Supporting Information

Nitrogen-Atom Insertion into Ir–S and C–S Bonds Initiated by Photolysis of Iridium(III)-Azido-Dithiocarbamato Complexes

Takayoshi Suzuki,* Antonio G. DiPasquale, and James M. Mayer*
Department of Chemistry, Box 351700, University of Washington, Seattle, WA 98195-1700
E-mai: suzuki@chem.sci.osaka-u.ac.jp; mayer@chem.washington.edu

Measurements

NMR spectra were acquired on Bruker DMX-750, AF-300 and AC-200 spectrometers at 298 K (unless otherwise noted). Proton NMR chemical shifts were referenced to the residual ^{1}H NMR signals of the deuterated solvents and are reported vs. TMS. External CD_3NO_2 and internal solvent CD_3CN was used as a reference for ^{15}N NMR chemical shifts. Absorption spectra were obtained using a HP 8453 UV-vis spectrophotometer at 293 K.

Materials

The following chemicals are used as received; $IrCl_3{\cdot}nH_2O$ from Pressure Chemical Co.; $C_5(CH_3)_5H$ (HCp^*), $Na(Me_2dtc){\cdot}2H_2O$ and $Na(Et_2dtc){\cdot}3H_2O$ from Aldrich, NaN_3 from J. T. Baker; $^{13}CS_2$ (^{13}C 97–99%) and $NaN_2{}^{15}N$ (singly ^{15}N-labeled sodium azide, 1-^{15}N 98%) from CIL; $HN(CH_3)_2$ from Matheson Gas Product Inc.; solvents for preparation of complexes from Fisher Chemicals. Acetonitrile-d_3 was purchazed from CIL, and dried by successive vacuum distillation over CaH_2, followed by P_2O_5 and again over CaH_2.

Preparation of complexes

The complex, $[\{Cp^*IrCl\}_2(\mu\text{-}Cl)_2]$ was prepared by the literature method.[1] Sodium *N,N*-dimethyldithiocarbamate-^{13}C, $Na[S_2{}^{13}CN(CH_3)_2]$, was prepared from $^{13}CS_2$ and $HN(CH_3)_2$ by a similar method for sodium *N,N*-dimethylthiocarbamate, $Na[SC(O)N(CH_3)_2]$.[2]

$Cp^*Ir(R_2dtc)Cl$ (R = Me or Et). These complexes were prepared by a similar method to that for the rhodium(III) analogues.[3] To an orange suspention of $[\{Cp^*IrCl\}_2(\mu\text{-}Cl)_2]$ (923 mg, 1.16 mmol) in methanol (60 cm^3) was added $Na(Me_2dtc){\cdot}2H_2O$ (416 mg, 2.32 mmol) with stirring. The mixture was stirred at room temperature for 2 h, giving a red solution. The filtered solution was evaporated to dryness under reduced pressure, and the residue was extracted with dichloromethane (5 cm^3). The extract was evaporated, again, to dryness under reduced pressure, and redissolved in methanol/dichloromethane (5:1, 6 cm^3).

Diffusion of diethyl ether vapor into the solution gave orange-red crystals, which were collected by filtration and dried in air. Yield: 1.068 g (95%). Anal. Found: C, 32.38; H, 4.44; N, 2.95%. Calcd for $C_{13}H_{21}ClIrNS_2$: C, 32.32; H, 4.38; N, 2.90%.

Complexes of $Cp^*Ir(Me_2dtc\text{-}^{13}C)Cl$ and $Cp^*Ir(Et_2dtc)Cl$ were prepared similarly with $Na[S_2{}^{13}CN(CH_3)_2]$ or $Na(Et_2dtc)\cdot 3H_2O$ in yields of 77–84%.

