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Structure and Reactivity of a Pyridine-1-imido-2-thiolato Complex of Iridium(III), Cp*Ir(1-N-2-Spy), Generated by Photolysis of the (Azido)(pyridine-2-thiolato) Complex, Cp*Ir(2-Spy)(N_3)

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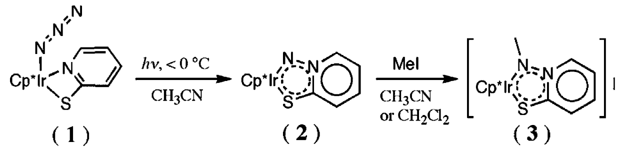
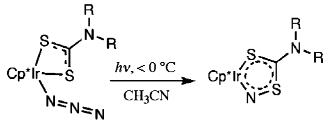
Photolysis of the (azido)(pyridine-2-thiolato)iridium(III) complex Cp*Ir(2-Spy)(N_3) (**1**) gave a pyridine-1-imido-2-thiolato complex, Cp*Ir(1-N-2-Spy) (**2**), in which one of the nitrogen atoms of the azide ligand has been inserted into the Ir–N(py) bond (Cp* = η^5-C_5Me_5). Complex **2** reacted quantitatively with methyl iodide to give the N-methylated product, [Cp*Ir(1-NMe-2-Spy)]I (**3**). X-ray crystallography revealed that both **2** and **3** have similar two-legged piano stool structures with planar 1-N-2-Spy^{2-} or 1-NMe-2-Spy^{-} ligands, which form iridacyclopentadienyl-like rings by moderate S(pπ)/N(pπ) to Ir(dπ) π donation.

Scheme 1. Photolysis of **1** and Methylation of the Resulting Pyridine-1-imido-2-thiolato Complex (**2**)



As a new synthetic methodology for nitrogen-containing organic/inorganic compounds, nitrogen atom transfer[1−3] has become of interest in recent years. By analogy with metal oxo complexes available for oxygen-atom-transfer reagents,[3c,4] the nitrido (or imido) complexes having a metal−nitrogen multiple bond could be effective for nitrogen-atom-transfer reactions.[5] We are exploring the chemistry of iridium(III) azido and potentially iridium(V or IV) nitrido complexes.[6] A previous study reported that photolysis of Cp*Ir(S_2CNR_2)(N_3) (Cp* = η^5-C_5Me_5, R = Me or Et) resulted in the insertion of a nitrogen atom of the azide ligand into an Ir−S bond, affording Cp*Ir[NSC(NR_2)S] (eq 1).[7] Described here



(1)

is the photolysis of Cp*Ir(2-Spy)(N_3) (**1**; 2-Spy$^-$ = pyridine-2-thiolate), which yields Cp*Ir(1-N-2-Spy) (**2**), the first metal complex bearing a pyridine-1-imido-2-thiolate (1-N-2-Spy^{2-}) ligand (Scheme 1).

The azido complex **1** was prepared from Cp*Ir(2-Spy)-Cl[8,9] and NaN_3 in MeOH.[9,10] Anaerobic photolysis[9] of a yellow-orange acetonitrile solution of **1** (ca. 10 mM) gave a gradual color change of the solution to dark red. ^{1}H NMR monitoring of the reaction solution indicated the formation of a main product (**2**) in 65% yield after 2 h, together with some unidentified byproducts (<5% each). When the photolysis was carried out with a nearly saturated (ca. 30 mM) acetonitrile solution of **1**, the main product **2** could be obtained as dark-red crystals in 16% isolated yield.[9] The ^{1}H NMR spectrum of isolated **2**, similar to that of the photolysis solution, shows a downfield-shifted Cp* signal at δ 2.11.

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(8) This complex was prepared from $[Cp^*IrCl_2]_2$, 2-pySH, and NaOMe (in a 1:2:2 molar ratio) in MeOH in 84% yield.

(9) See the Supporting Information for full details.

(10) Yield: 82%. Anal. Calcd for $C_{15}H_{19}IrN_4S$: C, 37.56; H, 3.99; N, 11.68. Found: C, 37.47; H, 3.88; N, 11.60. IR (Nujol mull): $\nu_{as}(N_3) = 2034$ cm^{-1}. ^{1}H NMR (CD_3CN, 303 K, 270 MHz): δ 1.76 (Cp*, 15H), 6.69, 6.90, 7.39, and 8.02 (py, 4H).

