Sulfur-Bonded 2-Methylthiopyridine (2-MeSpy) Complex of Iridium(III). Crystal Structure of [Cp*IrI_2-(2-MeSpy-κS)] (Cp* = η^5-C_5Me_5)

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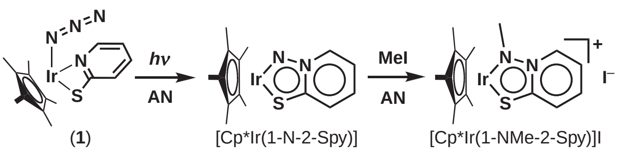
A reaction of [Cp*Ir(2-Spy)(N_3)] (Cp* = pentamethylcyclopentadienyl; 2-Spy = 2-pyridinethiolate) with two equivalents of methyl iodide afforded the diiodo complex bearing 2-MeSpy, [Cp*IrI_2(2-MeSpy)] (**3**). From X-ray crystallography and IR spectroscopy, the S atom of 2-MeSpy is coordinated to the metal ion in the solid state. In CD_2Cl_2, complex **3** exhibited a dissociation equilibrium of 2-MeSpy similar to the corresponding thioanisole complex of [Cp*IrI_2(MeSPh)].

Transiton-metal azide complexes often exhibit interesting reactivities on irradiation with UV–vis light or on addition of various electrophiles.[1–7] For instance, it has been well documented that photooxidation of early transition-metal(III) azido complexes gave the corresponding nitridometal(V) complexes.[2] In case of photolysis or acid decomposition of azidopentaammineiridium(III), a coordinated nitrene intermediate was postulated.[3] In addition, the azide complexes often react with alkynes or nitriles, affording triazolate or tetrazolate complexes via 1,3-dipolar cycloadditions.[4] Furthermore, it has recently been reported that a reaction of *cis*-di(azido)bis(2,2′-bipyridine)ruthenium(II) with methyl iodide produced a novel *N*-bonded methyleneimine (NH=CH_2-κN) complex.[5] We are investigating the reactivity of azido(pentamethylcyclopentadienyl)iridium(III) complexes incorporating short-bite didentate ligands, such as *N*,*N*-dialkyldithiocarbamate[6] or 2-pyridinethiolate (2-Spy).[7] Photolysis of [Cp*Ir(2-Spy)(N_3)] (**1**) in acetonitrile (AN) afforded a novel nitrogen-atom insertion product, [Cp*Ir(1-N-2-Spy)], which reacted further with MeI to give a *N*-methylated product, [Cp*Ir(1-NMe-2-Spy)]I (Scheme 1).[7] Here, we describe the reaction of complex **1** with MeI prior to photolysis and structural characterization of the product.



Scheme 1.

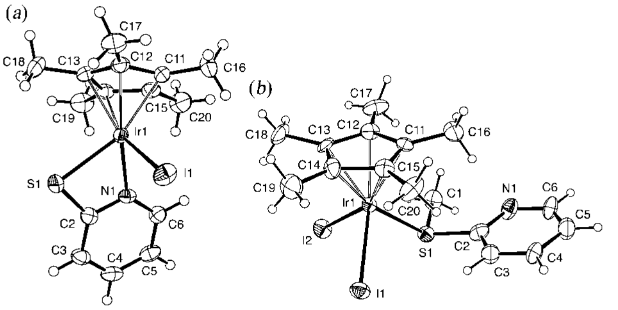
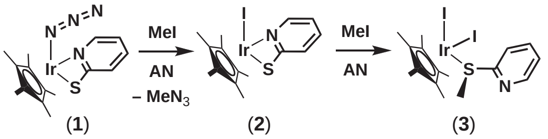


Fig. 1. Perspective views of (a) [Cp*Ir(2-Spy-$\kappa S,N$)I] (**2**) and (b) [Cp*IrI_2(2-MeSpy-κS)] (**3**).



Scheme 2.

