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# Reactivities of the N-Atom-inserted Ligands, $NSC(NR_2)S^{2-}$ and $SN{=}C(NR_2)S^{2-}$, in Iridium(III) Complexes

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Reactions of $[Cp^*Ir\{NSC(NR_2)S\}]$ ($Cp^* = \eta^5\text{-}C_5Me_5$, R = Me or Et,) with alkyl halides (MeI or BnBr) in acetonitrile gave the *N*-alkylated products, $[Cp^*Ir\{R'NSC(NR_2)S\}]^+$ (R′ = Me or Bn). These complexes readily reacted with $PPh_3$ to give adducts. In contrast, $[Cp^*Ir\{SN{=}C(NR_2)S\}]$ formed their $PPh_3$ adducts, which gave thermally stable *S*-alkylated products by reactions with alkyl halides.

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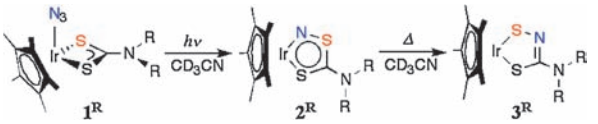
Transition-metal complexes make it feasible to investigate the reactivity of atomic and molecular ligands which are unstable in the metal-free states. Also, the ligands bound to a metal ion often exhibit novel physical and chemical properties, which cannot be achieved by themselves. Therefore, the study of reactivity of the coordinated ligands is efficient to develop new types of organic/inorganic compounds. In particular, the reaction at the ligating heteroatoms (i.e., N, O, P, etc.) is fascinating to evaluate,[1–3] because they often have very different electronic states in the metal complexes from those of the free ligands. In a previous study,[4] we have reported that photolysis of $[Cp^*Ir(N_3)(R_2dtc)]$ ($\mathbf{1^R}$: $R_2dtc$ = *N*,*N*-dialkyldithiocarbamate; R = Me or Et) gave an insertion of N-atom originated from the azido ligand into the Ir–S bond to afford thioimido complexes, $[Cp^*Ir\{NSC(NR_2)S\}]$ ($\mathbf{2^R}$), which were thermally converted to the iminethiolato isomers, $[Cp^*Ir\{SN{=}C(NR_2)S\}]$ ($\mathbf{3^R}$), as shown in eq 1. In this study we have examined the reactivities of these complexes toward methyl iodide (MeI), benzyl bromide (BnBr), and triphenylphosphane ($PPh_3$), in order to develop new chelate ligands having *N*-functional groups.



(1)