10.1021/ic051097z CCC: $30.25

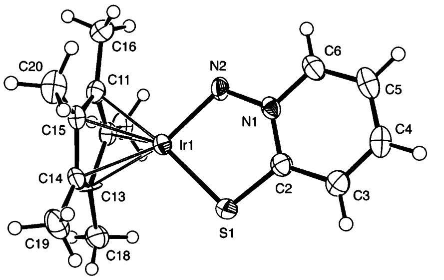

Figure 1. ORTEP (50% probability level) and selected bond lengths (Å) and angles (deg) for **2**: Ir1−S1 2.251(3), Ir1−N2 1.946(10), S1−C2 1.705(12), N1−N2 1.364(13), N1−C2 1.370(16), S1−Ir1−N2 85.4(3), Ir1−N2−N1 117.3(8), Ir1−S1−C2 99.6(4).

The IR spectrum of **2** (Nujol mull) did not show an azide stretch, and the EI-MS spectrum exhibited an isotopic distribution corresponding to that of $[C_{15}H_{19}IrN_2S]^+$ ($m/z = 452$). The UV−vis spectrum of **2** in acetonitrile showed three intense bands centered at 510 ($\epsilon = 4300$), 422 (5100), and 317 nm (16 000 M^{-1} cm^{-1}). Similar spectral features have been observed for Cp*Ir[NSC(NR_2)S][7] and Cp*Ir(1,2-$S_2C_6H_4$),[11] both of which have a five-coordinate (two-legged piano stool) structure.

The molecular structure of **2** (Figure 1) determined by single-crystal X-ray analysis[12] revealed a pyridine-1-imide-2-thiolate(2−) ligand (1-N-2-Spy^{2-}) in which an azide nitrogen atom has been inserted into the Ir−N(py) bond. The five-membered chelate ring formed by 1-N-2-Spy^{2-} is highly planar and coplanar to the pyridyl ring. The Ir−N2 bond of **2** [1.946(10) Å], close to that of Cp*Ir[NSC(NMe_2)S] [1.911(5) Å],[7] is longer than the Ir−N bonds in Bergman's Cp*Ir(NR) complexes (1.71−1.75 Å)[13] but shorter than the typical values for iridium(III) amine, amide, or imine complexes (2.01−2.18 Å).[14] Similarly, the Ir−S bonds of **2** [2.251(3) Å], Cp*Ir[NSC(NR_2)S] [2.272(2) Å],[7] and Cp*Ir(1,2-$S_2C_6H_4$) [2.249(6) Å][11] are shorter than those of the iridium(III) arenethiolate complexes (2.35−2.42 Å).[14] The N1−N2 and S1−C2 bond lengths of **2** [1.36(1) and 1.71(1) Å, respectively] are also intermediates between typical single and double bonds.[14,15] Therefore, the five-membered chelate ring formed by 1-N-2-Spy^{2-} can be treated as an iridacyclopentadienyl-like moiety, and the iridium(III) center approaches an 18-electron configuration because of effective π-electron donation from the imido and/or thiolato groups.

The two types of chemical mechanisms proposed for the photochemical N-atom-insertion reaction of the iridium(III) azido complexes Cp*Ir(S_2CNR_2)(N_3) (eq 1)[7] could also apply to the photolysis of **1** (Scheme 1). Photolytic cleavage of the azide ligand could generate N_2 and a transient nitridoiridium(V) species that rapidly inserts the N atom into a metal−ligand bond. Alternatively, photolysis could cause dissociation of a donor ligand, such as the pyridine in **1** or one sulfur of the $S_2CNR_2^-$ ligand in Cp*Ir(S_2CNR_2)(N_3), which then attacks the coordinated azide with displacement of N_2. The observation that photolysis of **1** leads to N-atom insertion into the Ir−N(py) bond rather than the Ir−S one seems to support the latter mechanism. The coordinated pyridine should not be reactive as a nucleophile to attack a putative nitrido ligand, especially compared with the coordinated S atom of the $S_2CNR_2^-$ or 2-Spy^- ligands. In addition, the neutral donor N(py) seems more likely to dissociate upon photolysis rather than an anionic S donor in 2-Spy^- or $S_2CNR_2^-$.

