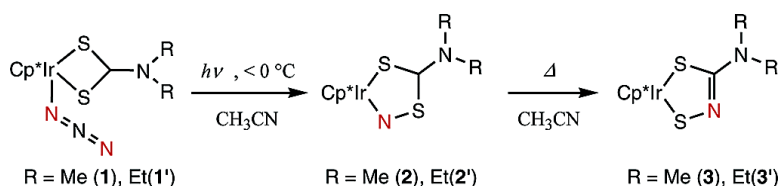## Communication

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

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

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Nitrogen atom transfer has in general received much less attention than related oxygen atom transfer processes.[1] This is changing as metal—nitrido complexes have been implicated in the splitting of N_2 and other small molecules and have seen increased usage as oxidants.[2] For instance, we and others have been investigating oxidizing osmium—nitrido complexes.[2d–g] This report describes an attempt to extend this chemistry to iridium via photolysis of azide complexes, a well-established route to high-valent nitrido complexes.[3] Although no high-valent iridium—nitrido complexes are known,[4] Basolo et al. have described photolyses of aqueous $[Ir(NH_3)_5(N_3)]^{2+}$ that apparently give a highly reactive intermediate, $[Ir(NH_3)_5(NH)]^{3+}$, which could be formulated either as an iridium(III) nitrene or as an iridium(V) imido.[5] In contrast, photolysis of the iridium bis(azido) complex $Cp*Ir(PR_3)(N_3)_2$ ($Cp* = \eta^5$-C_5Me_5) generates a reduced intermediate, $Cp*Ir^I(PR_3)$.[6] Here, we describe the photochemical and the subsequent thermal reactions of iridium(III)—azido complexes containing *N,N*-dialkyldithiocarbamate ligands, $Cp*Ir(R_2dtc)(N_3)$ [R = Me (**1**) or Et (**1′**)], involving novel nitrogen atom insertions.

The azido complexes $Cp*Ir(R_2dtc)(N_3)$ (**1** or **1′**) are prepared from $Cp*Ir(R_2dtc)Cl$, AgOTf, and NaN_3 in MeCN/MeOH.[7] Anaerobic photolyses of acetonitrile solutions of **1** or **1′** with a Hg lamp at temperatures below 0 °C causes the original orange-yellow solution to turn red. ${}^1H$ NMR monitoring of photochemical reaction mixtures showed formation of a main product, **2** or **2′**, in more than 70% yield after 5 h, together with a few byproducts. ${}^1H$ NMR spectra for **2** show singlets for the Cp* and $N(CH_3)_2$ groups at δ 2.04 and 3.38, respectively, both of which are significantly downfield-shifted vs those of **1** (δ 1.77 and 3.11). Solutions of **2** or **2′** are stable below −20 °C in the dark for at least a couple of days, but over 1 d at room-temperature quantitative conversion to a new product (**3** or **3′**) is observed. Complex **3** also shows downfield ${}^1H$ NMR chemical shifts, δ 2.09 (Cp*) and 3.27 $[N(CH_3)_2]$.

Red, columnar crystals of **2** were obtained from a photolysis reaction mixture at −30 °C. An X-ray crystal structure (Figure 1a)[8] shows a Cp*Ir^{III} complex with a novel $NSC(NMe_2)S^{2-}$ ligand bound via the terminal N and S atoms. One nitrogen atom of the azide ligand has been inserted into an Ir—S bond, forming an N—S bond. The five-membered chelate ring is nearly planar. The Ir(1)—N(1) bond, 1.911(5) Å, is substantially shorter than the Ir—N(azide) bond in **1** (2.120(6) Å),[9] which is similar to Ir^{III}—N distances in amine and nitrile complexes.[10] This indicates significant double-bond character for the Ir—N linkage in **2**. The Ir(1)—S(2) bond, 2.272(2) Å, is also shorter than the ones in **1** and in Ir(Et$_2$dtc)$_3$ (2.365(2)–2.370(2) Å).[11] Short Ir—S bonds have also been observed in the structurally related 1,2-benzenedithiolate complex, Cp*Ir-(1,2-S$_2$C$_6$H$_4$).[12] The N(2)—C(11) bond, 1.359 (8) Å, is longer than typical C—N bonds (1.30–1.32 Å) in Me$_2$dtc complexes.[9,11] This
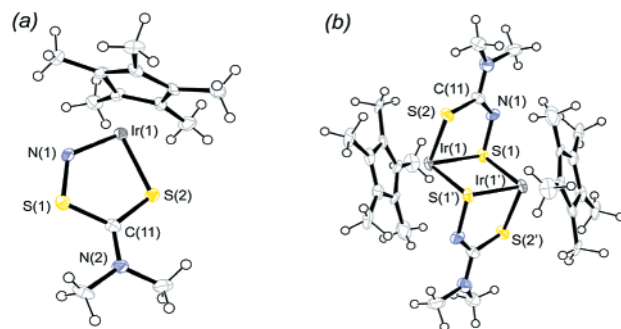

Figure 1. ORTEPs and selected bond lengths (Å) for (a) Cp*Ir[NSC-(NMe$_2$)S] (**2**): Ir(1)—S(2) 2.272(2), Ir(1)—N(1) 1.911(5), S(1)—N(1) 1.628(5), S(1)—C(11) 1.706(6), S(2)—C(11) 1.712(6), N(2)—C(11) 1.359(8). (b) One of the crystallographically independent molecules of {Cp*Ir[μ-SN=C(NMe$_2$)S]}$_2$ (**4**): Ir(1)—S(1) 2.328(3), Ir(1)—S(2) 2.339(3), Ir(1)—S(1′) 2.370(3), S(1)—N(1) 1.695(10), S(2)—C(11) 1.78(1), N(1)—C(11) 1.31(2), N(2)—C(11) 1.38(2).

elongation is consistent with the observation of a single unbroadened $N(CH_3)_2$ NMR resonance even at −40 °C, indicating that rotation about the C—N bond is fast on the NMR time scale. The bonding in **2** thus has a delocalized character within the chelate ring, and an exocyclic C—N single bond.