$Cp^*Ir(R_2dtc)(N_3)$ {R = Me (1) or Et (1')}. To a solution of $Cp^*Ir(R_2dtc)Cl$ (100 mg, 0.204 mmol) in a mixture of methanol and acetonitrile (1:1, 2 cm^3) was added a methanol solution (1 cm^3) of AgOTf (53.2 mg, 0.207 mmol) with stirring. The mixture was stirred in the dark at room temperature for 20 min, and filtered to remove a white precipitate of AgCl. The precipitate was washed with methanol (3 × 1 cm^3) and acetonitrile (1 cm^3), and the filtrate and washings were combined. Sodium azide NaN_3 (14.8 mg, 0.230 mmol) was added, and the mixture was stirred in the dark at room temperature for 10 min. After the solution was evaporated to dryness under reduced pressure, the residue was extracted with dichloromethane (2 cm^3). Methanol (2 cm^3) was added to the filtered extract, and the mixture was concentrated to ca. 2 cm^3 by flow of N_2 gas. The concentrate was kept in a freezer for a while, and the deposited orange crystals were collected by filtration, and dried in vacuo. Yield: 77.8 mg (77%). Anal. Found: C, 31.97; H, 4.32; N, 11.35%. Calcd for $C_{13}H_{21}IrN_4S_2$: C, 31.89; H, 4.32; N, 11.44%. Crystals of **1** suitable for X-ray analysis were grown from a CH_2Cl_2 solution by vapor diffution of Et_2O at ambient temperature.

The Et_2dtc complex (**1'**) and the ^{15}N labeled complexes, $Cp^*Ir(Me_2dtc)(N_3\text{-}^{15}N)$ (**1**-^{15}N) and $Cp^*Ir(Et_2dtc)(N_3\text{-}^{15}N)$ (**1'**-^{15}N) (singly labeled $NaN_3\text{-}^{15}N$ was used), were prepared similarly in the yields of 75–80%.

Photolysis

Sample solutions for photolysis experiments were prepared under a nitrogen atmosphere with dry acetonitrile-d_3 (10 mg of sample in 1 cm^3 of CD_3CN; ca. 20 mM), and placed in a screw-top (J-Young brand) NMR tube. A Hg lamp was used for photolysis, and the lamp and the samples were cooled in an aqueous ethanol bath with a Neslab cryocool. During photolysis the bath temperature was monitored beside the samples.

Isolation of the photochemical product, $Cp^*Ir\{NSC(NMe_2)S\}$ (2)

An acetonitrile-d_3 solution of $Cp^*Ir(Me_2dtc)(N_3)$ (**1**, 10 mg in 1 cm^3) was photolyzed at –10 °C for 5 h. The ^1H NMR spectrum of this photolyzed solution confirmed that more than 70% of **1** turned to **2** without detectable formation of thermal product **3** (a few by-products were also detected <10%). The solution was allowed to stand in a freezer (–30°C)

for a couple of days, giving a small amount of red columnar crystals (~0.3 mg), which were suitable for X-ray analysis.

Isolation of the dimer product, {Cp*Ir[SN=C(NMe$_2$)S]}$_2$ (4)

An acetonitrile solution of **1** was photolyzed in the same manner as the above, and the solution was allowed to stand at ambient temperature for two days. The initial red reaction solution (containing **2** as a main photochemical product) turned to reddish purple on standing (**2** converted quantitatively to **3**, as revealed by the ^{1}H NMR spectrum). The solution was evaporated slowly in an inert atmosphere, affording yellow plate crystals of **4** suitable for X-ray analysis. More microcrystals of **4** were obtained by evaporation of the reddish purple solution to nearly dryness, followed by washing the residue with a small amount of acetonitrile, in a ~40% isolated yield.

Cross reaction between Cp*Ir{^{15}NSC(NMe$_2$)S} (2-^{15}N) and Cp*Ir{NSC(NEt$_2$)S} (2')

Separate solutions of Cp*Ir(Me$_2$dtc)(N$_3$-^{15}N) (**1**-^{15}N) and Cp*Ir(Et$_2$dtc)(N$_3$) (**1'**) in dry CD$_3$CN (10 mg cm^{-3}) were photolyzed at temperatures below –2°C for 5 h. The existance of the photochemical product, Cp*Ir{NSC(NMe$_2$)S} (**2**) or Cp*Ir{NSC(NEt$_2$)S} (**2'**), in each reaction mixture was confirmed by ^{1}H NMR spectroscopy. These solutions were mixed together, and kept in a freezer (–20°C) overnight. The ^{1}H NMR spectrum of this mixture showed that less than 5% of **2** and **2'** had converted to **3** and **3'**, respectively. In the ^{15}N NMR spectrum of this mixture (measured at –20°C) a resonance corresponding to Cp*Ir{^{15}NSC(NMe$_2$)S} (**2**-^{15}N) was observed as a main peak, but a weak (1/6 in height) signal due to Cp*Ir{^{15}NSC(NEt$_2$)S} (**2'**-^{15}N) was also detected. Then, this solution was kept at room temperature for 4 h; at that time ca. 1/4 of each **2** and **2'** were converted thermally to **3** and **3'**, which was confirmed by ^{1}H NMR. The mixture was, again, cooled to –20°C to measure the ^{15}N NMR spectrum, in which two resonances due to **2**-^{15}N and **2'**-^{15}N were observed in almost equal intensities (height ratio was ca. 7:5). After complete thermal convertion, the resonancec for **3** and **3'** were also of almost equal intensity.