Photolysis of **1** in pyridine-d_5 was explored with the goal of trapping a photogenerated intermediate. ^{1}H NMR monitoring showed **2** to be the major product even in this coordinating solvent, with a complicated mixture of byproducts. The related NCO complexes Cp*Ir(L_2)(NCO) (L_2 = S_2CNMe_2 or 2-Spy) have been prepared, in which the coordinated NCO^- was expected to be more reactive toward attack by a dangling pyridine but less eager to lose CO. However, these complexes were unreactive toward photolysis, with no spectral change being observed.

The optical spectrum of **1** shows an intense absorption at 290 nm ($\epsilon = 10\,400$ M^{-1} cm^{-1}), with broad shoulders at 360 and 450 nm ($\epsilon = \sim 2500$ and ~ 400 M^{-1} cm^{-1}).[9] Filtering the photolysis light through a solution of benzene in isooctane (1.3 M; half cutoff wavelength = 275 nm) gave no effect on the photochemical conversion of **1** to **2**. However, the rate of conversion of **1** to **2** was about half as fast when photolysis was conducted using a naphthalene filter solution (0.1 M in isooctane; half cutoff wavelength = 325 nm).[9] This suggests that the reactive excited state is best formed by irradiation into the 290-nm absorption. This result is not mechanistically informative, however, in the absence of assignments for the electronic transitions.

Complex **2** is thermally stable in the solid state and in solution under an inert atmosphere. The reaction of **2** with an equimolar amount of methyl iodide in dichloromethane or acetonitrile gave a gradual color change of the solution from red to orange within 20 min at ambient temperature. ^{1}H NMR spectra indicate that **2** is quantitatively converted to an addition product (**3**) exhibiting its Cp* resonance at δ 2.07 and the added CH_3 signal at δ 4.23 (with the integration ratio of 15:3:4 for Cp*/CH_3/pyridyl moieties). After evaporation of the reaction solution, recrystallization from acetonitrile/diethyl ether deposited red-orange crystals of **3**.[9,16] The UV−vis absorption spectrum of **3** in acetonitrile exhibited three absorption bands at 483 ($\epsilon = 730$), 368 (4400), and

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(12) Crystallographic data for **2**: $C_{15}H_{19}IrN_2S$, $M = 451.58$, $T = 200(2)$ K, monoclinic, $P2_1/c$, $a = 13.087(8)$ Å, $b = 8.418(4)$ Å, $c = 13.617(7)$ Å, $\beta = 99.12(5)°$, $V = 1481(1)$ Å^3, $Z = 4$, $\rho_c = 2.025$ Mg m^{-3}, μ(Mo Kα) = 9.143 mm^{-1}, 13 593 reflns collected, 3356 unique ($R_{int} = 0.066$), $R1\{I > 2\sigma(I)\} = 0.055$, $wR2$(all data) = 0.145.

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(15) Typical bond lengths: N−N in hydrazine, ∼1.47 Å; N−N in pyrazine, ∼1.34 Å; N═N in diazene, ∼1.15 Å; C−S, ∼1.82 Å; C═S, ∼1.55 Å.

(16) Yield: ca. 70%. Anal. Calcd for $C_{16}H_{22}IIrN_2S$: C, 32.38; H, 3.74; N, 4.72. Found: C, 32.51; H, 3.66; N, 4.89. Crystallographic data: $M = 593.52$, $T = 200(2)$ K, triclinic, $P\bar{1}$, $a = 7.100(7)$ Å, $b = 10.183(11)$ Å, $c = 12.694(13)$ Å, $\alpha = 88.28(3)°$, $\beta = 87.04(3)°$, $\gamma = 84.64(2)°$, $V = 912.2(16)$ Å^3, $Z = 2$, $\rho_c = 2.161$ Mg m^{-3}, μ(Mo Kα) = 9.120 mm^{-1}, 8844 reflns collected, 4085 unique ($R_{int} = 0.025$), $R1\{I > 2\sigma(I)\} = 0.031$, $wR2$(all data) = 0.075.

