.20
symmetry	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	<i>P2₁/a</i> (#14)	<i>P2₁/c</i> (#14)	<i>P2₁/c</i> (#14)	<i>P2₁2₁2₁</i> (#19)	<i>Pbca</i> (#61)
<i>a</i> , Å	14.045(4)	10.474(4)	11.945(3)	12.605(3)	14.832(5)
<i>b</i> , Å	18.430(5)	19.550(7)	18.337(4)	14.305(4)	19.130(7)
<i>c</i> , Å	22.740(6)	20.356(7)	17.387(4)	18.654(5)	30.389(11)
α , °	90	90	90	90	90
β , °	98.606(3)	91.550(5)	104.708(3)	90	90
γ , °	90	90	90	90	90
<i>V</i> , Å ³	5820(2)	4167(2)	3683.8(15)	3363.5(14)	8623(5)
<i>Z</i>	8	4	4	4	8
<i>D</i> _{calc} , g cm ⁻³	1.652	1.572	1.605	1.653	1.564
<i>F</i> ₀₀₀	2880.00	1992.00	1800.00	1664.00	4080.00
μ , cm ⁻¹	48.187	34.253	38.701	43.367	34.062
exposure rate, sec/°	10.0	6.0	2.0	4.0	10.0
no. of data collected	51953 (<i>R</i> _{int} = 0.059)	37870 (<i>R</i> _{int} = 0.065)	33325 (<i>R</i> _{int} = 0.073)	31426 (<i>R</i> _{int} = 0.049)	88525 (<i>R</i> _{int} = 0.091)
no. of unique data (2 θ < 55°)	13188	9542	8396	7623	9869
transmission factors	0.250–0.381	0.306–0.504	0.048–0.144	0.118–0.272	0.348–0.506
no. variables	719	546	465	408	542
<i>R</i> (all data)	0.0801	0.0911	0.0480	0.0351	0.0928
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)] ^a	0.0394	0.0527	0.0370	0.0284	0.0382
<i>wR</i> 2 ^a	0.1302	0.1191	0.1053	0.0924	0.1386
gof ^a	1.008	1.009	1.000	1.006	1.000
max/min residuals, e Å ⁻³	4.35, -4.34	3.60, -2.45	2.22, -1.59	2.20, -1.35	3.68, -2.16

^a $R1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|}$. $wR2 = \frac{[\sum (w(F_o^2 - F_c^2)^2)]^{1/2}}{[\sum w(F_o^2)^2]^{1/2}}$. $gof = \frac{[\sum w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{params})]^{1/2}}{[\sum w(F_o^2)^2]^{1/2}}$.