Crystal structure analyses

Each crystal of **1**, **2**, and **3** suitable for X-ray analysis was mounted on a glass capillary with oil. X-ray diffraction data were collected on a Nonius KappaCCD diffractometer. One set of ψ-scan exposure was collected (details: see Table S1). The data were integrated and scaled using hkl-2000,[(4)] and empirical absorption corrections were applied with the same program. The structures were solved by direct method (SIR97[(5)]), and refined by full-matrix least-squares[(6)] with anisotropic thermal parameters for all non-

hydrogen atoms. Hydrogen atoms were placed using a riding model. Crystal data, experimental conditions, and refinement details are collected in Table S1. Perspective views of complexes **1**, **2**, and **4** are shown in Figures S1–S3, and selected bond lengths and angles are listed in Tables S2–S4, respectively.

References

(1) White, C.; Yates, A.; Maitlis, P. M. *Inorg. Synth.* **1992**, *29*, 228–234.

(2) Hawthorne, S. L.; Bruder, A. H.; Fay, R. C. *Inorg. Chem.* **1978**, *17*, 2114–2120.

(3) (a) Robertson, D. R.; Stephenson, T. A. *J. Chem. Soc., Dalton Trans.* **1978**, 486–495. (b) Russell, M. J. H.; White, C.; Yates, A.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 849–857.

(4) Otinowski, Z.; Minor, W. *Methods in Enzymology*, Carter, Jr., C. W.; Sweet, R. M. Eds. **1996**, *276*, 307–325, Academic Press.

(5) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Cryst.* **1994**, *27*, 435–442.

(6) Sheldrich, G. M. *SHELXL97*, Univ. of Göttingen, Germany, 1997.

Table S1 Crystal data, experimental conditions, and refinement details.

Complex	**1**	**2**	**4**
Formula	$C_{13}H_{21}IrN_4S_2$	$C_{13}H_{21}IrN_2S_2$	$C_{26}H_{42}Ir_2N_4S_4$
FW	489.66	461.64	923.28
T / K	130(2)	130(2)	130(2)
λ(Mo Kα) / Å	0.71073	0.71073	0.71073
Crystal color/habit	orange/prism	red/prism	orange/prism
Crystal size / mm	0.08×0.04×0.03	0.20×0.20×0.12	0.19×0.17×0.12
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	*Pnma* (no. 62)	*P*2/*c* (no. 14)	$P\bar{1}$ (no. 2)
a / Å	15.5070(2)	9.7290(3)	10.4540(4)
b / Å	12.0280(3)	11.2510(4)	11.1600(6)
c / Å	8.8740(6)	14.1330(6)	14.1330(10)
α / °	90	90	84.1170(17)
β / °	90	101.8080(14)	87.4570(16)
γ / °	90	90	66.235(4)
V / Å^3	1655.16(12)	1514.28(10)	1501.08(15)
Z, ρ_c / Mg m^{-3}	4, 1.965	4, 2.025	2, 2.043
μ(Mo Kα) / mm^{-1}	8.315	9.078	9.158
F(000)	944	888	888
θ_{min}, θ_{max} collected	3.49, 28.27	3.62, 28.28	3.37, 24.71
Collect/unique reflns	3363/1892	5827/3575	7062/4658
R_{int}	0.0397	0.0486	0.0609
Completeness	0.883	0.954	0.911
T_{min}, T_{max}	0.5560, 0.7885	0.2640, 0.4088	0.2751, 0.4062
Data/parameters	1892/107	3575/170	4658/339
R1, *wR2* [$I > 2\sigma(I)$]	0.0302, 0.0536	0.0384, 0.0720	0.0505, 0.1115
R1, *wR2* (all data)	0.0498, 0.0572	0.0629, 0.0776	0.0783, 0.1228
S (GoF)	1.000	1.005	0.999
$\Delta\rho$ / e Å^{-3}	–1.726, 0.962	–1.720, 0.946	–2.733, 2.504