Complex $\mathbf{2^R}$ was inactive toward the addition of $PPh_3$, but reacted immediately with MeI, similar to the related pyridine-1-imido-2-thiolato complex, $[Cp^*Ir(1\text{-}N\text{-}2\text{-}Spy)]$.[5] When a small excess of MeI was added to a $CD_3CN$ solution of $\mathbf{2^{Me}}$, the $^1H$ NMR for the $Cp^*$ group ($\delta$ 2.04 for $\mathbf{2^{Me}}$) was observed at $\delta$ 1.96 (the conversion proceeded nearly quantitatively: Figure S1).[5] Such a small shift to higher-field was similarly observed in the reaction of $[Cp^*Ir(1\text{-}N\text{-}2\text{-}Spy)]$ with MeI, which resulted in *N*-methylation to afford $[Cp^*Ir(1\text{-}NMe\text{-}2\text{-}Spy)]I$.[6] Therefore, the formation of *N*-methylated complex with a two-legged piano-stool structure, $[\mathbf{4^{Me}}Me]I$, was suggested (eq 2). A similar spectral change was also observed when a solution of $\mathbf{2^R}$ reacted with BnBr. The products, $[\mathbf{4^R}Bn]Br$, could be isolated as red plate (R = Me) or dark purple block (R = Et) crystals by diffusion of diethyl ether vapor.[5] The X-ray analysis[7] of $[\mathbf{4^{Et}}Bn]Br\cdot CH_3CN\cdot H_2O$ revealed the two-legged piano-stool structure of the complex cation (Figure 1). The five-membered iridacycle in $[\mathbf{4^{Et}}Bn]^+$ is nearly planar, and the benzylic carbon, C16, is located in the plane; the benzyl(sulfanyl)amide-N atom, N1, has a trigonal-planar geometry. The Ir1–S2 bond length is 2.264(1) Å, which is comparable to that in $\mathbf{2^{Me}}$ (2.272(2) Å), while the Ir1–N1 bond of 1.943(3) Å is slightly longer than that in $\mathbf{2^{Me}}$ (1.911(5) Å). The S1–N1 bond is further elongated upon *N*-benzylation: 1.693(3) Å in $[\mathbf{4^{Et}}Bn]Br$ vs. 1.628(5) Å in $\mathbf{2^{Me}}$. These metrical differences indicate that the $\pi$-electron delocalization in the iridacycle found in $\mathbf{2^{Me}}$ would be no longer effective in $[\mathbf{4^{Et}}Bn]Br$, and the $\pi$-bonding interaction that stabilizes a coordinatively unsaturated structure would become weaker upon *N*-benzylation. However, the two-legged piano-stool structure was still maintained in an acetonitrile solution, as the $^1H$ NMR spectrum of $[\mathbf{4^{Et}}Bn]Br$ in $CD_3CN$ gave a singlet resonance for the benzylic $CH_2$ protons ($\delta$ 5.52).

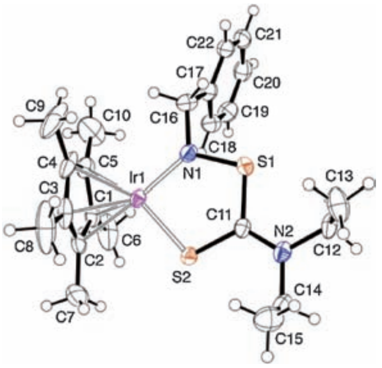
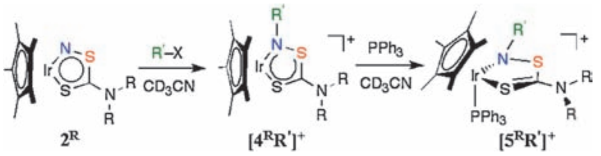


**Figure 1.** ORTEP (50% probability level) of the cationic complex in $[Cp^*Ir\{BnNSC(NEt_2)S\}]Br\cdot CH_3CN\cdot H_2O$ ($[\mathbf{4^{Et}}Bn]Br\cdot CH_3CN\cdot H_2O$).



(2)

Complex $[\mathbf{4^R}Me]I$ was thermally unstable in solution, and gradually lost the "MeN" moiety to give $[Cp^*Ir(R_2dtc)I]$,[5] which was confirmed by $^1H$ NMR spectroscopy (Figure S2). However, characterization has not been successful yet for the product from the methylnitrene moiety.

When $PPh_3$ was added to the reaction mixture containing $[\mathbf{4^R}Me]I$ at below 0 °C, the $^1H$ NMR for the $Cp^*$ group was observed at the typical region ($\delta \sim 1.5$) for coordinatively saturated $[Cp^*Ir^{III}L_3]$-type complexes, suggesting the quantitative formation of the $PPh_3$ adduct, $[\mathbf{5^R}Me]^+$ (eq 2). The NMR

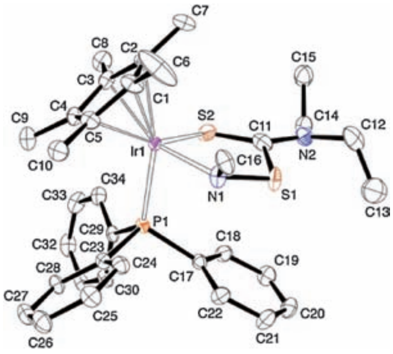


**Figure 2.** ORTEP of the cationic complex of [Cp*Ir{MeNSC(NEt$_2$)S}]$^+$ in a cocrystal of [**5$^{Et}$**Me]I and [**6$^{Et}$**]I (50% probability level, H atoms omitted).