A reaction of [Cp*Ir(2-Spy)(N_3)] (**1**) (0.035 mol dm^{-3} in CD_3CN) with two equivalent amounts of MeI at 30 °C was monitored by ^{1}H NMR spectroscopy. As the peaks for complex **1** decreased in intensity, the peaks corresponding to the iodo complex [Cp*Ir(2-Spy)I] (**2**), of which the molecular structure (Fig. 1a) and chemical shifts were confirmed by the sample prepared independently from [Cp*Ir(2-Spy)Cl] and NaI, appeared. After standing the reaction mixture for 8 h, the ^{1}H NMR spectrum indicated the formation of at least four complexes having a Cp*Ir fragment. The main product (**3**: ≈60% by integration) exhibited both Cp* and py resonances, which were different from those of **2** (complex **2** still remained in this mixture), together with a SMe resonance at δ 2.53. Two other weak Cp* resonances were assigned to [(Cp*IrI)$_2$(μ-I)$_2$][8] and [(Cp*IrI)$_2$(μ-N_3)$_2$].[9] In addition, the spectrum of the reaction mixture showed a broad singlet resonance at δ 2.98, which was probably due to methyl azide[10] generated in the reaction. When the reaction solution was allowed to stand for 2 days, red prismatic crystals of product **3** were deposited (together with a few red-brown platelet crystals of [(Cp*IrI)$_2$(μ-N_3)$_2$][9]). The crystal structure of **3** was determined by X-ray analysis; complex **3** is a diiodo complex containing a sulfur-bonded 2-methylthiopyridine, [Cp*IrI_2(2-MeSpy-κS)] (Fig. 1b). Thus, the reaction of **1** with MeI can be outlined as Scheme 2 (the minor by-products are omitted).

The Ir–S bond length in **3** is 2.380(4) Å, which is comparable to those in the related Cp*Ir^{III} thioether-κS complexes: [Cp*$IrCl_2$(dbt)] (dbt = dibenzothiophene) 2.375(2) Å,[11] [Cp*-$IrCl_2$(PhSCH_2SPh-κS)] 2.385(1) Å.[12] The structural parameters around the S atom in **3** are normal for a coordinated thioether ligand:[13] S1–C1 1.80(2), S1–C2 1.78(2) Å, Ir1–S1–C1 109.6(7), Ir1–S1–C2 111.4(5), and C1–S1–C2 101.7(9)°. The Ir–I bond lengths are 2.712(1) and 2.714(1) Å, and the I1–Ir1–I2 angle is 91.14(4)°. In contrast, in the chelating 2-Spy complex, **2**, the structural parameters associated with the four-membered chelate ring are highly strained; the S1–Ir1–N1, Ir1–S1–C2, and Ir1–N1–C2 bond angles are only 67.0(1), 80.4(2), and 102.5(4)°, respectively. The Ir1–S1 bond in **2**, 2.431(2) Å, is 0.05 Å longer than that in **3**.

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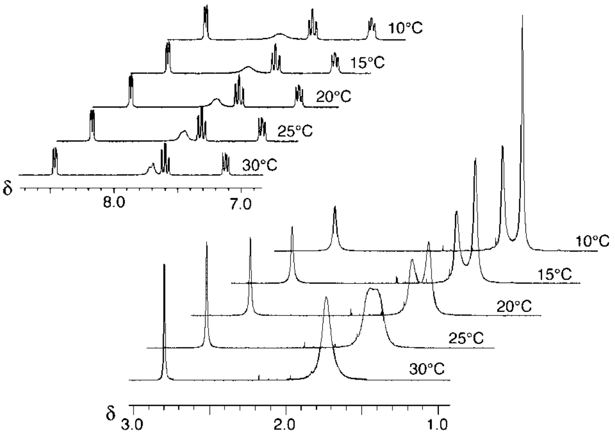

Fig. 2. Variable-temperature ^{1}H NMR spectra of complex **3** in CD_2Cl_2 in the pyridyl and the methyl region.