Table S2 Selected bond lengths (Å) and angles (°) for $Cp^*Ir(Me_2dtc)(N_3)$ (**1**).

Ir(1)–N(1)	2.120(6)	Ir(1)–S(1)	2.390(1)
S(1)–C(7)	1.723(4)		
N(1)–N(2)	1.197(8)	N(2)–N(3)	1.157(9)
N(4)–C(7)	1.322(8)	N(4)–C(8)	1.463(6)
S(1)– Ir(1)–S(1')	72.54(5)	N(1)– Ir(1)–S(1)	90.06(13)
Ir(1)– S(1)– C(7)	88.59(19)	S(1)–C(7)–S(1')	110.3(4)
N(2)–N(1)– Ir(1)	122.5(5)	N(3)–N(2)–N(1)	176.3(8)
C(7)–N(4)–C(8)	121.9(3)	C(8)–N(4)–C(8')	116.2(5)
N(4)–C(7) –S(1)	124.9(2)		

Table S3 Selected bond lengths (Å) and angles (°) for $Cp^*Ir\{NSC(NMe_2)S\}$ (**2**)

Ir(1)–S(2)	2.272(2)	Ir(1)–N(1)	1.911(5)
S(1)–C(11)	1.706(6)	S(2)–C(11)	1.712(6)
S(1)–N(1)	1.628(5)	N(2)–C(11)	1.359(8)
N(2)–C(12)	1.456(7)	N(2)–C(13)	1.451(8)
S(2)– Ir(1)–N(1)	88.52(14)		
Ir(1)–N(1)–S(1)	123.3(3)	Ir(1)–S(2)–C(11)	105.2(2)
N(1)–S(1)–C(11)	107.2(3)	S(1)–C(11)–S(2)	115.8(3)
S(1)–C(11)–N(2)	121.8(4)	S(2)–C(11)–N(2)	122.4(5)
C(11)–N(2)–C(12)	119.2(5)	C(11)–N(2)–C(13)	121.6(5)
C(12)–N(2)–C(13)	119.2(5)		

Table S4 Selected bond lengths (Å)·and angles (°) for $\{Cp^{*}Ir[SN{=}C(NMe_2)S]\}_2$ (**4**).

Ir(1)–S(1)	2.328(3)	Ir(2)–S(3)	2.333(4)
Ir(1)–S(2)	2.339(3)	Ir(2)–S(4)	2.333(3)
Ir(1)–S(1')	2.370(3)	Ir(2)–S(3*)	2.378(4)
S(1)–N(1)	1.695(10)	S(3)–N(3)	1.718(11)
S(2)–C(11)	1.777(12)	S(4)–C(31)	1.774(13)
N(1)–C(11)	1.305(15)	N(3)–C(31)	1.274(16)
N(2)–C(11)	1.378(16)	N(4)–C(31)	1.356(15)
N(2)–C(12)	1.447(16)	N(4)–C(32)	1.441(17)
N(2)–C(13)	1.445(15)	N(4)–C(33)	1.444(16)
S(1)– Ir(1)–S(2)	82.77(11)	S(3)– Ir(2)–S(4)	83.41(12)
S(1)– Ir(1)–S(1')	80.84(11)	S(3)– Ir(2)–S(3*)	78.33(15)
S(2)– Ir(1)–S(1')	86.07(11)	S(4)– Ir(2)–S(3*)	88.16(12)
Ir(1)–S(1)–Ir(1')	99.16(11)	Ir(2)–S(3)–Ir(2*)	101.67(15)
Ir(1)–S(1)–N(1)	106.8(3)	Ir(2)–S(3)–N(3)	104.9(4)
Ir(1')–S(1)–N(1)	107.8(3)	Ir(2*)–S(3)–N(3)	107.1(4)
Ir(1)–S(2)–C(11)	100.6(4)	Ir(2)–S(4)–C(31)	102.1(4)
S(1)–N(1)–C(11)	116.3(9)	S(3)–N(3)–C(31)	119.4(9)
S(2)–C(11)–N(1)	125.3(10)	S(4)–C(31)–N(3)	123.7(9)
S(2)–C(11)–N(2)	115.8(9)	S(4)–C(31)–N(4)	115.7(9)
N(1)–C(11)–N(2)	118.9(11)	N(3)–C(31)–N(4)	120.6(12)
C(11)–N(2)–C(12)	122.7(19)	C(31)–N(4)–C(32)	123.0(11)
C(11)–N(2)–C(13)	119.6(10)	C(31)–N(4)–C(33)	120.5(11)
C(12)–N(2)–C(13)	114.7(11)	C(32)–N(4)–C(33)	116.4(11)