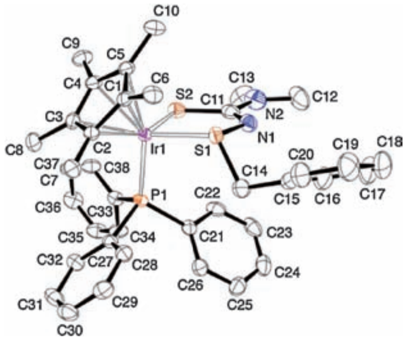
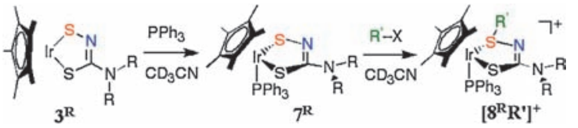


**Figure 3.** ORTEP of the cationic complex in [Cp*Ir{BnSN=C(NMe$_2$)S}]Br·CH$_3$CN ([**8$^{Me}$**Bn]Br·CH$_3$CN) (50% probability level, H atoms omitted).

spectroscopic investigation revealed that this adduct [**5$^{R}$**Me]$^+$ was also thermally unstable and converted gradually to [Cp*Ir(R$_2$dtc)(PPh$_3$)]$^+$ ([**6$^{R}$**]$^+$) at room temperature. From the reaction mixture of [**4$^{Et}$**Me]I and PPh$_3$, we could isolate orange crystals, one of which was subjected to X-ray analysis.[7] The results indicated that it was a cocrystal of [**5$^{Et}$**Me]I and [**6$^{Et}$**]I in an approximately 1:3 ratio.[5] The molecular structure of cationic complex, [**5$^{Et}$**Me]$^+$, is shown in Figure 2, which reveals the *N*-methylation of the bidentate ligand, {MeNSC(NEt$_2$)S}$^-$. The Ir1–N1 bond length is 2.205(11) Å, which is extremely long compared to those in the above-mentioned coordinatively unsaturated complexes of **2$^{Me}$** and [**4$^{Et}$**Bn]Br. The Ir1–S2 bond, 2.343(3) Å, is also longer by ca. 0.07 Å than those of **2$^{Me}$** and [**4$^{Et}$**Bn]Br, but comparable to the Ir–S bonds of [Cp*Ir$^{III}$-(R$_2$dtc)L] complexes (e.g., [**6$^{Et}$**]I of the cocrystallized complex). These elongations indicate that there is no more multiple-bond character in the Ir–N and Ir–S coordination bond when PPh$_3$ is bound to the Ir$^{III}$ center. The coordination of PPh$_3$ also makes the S1–C11 bond remarkably longer to 1.875(11) Å, as compared to the S2–C11 bond (1.699(12) Å), while the N1–S1 bond shortens to 1.639(11) Å from the corresponding bond length (1.693(3) Å) in [**4$^{Et}$**Bn]Br. The bond angles around N1 are Ir1–N1–S1 116.4(5)°, Ir1–N1–C16 119.7(10)°, and S1–N1–C16 110.1(10)°, which were indicative of the nonplanarity of the methyl(sulfanyl)amido-N atom (Figure 2). This fact is in contrast to the planar nature of {BnNSC(NEt$_2$)S}$^-$ in [**4$^{Et}$**Bn]Br and would be related to diminution of the $\pi$-donation from bidentate {R′NSC(NR$_2$)S}$^-$ ligand.