Complex **3** was directly prepared by reacting **2** and MeI in a nearly quantitative yield. Methylation at thiolate-S atom is a commonplace reaction,[14] but the resulting *S*-bonded 2-methylthiopyridine complex is rare (vide infra). We have, also, confirmed by IR spectroscopy that the pyridyl-N atom of 2-MeSpy in complex **3** does not coordinate to the Ir^{III} center in the solid state. In the spectrum of complex **2**, the absorption band due to an in-plane ring deformation of pyridyl moiety was observed at 652 cm^{-1}, which was indicative of the *N*-bonded pyridyl ligand, while complex **3** showed a band in the region for a free pyridyl group (607 cm^{-1}).[15]

Complex **3** in CD_3CN at 30 °C exhibited sharp ^{1}H NMR signals (see Experimental), while in CD_2Cl_2 at the same temperature the Cp* and py-3H resonances were broadened. On cooling the Cp* resonance (δ 1.74 at 30 °C) was split into two signals, and the py-3H and SMe resonances (δ 7.69 and 2.80, respectively, at 30 °C) became much broader (Fig. 2). At 0 °C two Cp* resonances were observed at δ 1.64 and 1.77 with an integration ratio of ca. 2:1. The lower-field signal seems to correspond to $[(Cp^*IrI)_2(\mu\text{-}I)_2]$, being indicative of the dissociation of 2-MeSpy from the Ir^{III} center. These variable-temperature ^{1}H NMR spectral behaviors were similarly observed for the analogous thioanisole complex $[Cp^*IrI_2(MeSPh)]$ (**4**), which was obtained as orange threadlike crystals. In CD_2Cl_2, the Cp* resonance of **4** was observed as a broad singlet (δ 1.69) at 30 °C and split into two signals (δ 1.64 and 1.77) on decreasing the temperature to 0 °C. The SMe and *ortho*-H (of Ph) resonances became broader on cooling (see Supporting Information). This spectral similarity of complexes **3** and **4** implies that the pyridyl-N atom of 2-MeSpy does not participate in coordination to the Cp^*IrI_2 fragment either in solution.

We have also attempted to prepare the corresponding 2-methoxypyridine (2-MeOpy) complex, but $[(Cp^*IrI)_2(\mu\text{-}I)_2]$ did not react with (excess) 2-MeOpy to give the desired complex. Instead, the pyridine complex $[Cp^*IrI_2(py)]$ (**5**) was isolated as an orange powdery solid by a reaction of $[(Cp^*IrI)_2(\mu\text{-}I)_2]$ and pyridine in dichloromethane. These results suggest that the unfavorable formation of the *N*-bonded 2-MeSpy or 2-MeOpy complexes must result from a severe steric hindrance between the Cp^*IrI_2 fragment and the MeS or MeO *ortho*-substituent of (coordinated) pyridine.

In summary, the reaction of $[Cp^*Ir(2\text{-}Spy)(N_3)]$ and two equivalent amounts of MeI afforded the diiodo complex of $[Cp^*IrI_2(2\text{-}MeSpy)]$ (**3**), in which 2-MeSpy acted as a monodentate *S*-bonded (κS) ligand; neither in the solid state nor in solution was detected any evidence for the κN coordination mode of 2-MeSpy. Contrary to the rich chemistry of transition-metal thiolate complexes, surprisingly few studies have been reported so far for 2-MeSpy or 2-RSpy (R = alkyl) complexes.[16,17] In most reported complexes, the alkylthiopyridines act as a monodentate *N*-bonded (κN), a didentate chelating ($\kappa^2 N,S$), or a bridging ($\mu\text{-}\kappa N{:}\kappa S$) ligand. For the gold(I) complexes of $[Au(2\text{-}MeSpy)_2]ClO_4$ and $[Au(2\text{-}MeSpy)(tht)]ClO_4$ (tht = tetrahydrothiophene), a κS-coordination mode of 2-MeSpy was speculated but without enough structural evidences.[16] To the best of our knowledge, the present Cp^*Ir^{III} complex of **3** is the first example in which the *S*-bonded 2-MeSpy was confirmed crystallographically and spectroscopically.

Experimental

Caution. Transition-metal azido complexes are, in general, potentially explosive, so that should be handled with great caution, although we did not have any accident with this Cp^*Ir^{III}–N_3 system.