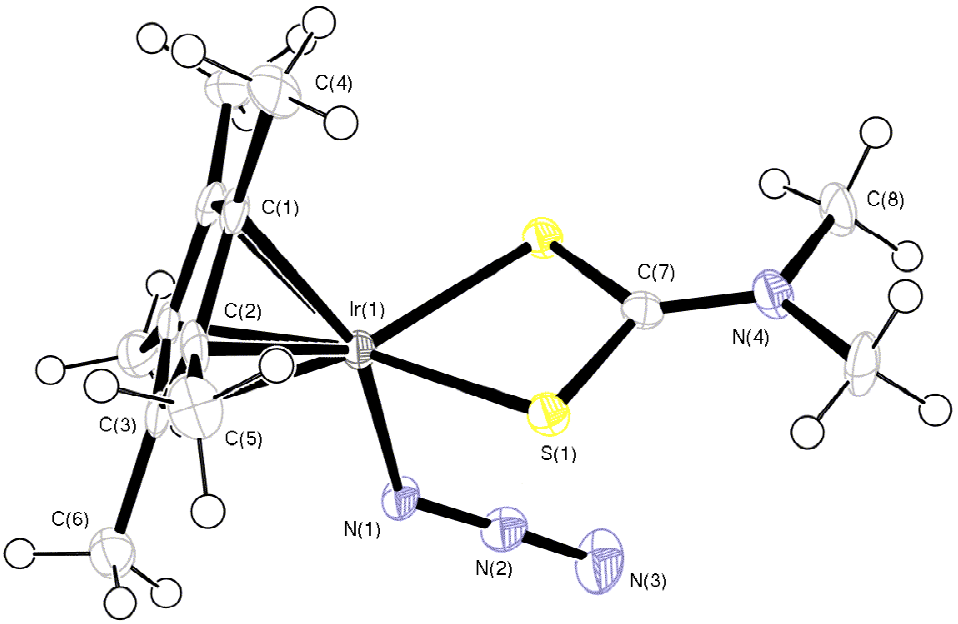


Figure S1 ORTEP of $Cp^{*}Ir(Me_2dtc)(N_3)$ (**1**).