The 1:3 occupancy ratio of [**5$^{Et}$**Me]I and [**6$^{Et}$**]I in the isolated cocrystals was consistent with the molecular ratio confirmed by $^1$H NMR spectroscopy. When this sample solution in CD$_3$CN stood at room temperature overnight, the resonances due to [**5$^{Et}$**Me]$^+$ completely disappeared, and only the resonances of [**6$^{Et}$**]$^+$ were detected. Here, the most important question related to this observation is what would be the product from the released "MeN" group. The formation of methyleneimine (CH$_2$NH) complexes would be one of the possibilities,[8] but we cannot give an explicit answer for this query at present, and experiments in this line are now in progress.

In contrast to **2$^{R}$**, the thermally *N*,*S*-exchanged products of **3$^{R}$** were unreactive with MeI or BnBr; no spectral changes were observed on addition of these reagents to a CD$_3$CN solution containing **3$^{R}$**. It has been reported previously that complex **3$^{R}$** crystallized as a *S*-bridged dimer while it existed as a monomer in solution,[4] suggesting that the $\pi$-donicity of bidentate {SN=C(NR$_2$)S}$^{2-}$ ligand is competitive with the nucleophilicity of the coordinated S donor of the iminethiolate. Complex **3$^{R}$** readily reacted with PPh$_3$, and the Cp* resonance of the product in the $^1$H NMR spectrum was quantitatively shifted to $\delta \sim 1.5$, indicating the formation of a PPh$_3$ adduct, [Cp*Ir{SN=C(NR$_2$)S}(PPh$_3$)] (**7$^{R}$**) (eq 3). Isolation of complex **7$^{R}$** was attempted in vain, however the reaction products with MeI ([**8$^{R}$**Me]I) or BnBr ([**8$^{R}$**Bn]Br) were isolated.[5] The $^1$H NMR spectroscopy suggested that alkylation occurred in a nearly quantitative yield, and X-ray diffraction of [**8$^{Me}$**Bn]Br·CH$_3$CN[7] revealed the product has a *S*-alkylated structure, [Cp*Ir{BnSN=C(NMe$_2$)S}(PPh$_3$)]$^+$ (Figure 3). Complexes [**8$^{R}$**R′]$^+$ are stable in air in the solid state and in solution, and are rare examples of complexes with a alkylsulfanyliminethiolate, {RSN=C(NR$_2$)S}$^-$, as a chelate ligand.[9]

 (3)

**3$^{R}$** **7$^{R}$** [**8$^{R}$R′**]$^+$

The five-membered chelate ring in [**8$^{Me}$**Bn]Br·CH$_3$CN is planar, and the chelate bite angle of S1–Ir1–S2 is 83.32(3)°. The benzylated S atom gives typical tetrahedral bond angles: Ir–S1–N1 109.9(1)°, Ir1–S1–C14 119.4(1)°, and N1–S1–C14 99.6(1)°. The S1–N1 and N1–C11 bond lengths in [**8$^{Me}$**Bn]Br·CH$_3$CN are 1.674(3) and 1.281(4) Å, indicating the single- and double-bond characters of these bonds, respectively. The S2–C11 and N2–C11 bonds are 1.775(3) and 1.372(4) Å, respectively, and they are remarkably elongated from those in the related R$_2$dtc complexes and in [**5$^{Et}$**Me]I. These structural characteristics are comparable to those in the *S*-bridged dimer structure of [Cp*Ir{$\mu$-SN=C(NMe)$_2$S}]$_2$ (**3$^{Me}$**)$_2$.[4] Consistent with the long C–N(Me$_2$) bond with single bond character, the $^1$H NMR spectrum of [**8$^{Me}$**Bn]$^+$ indicated the equivalency of two Me groups in the {BnSN=C(NMe$_2$)S}$^-$ ligand. In the structure of [**8$^{Me}$**Bn]$^+$ it is remarkable that the Ir and sulfane-S bond, Ir1–S1 2.3111(7) Å, is apparently shorter than the Ir and thiolate-S bond, Ir1–S2 2.3567(7) Å.