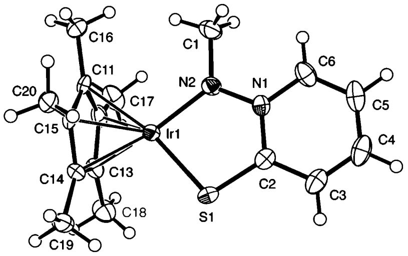

Figure 2. ORTEP (50% probability level) of the cationic part in **3**. Selected bond lengths (Å) and angles (deg): Ir1−S1 2.243(2), Ir1−N2 1.965(5), S1−C2 1.710(6), N1−N2 1.389(6), N1−C2 1.371(7), N1−C6 1.381(7), S1−Ir1−N2 83.4(1), Ir1−N2−N1 121.2(3), Ir1−S1−C2 100.7(2).

313 nm (25 000 M^{-1} cm^{-1}), and the FAB-MS spectrum gave an isotopic distribution corresponding to that of $[C_{16}H_{22}IrN_2S]^+$ ($m/z = 467$). X-ray crystallography for **3**[16] revealed that the crystal consisted of the N-methylated cationic complex having a two-legged-piano-stool structure (Figure 2) and an iodide anion, [Cp*Ir(1-NMe-2-Spy)]I (**3**). The iodide does not show any significant contact either to the Ir center or to the ligands. Methylation of the 1-N-2-Spy^{2-} ligand occurred at the imide N atom, in contrast to the typical methylation of 2-Spy^- at the S atom. The structure of the cationic complex in **3** is very similar to that of **2**. In particular, the iridacyclopentadienyl-like structure of the five-membered chelate ring is maintained upon N-methylation to 1-N-2-Spy^{2-}. The only substantial differences are small changes in bond angles, such as a widening of ∠Ir−N2−N1 from 117.3(8)° in **2** to 121.2(3)° in **3**. Furthermore, the isolation of the iodide anion indicates the stability of the coordinatively unsaturated complex **3** toward the attack of nucleophiles.

Complexes **2** and **3** bear new ligands, pyridine-1-imide-2-thiolate(2−) (1-N-2-Spy^{2-}) and pyridine-1-methylimine-2-thiolate (1-NMe-2-Spy^-), respectively. Related organic compounds with an NAr group attached to the pyridyl nitrogen have been prepared, 2-sulfanylpyridinium *N*-arylimides 1-NAr-2-(SR)py.[17] A structurally similar imido/thiolate bidentate ligand with a phenylene bridge instead of a pyridyl one, 2-imidothiophenolate(3−), has been reported in $Mo(S_2CNEt_2)_2X(NC_6H_4S)$ (X = Cl or OMe).[18] In addition, many complexes with the 2-amidothiophenolate(2−) ligand have been characterized since the first X-ray analysis of $Mo(SC_6H_4NH)_3$ was described in 1978.[19] Among them, cobalt(III) complexes having a two-legged-piano-stool structure, $Cp'Co(SC_6H_4NH)$ (Cp′ = Cp* or η^5-C_5H_5),[20] are closely related to **2** and **3**. In recent years, these 2-amino- or iminothiophenolates have attracted attention as redox noninnocent ligands.[21] The novel ligands of 1-N(R)-2-Spy^{n-} synthesized in this study could also be interesting in this regard.

In summary, photolysis of **1** gave a pyridine-1-imido-2-thiolato complex, **2**, a result of N-atom insertion into the Ir−N(py) bond. This complex can be methylated at the imide N site with CH_3I, affording **3**. X-ray crystallography revealed that complexes **2** and **3** have two-legged-piano-stool structures in which a planar 1-N-2-Spy^{2-} or 1-NMe-2-Spy^- ligand forms an iridacyclopentadienyl-like chelate ring with moderate S(pπ)/N(pπ) to Ir(dπ) π donation.

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Supporting Information Available: Experimental procedures including syntheses and spectra of Cp*Ir(2-Spy)Cl and **1**−**3**, photolysis experiments, and X-ray crystallographic information for **2** and **3** (PDF/CIF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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