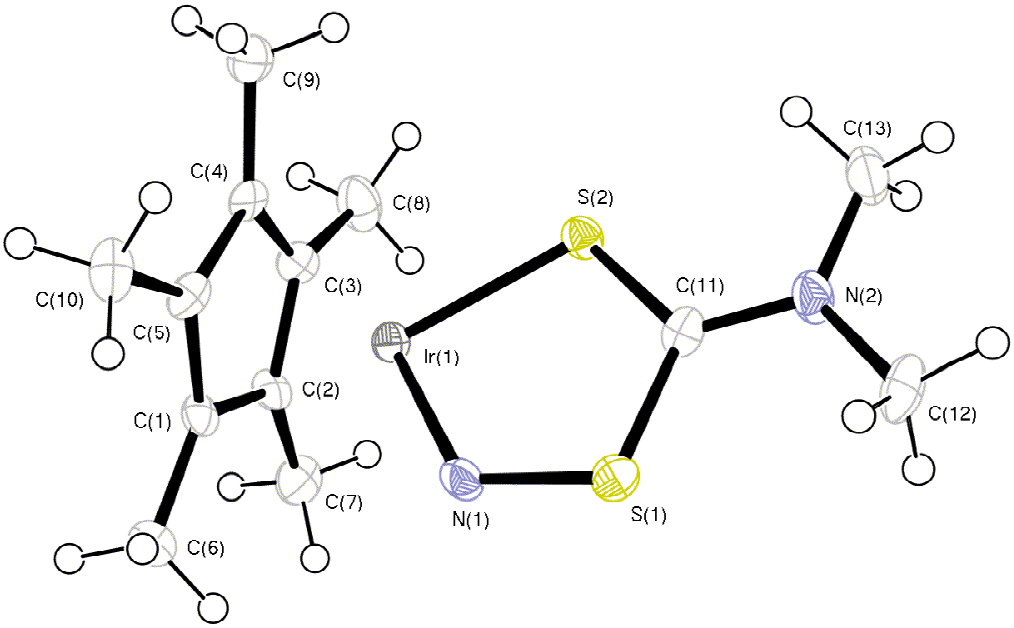
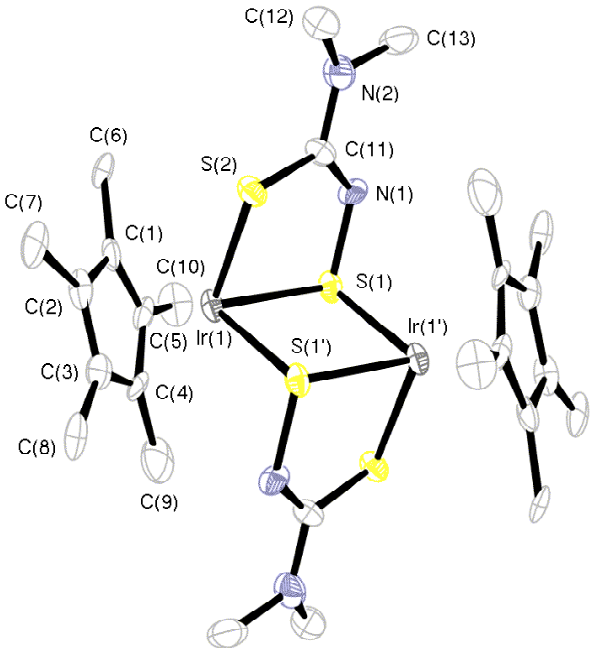


Figure S2 ORTEP of $Cp^{*}Ir\{NSC(NMe_2)S\}$ (**2**).

(*a*)



(*b*)

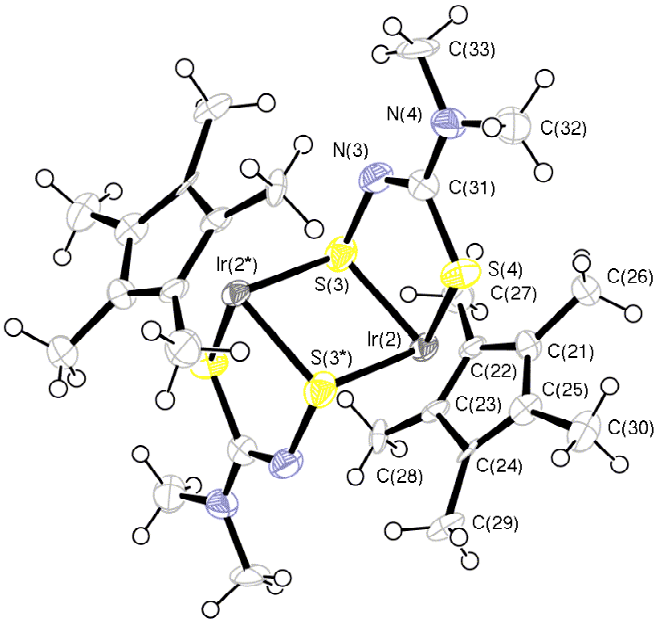


Figure S3 ORTEPs of two crystallographically independent molecules in $\{Cp^{*}Ir[SN{=}C(NMe_2)S]\}_2$ (**4**).