General. The preparations of the azido complex **1** and the chloro analogue, $[Cp^*Ir(2\text{-}Spy)Cl]$, were reported previously.[7] Sodium iodide, methyl iodide, thioanisole, 2-methoxypyridine, and solvents were purchased from Nacalai Tesque, Inc. or Wako Pure Chemicals Industry, Ltd., and used as received. Variable-temperature ^{1}H NMR spectra were acquired on a JEOL EX-270 spectrometer. Chemical shifts were referenced to the residual ^{1}H NMR signals of the deuterated solvents and reported vs TMS. Infrared spectra were measured on a Jasco FT-IR 410 spectrophotometer using Nujol mulls.

$[Cp^*Ir(2\text{-}Spy)I]$ (2). A mixture of $[Cp^*Ir(2\text{-}Spy)Cl]$ (280 mg, 0.59 mmol) and NaI (490 mg, 3.3 mmol) in methanol (60 cm^3) was stirred at ambient temperature for 3 h. After evaporation of the solvent, the residue was extracted with dichloromethane. The filtered extract was concentrated (to ca. 2 cm^3) under reduced pressure, and diethyl ether vapor was diffused into the concentrate to give red block crystals. Yield: 303 mg (91%). Anal. Found: C, 31.63; H, 3.36; N, 2.42%. Calcd for $C_{15}H_{19}IIrNS$: C, 31.92; H, 3.39; N. 2.48%. ^{1}H NMR (CD_3CN, 303 K): δ 1.82 (s, Cp*, 15H), 6.54 (dt, J = 8.2, 1.1 Hz, py-3H, 1H), 6.81 (ddd, J = 7.4, 5.7, 1.1 Hz, py-5H, 1H), 7.33 (ddd, J = 8.2, 7.4, 1.7 Hz, py-4H, 1H), 8.00 (ddd, J = 5.7, 1.7, 1.1 Hz, py-6H, 1H).

$[Cp^*IrI_2(2\text{-}MeSpy)]$ (3). To an acetonitrile solution (10 cm^3) of complex **2** (105 mg, 0.186 mmol) was added MeI (200 mg, 1.4 mmol). After standing for a day at room temperature, the mixture was allowed to evaporate slowly (to ca. 2 cm^3), depositing red prismatic crystals. Yield: 91 mg (69%). Anal. Found: C, 26.99; H, 3.13; N, 1.97%. Calcd for $C_{16}H_{22}I_2IrNS$: C, 27.20; H, 3.14; N, 1.98%. ^{1}H NMR (CD_3CN, 303 K): δ 1.81 (s, Cp*, 15H), 2.53 (s, SMe, 3H), 7.04 (ddd, J = 7.4, 4.9, 1.0 Hz, py-5H, 1H), 7.26 (dm, J = 8.3 Hz, py-3H, 1H), 7.57 (ddd, J = 8.3, 7.4, 1.9 Hz, py-4H, 1H), 8.39 (dm, J = 4.9 Hz, py-6H, 1H).

$[Cp^*IrI_2(MeSPh)]$ (4). Diethyl ether vapor was diffused into a dichloromethane (2 cm^3) solution of $[(Cp^*IrI)_2(\mu\text{-}I)_2]$[8] (130 mg, 0.11 mmol) and MeSPh (230 mg, 1.85 mmol) in a closed vessel. The resulting orange threadlike crystals were collected by filtration and dried in vacuo. Yield: 121 mg (77%). Anal. Found: C, 28.77; H, 3.35%. Calcd for $C_{17}H_{23}I_2IrS$: C, 28.94; H, 3.29%.

^{1}H NMR (CD_3CN, 303 K): δ 1.78 (s, Cp*, 15H), 2.61 (s, SMe, 3H), 7.20–7.41 (m, SPh, 5H).