When the reaction solution containing complex **7$^{Et}$** was exposed to air (eq 4) and treated with a methanolic solution of K(CF$_3$SO$_3$), yellow block crystals of the oxidized product were obtained after recrystallization from acetonitrile/diethyl ether.[5]

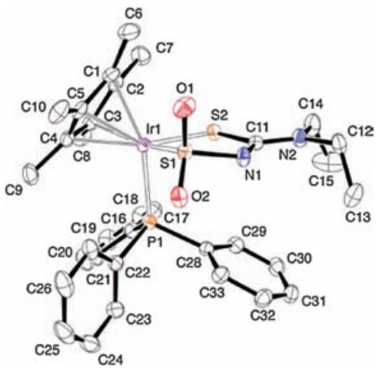
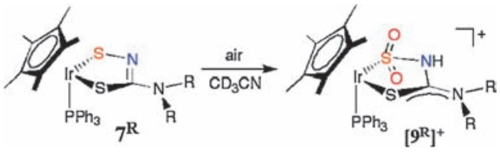


**Figure 4.** ORTEP of the cationic portion of [Cp*Ir{$O_2$SNH-C($NEt_2$)S}]$CF_3SO_3$ ([$\mathbf{9}^{Et}$]OTf) (50% probability level, H atoms omitted).

The single-crystal X-ray analysis[7] revealed that the complex is [Cp*Ir{$O_2$SNHC($NEt_2$)S}]($CF_3SO_3$) ([$\mathbf{9}^{Et}$]OTf), where only the S atom attached to the inserted N atom was oxidized to aminosulfonyl group (Figure 4). The existence of H attached to the N was confirmed by $^1$H NMR spectroscopy; the N–H resonance was too broad to detect at 22 °C, but observed as a broad signal around $\delta$ 9.42 at −20 °C. The oxidized S atom has a tetrahedral geometry, the bond angles around the S atom being 101.4(1)–118.01(8)°. The Ir1–S2 bond length, 2.3447(6) Å, is comparable to that in [$\mathbf{8}^{Me}$Bn]Br•$CH_3CN$, but the Ir–S1 bond is as short as 2.2654(6) Å. Because the N1 atom is protonated, both S1–N1 and N1–C11 bond lengths (1.720(7) and 1.336(3) Å, respectively) become longer than those in [$\mathbf{8}^{Me}$Bn]Br•$CH_3CN$. In contrast, the S2–C11 and N2–C11 bonds (1.735(2) and 1.323(3) Å) are shorter by ca. 0.05 Å than the corresponding bonds in [$\mathbf{8}^{Me}$Bn]Br•$CH_3CN$. This is coincident with the nonequivalency of two ethyl groups observed in the $^1$H NMR spectrum of [$\mathbf{9}^{Et}$]OTf (Figure S3).[5]



(4)

It is interesting to note that complexes [$\mathbf{5}^{R}$Me]I and [$\mathbf{8}^{R}$Me]I are structural isomers, similar to their parent complexes $\mathbf{2}^{R}$ and $\mathbf{3}^{R}$. The methyl(sulfanyl)amido complex [$\mathbf{5}^{R}$Me]I was prepared first by alkylation of $\mathbf{2}^{R}$ followed by coordination of $PPh_3$, while the methyl(imino)sulfane complex [$\mathbf{8}^{R}$Me]I was obtained by alkylation of the $PPh_3$ adduct from $\mathbf{3}^{R}$. The order of the reactants is essential for preparation of these isomers. These complexes are similar in their molecular structures, but their thermal stabilities are remarkably different. Complex [$\mathbf{5}^{R}$Me]I was converted gradually to [$\mathbf{6}^{R}$]$^+$ with a release of the "methylnitrene" moiety, while complex [$\mathbf{8}^{R}$Me]I was stable in air. The imine (or niterene) group transfer observed in this study is a current topic in inorganic reaction mechanisms,[10] and further study on this line are now in progress.

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5 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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7 Crystallographic data reported in this manuscript have been deposited with Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-823647–823650. 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; or deposit@ccdc.cam.ac.uk).

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