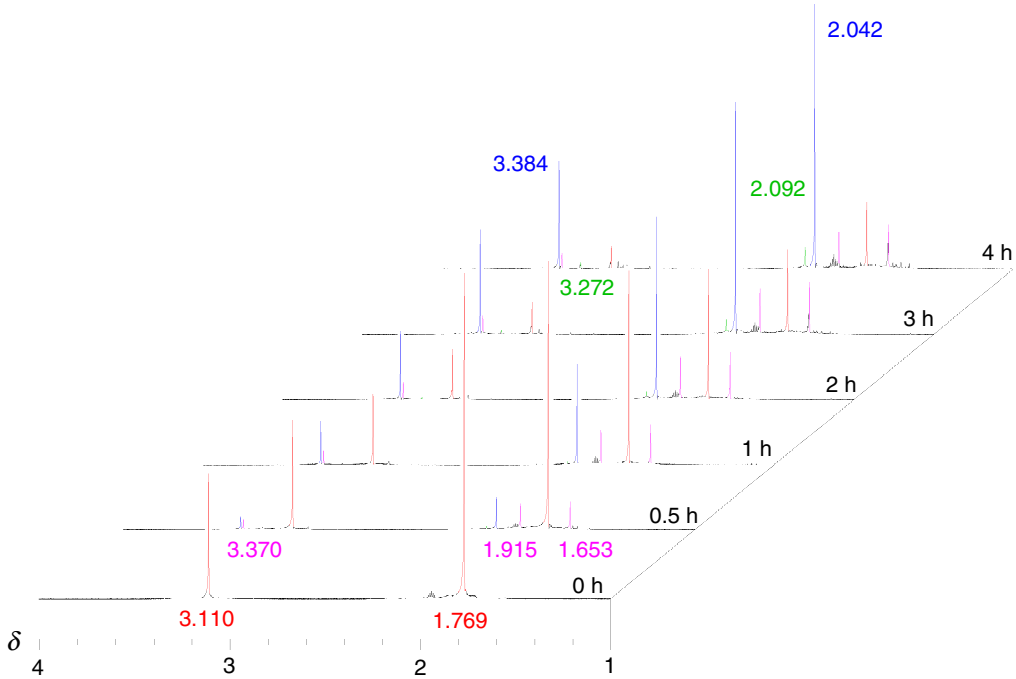


Figure S4 ^{1}H NMR spectral change on photolysis of Cp*Ir(dtc)(N_3) (**1**) in dry CD_3CN at temperature below 0 °C. Resonances in color are red **1**, blue **2**, green **3**, and purple by-product(s).

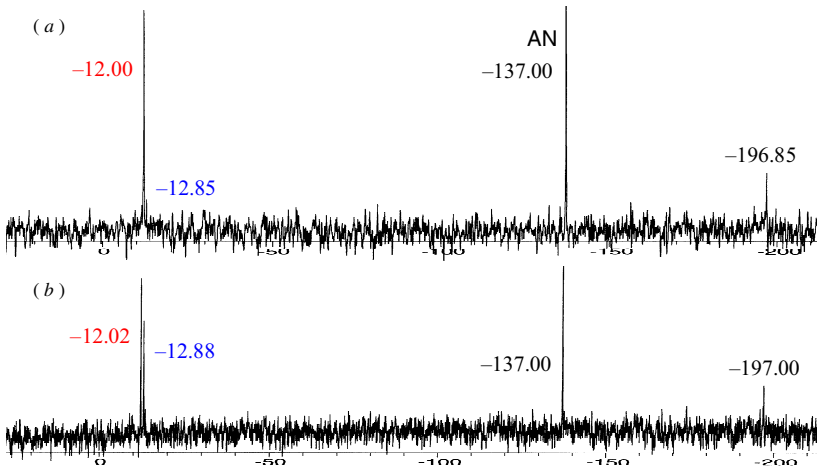


Figure S5 ^{15}N NMR spectra (at –20°C) of a mixture of Cp*Ir[^{15}NSC(NMe_2)S] (**2**-^{15}N) and Cp*Ir[NSC(NMe_2)S] (**2'**), after standing (*a*) in a freezer overnight and (*b*) at room temperature for 4 h. The resonances at δ –12.0 and –12.9 are due to **2**-^{15}N and **2'**-^{15}N, respectively. The peak at δ –197 is due to a minor by-product.