[Cp*IrI$_2$(py)] (5). Pyridine (2 cm^3) was added with sitirring to a red solution of [(Cp*IrI)$_2$(μ-I)$_2$] (50 mg) in dichloromethane (6 cm^3). The color of the mixture immediately turned orange, and an orange precipitate formed after a few minutes. After stirring for 30 min, the product was collected by filtration, washed with CH_2Cl_2 (2 cm^3) and Et_2O (3 cm^3), and dried in vacuo. Yield: 42 mg (74%). Anal. Found: C, 27.35; H, 3.04; N, 2.19%. Calcd for $C_{15}H_{20}I_2IrN$: C, 27.28; H, 3.05; N, 2.12%. ^{1}H NMR (dmso-d_6, 303 K): δ 1.88 (s, Cp*, 15H), 7.38 (ddd, $J = 7.6$, 4.2, 1.6 Hz, py-3,5H, 2H), 7.78 (tt, $J = 7.6$, 2.0 Hz, py-4H, 1H), 8.57 (dt, $J = 4.2$, 1.6 Hz, py-2,6H, 2H). IR (Nujol): ν(py) = 639 cm^{-1}.

Crystallography. A red block crystal of **2** suitable for the X-ray diffraction study (approximate dimension of 0.25 × 0.15 × 0.15 mm^3) was mounted with a cryoloop and flash-cooled by a cold nitrogen stream. The intensity data were obtained at −73(2) °C on a Rigaku R-axis rapid diffractometer [$8 \le 2\theta \le 55°$, λ(Mo Kα) = 0.71073 Å], and numerical absorption collections from crystal shape were applied.[18] The X-ray diffraction data of a red prismatic crystal of **3** (0.24 × 0.24 × 0.16 mm^3) sealed in a glass capillary tube were collected on a Rigaku AFC5R diffractometer at 23(2) °C [$2\theta \le 60°$, λ(Mo Kα) = 0.71073 Å]. Absorption effects were corrected by an empirical method based on three sets of Ψ-scan data.[19] The structures were solved by the direct method using SIR92 program,[20] and refined on F^2 by full-matrix least-squares using SHELXL97 program.[21] All non-H atoms were refined anisotropically, and H atoms were treated as riding models.

The crystallographic data for **2**: $C_{15}H_{19}IIrNS$, MW = 564.47, $T = 200(2)$ K, orthorhombic, *Pbca*, $a = 8.5551(4)$ Å, $b = 16.7071(7)$ Å, $c = 23.6078(9)$ Å, $V = 3374.3(2)$ Å^3, $Z = 8$, $D_{\rm calcd} = 2.222$ Mg m^{-3}, $R_{\rm int} = 0.040$, $F(000) = 2096$, μ(Mo Kα) = 9.855 mm^{-1}, No. of independent reflns = 3765, No. of param = 173, $R1[F^2\colon F^2 > 2\sigma(F^2)] = 0.032$, $wR2(F^2\colon \text{all data}) = 0.071$. For **3**: $C_{16}H_{22}I_2IrNS$, MW = 706.41, $T = 296(2)$ K, orthorhombic, *Pbca*, $a = 16.710(2)$ Å, $b = 16.706(2)$ Å, $c = 14.044(2)$ Å, $V = 3920.6(9)$ Å^3, $Z = 8$, $D_{\rm calcd} = 2.394$ Mg m^{-3}, $R_{\rm int} = 0.052$, $F(000) = 2592$, μ(Mo Kα) = 10.06 mm^{-1}, No. of independent reflns = 5721, No. of param = 191, $R1[F^2\colon F^2 > 2\sigma(F^2)] = 0.056$, $wR2(F^2\colon \text{all data}) = 0.173$.

Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposition numbers CCDC-613445 and 613446 for compounds **2** and **3**, respectively. Copies of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information

Variable-temperature ^{1}H NMR spectra of complex **4** in CD_2Cl_2. This material is available free of charge on the Web at: http://www.csj.jp/journals/bcsj/.

References

1 Z. Dori, R. F. Ziolo, *Chem. Rev.* **1973**, *73*, 247; J. Strähle, *Comments Inorg. Chem.* **1985**, *4*, 295.

2 J. Du Bois, C. S. Tomooka, J. Hong, E. M. Carreira, *Acc. Chem. Res.* **1997**, *30*, 364; C. A. Grapperhaus, B. Mienert, E. Bill, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **2000**, *39*, 5306; M. Tsuchimoto, N. Yoshioka, S. Ohba, *Eur. J. Inorg. Chem.* **2001**, 1045.