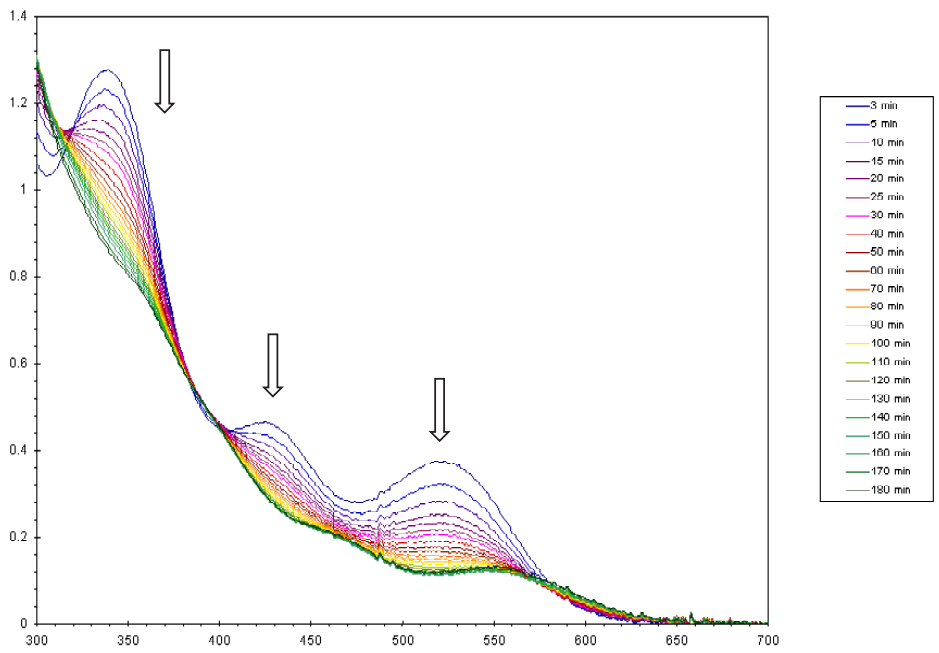


Figure S6 UV-vis absorption spectral change from the photochemical product (**2**) to the thermal product (**3**) (some decomposition accompanied) in CH_3CN at room temperature.

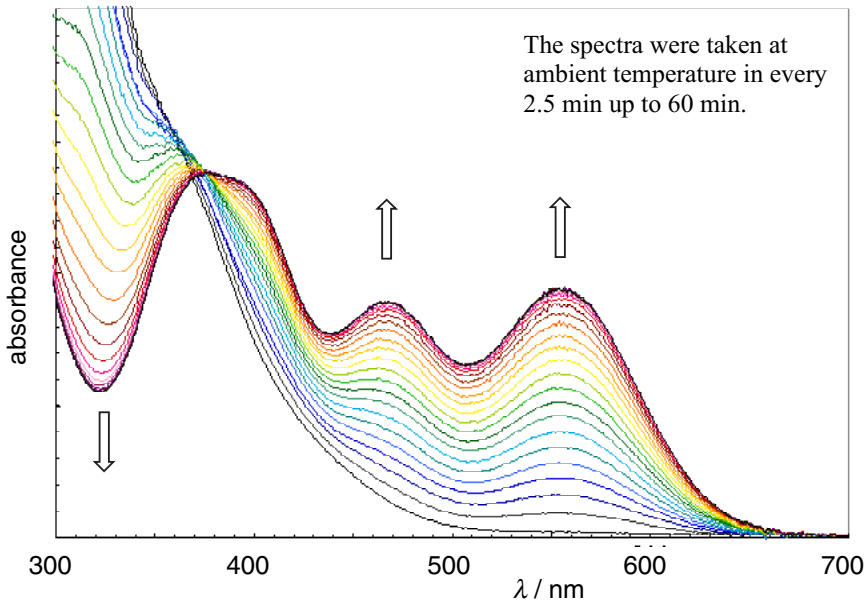


Figure S7 UV-vis absorption spectral change of a CH_2Cl_2 solution of yellow dimer product, $\{Cp^*Ir[SN{=}C(NMe_2)S]\}_2$ (**4**), to the corresponding monomer **3** at room temperature.