3 B. C. Lane, J. W. McDonald, V. G. Myers, F. Basolo, R. G. Pearson, *J. Am. Chem. Soc.* **1971**, *93*, 4934; E. D. Johnson, F. Basolo, *Inorg. Chem.* **1977**, *16*, 554.

4 W. Rigby, P. M. Bailey, J. A. McCleverty, P. M. Maitlis, *J. Chem. Soc., Dalton Trans.* **1979**, 371; C.-W. Chang, G.-H. Lee, *Organometallics* **2003**, *22*, 3107; K. S. Singh, C. Thöne, M. R. Kollipara, *J. Organomet. Chem.* **2005**, *690*, 4222.

5 H. Nagao, T. Kikuchi, M. Inukai, A. Ueda, T. Oi, N. Suzuki, M. Yamasaki, *Angew. Chem., Int. Ed.* **2006**, *45*, 3131.

6 T. Suzuki, A. G. Dipasquale, J. M. Mayer, *J. Am. Chem. Soc.* **2003**, *125*, 10514.

7 Y. Sekioka, S. Kaizaki, J. M. Mayer, T. Suzuki, *Inorg. Chem.* **2005**, *44*, 8173.

8 M. R. Churchill, S. A. Julis, *Inorg. Chem.* **1979**, *18*, 1215.

9 The crystal structure of the μ-N_3 dimer was also analyzed by X-ray, but the results were not sufficient to report here, because of the highly efflorescent nature of the crystal and the partial co-crystallization of the μ-I dimer. However, the resulting atomic arrangement of [(Cp*IrI)$_2$(μ-N_3)$_2$] was believed to be correct.

10 A. Mertens, K. Lammertsma, M. Arvanaghi, G. A. Olah, *J. Am. Chem. Soc.* **1983**, *105*, 5657.

11 K. M. Rao, C. L. Day, R. A. Jacobson, R. J. Angelici, *Inorg. Chem.* **1991**, *30*, 5046.

12 M. Valderrama, R. Contreras, V. Arancibia, D. Boys, *J. Organomet. Chem.* **2001**, *620*, 256.

13 S. Ye, W. Kaim, M. Albrecht, F. Lissner, T. Schleid, *Inorg. Chim. Acta* **2004**, *357*, 3325.

14 M. Lissel, S. Schmidt, B. Neumann, *Synthesis* **1986**, 382; N. Furukawa, F. Takahashi, T. Kawai, K. Kishimoto, S. Ogawa, S. Oae, *Phosphorus, Sulfur* **1983**, *16*, 167.

15 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 5th ed., John Wiley & Sons, New York, U.S.A., **1997**, Part B, p. 23; T. Suzuki, M. Kita, K. Kashiwabara, J. Fujita, *Bull. Chem. Soc. Jpn.* **1990**, *63*, 3434.

16 J. Vicente, M.-T. Chicote, C. Rubio, *Chem. Ber.* **1996**, *129*, 327; J. Vicente, M.-T. Chicote, S. Huertas, M. C. R. de Arellano, P. G. Jones, *Eur. J. Inorg. Chem.* **1998**, 511.

17 A. J. Deeming, M. N. Meah, P. A. Bates, M. B. Hursthouse, *Inorg. Chim. Acta* **1988**, *142*, 37; G. F. de Sousa, C. A. L. Filgueiras, *Trans. Met. Chem.* **1990**, *15*, 290.

18 T. Higashi, *Shape*, Rigaku Corporation, Akishima, Tokyo, **1999**.

19 A. C. T. North, D. C. Phillips, F. S. Mathews, *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

20 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. Burla, G. Polidori, M. Camalli, *J. Appl. Crystallogr.* **1994**, *27*, 435.

21 G. M. Sheldrich, *SHELXL97*, University of Göttingen, Germany, **1997**.