Complex **2** and Cp*Ir(1,2-S$_2$C$_6$H$_4$) are formally five-coordinate, in contrast to most Cp*Ir^{III} complexes which are six-coordinate, 18-electron species. As described for Cp*Ir(1,2-S$_2$C$_6$H$_4$), the short Ir—L distances indicate partial π-donation from the ligand so that the molecules approach an 18-electron configuration.[12] This electronic structure is the origin of the intense optical absorptions of Cp*Ir(1,2-S$_2$C$_6$H$_4$) and **2** (for the latter in acetonitrile, $\lambda_{max} = 340$, 425, and 520 nm, $\epsilon \approx 10^4$ M^{-1} cm^{-1}). Six-coordinate Cp*IrL$_3$ complexes typically do not have strong visible absorptions. The thermal product **3** has an optical spectrum similar to that of **2** ($\lambda_{max} = 370$, 460, and 550 nm), indicating a five-coordinate (two-legged piano stool) structure. This structure also leads to the unusually downfield Cp* chemical shifts in **2**, **3**, and Cp*Ir(1,2-S$_2$C$_6$H$_4$).

Slow evaporation of MeCN solutions of dark red **3** in an inert atmosphere gives yellow crystals of a new compound, **4**. The X-ray crystal structure of **4** (Figure 1b) shows a dinuclear Cp*Ir^{III} complex {Cp*Ir[μ-SNC(NMe$_2$)S-κ^3S:S,S']}$_2$[8] with novel SNC(NMe$_2$)S^{2-} bridging ligands.[13] A nitrogen atom has now been inserted into a C—S bond of the Me$_2$dtc ligand, forming a new C—N bond. The N(1)—C(11) bond length of 1.31(2) Å shows substantial double-bond character; thus, the ligand is 2-(dimethylamino)-1-azaethene-1,2-dithiolate, SN=C(NMe$_2$)S^{2-}. Each iridium center in **4** has a three-legged piano-stool configuration with two bridging and one terminal S atom. The Ir—S bond lengths of 2.328(3)–2.370(3) Å are typical of Ir^{III}(R$_2$dtc) complexes.[9,10a,11] The six-coordinate structure of **4** is consistent with its yellow color [λ_{max}(shoulder) $\approx$ 360 nm] and its normal ${}^1H$ NMR chemical shifts [δ 1.68 (Cp*) and 3.22 $N(CH_3)_2$ in CD$_2$Cl$_2$].

Scheme 1. Photochemical and Subsequent Thermal Reactions of Cp*Ir(R₂dtc)(N₃)
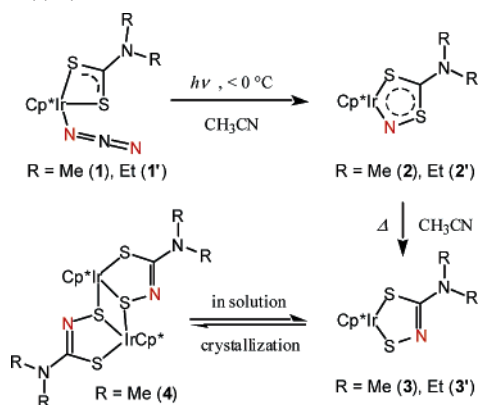
Yellow solutions of **4** convert back to dark red **3** on standing for 1 h at ambient temperatures (by both ¹H NMR and UV/vis spectroscopies). This and the spectral data above indicate that the thermal products **3** (and **3′**) are five-coordinate monomer complexes with a chelating $SN=C(NR_2)S^{2-}$ ligand. A similar dimer-to-monomer conversion in solution has been observed for a related Rh^III complex, Cp*Rh(1,2-S₂C₆H₄).[12]

The reactions described here are summarized in Scheme 1. The movement of nitrogen atoms was followed, starting with **1**- and **1′**-¹⁵N, where each end of the azide ligand was 50% labeled.[14] Photolysis gives **2** or **2′** with ¹⁵N in the chelate ring, and the ¹⁵N NMR spectrum also shows N₂. Photolysis likely cleaves the azide ligand, generating N₂ and the iridium(V) nitrido species [Cp*Ir-(N)(S₂CNR₂)]. This reactive transient is then rapidly stabilized by formation of an N—S bond between the nitrido and R₂dtc ligands, forming **2**. Attempts to trap the proposed nitrido complex by photolysis in neat Me₂S were not successful, presumably because bimolecular trapping cannot compete with the unimolecular rearrangement. (Phosphines cannot be used as traps because they displace the azide ligand from **1**.) It is also possible that photolysis causes dissociation of one sulfur of the R₂dtc ligand, which then attacks the azide ligand with displacement of N₂.[15]

The thermal rearrangement of **2** to **3** involves a switch of the N and S atoms within the chelate ring. The nitrogen atom is effectively inserted into a C—S bond. We know of no precedent for such a transformation. To probe the mechanism, a crossover experiment was performed by mixing Cp*Ir[¹⁵NSC(NMe₂)S] (**2**-¹⁵N) with Cp*Ir[NSC(NEt₂)S] (**2′**) in acetonitrile solution. Remarkably, ¹⁵N NMR spectra showed exchange of the ¹⁵N label between **2**-¹⁵N and **2′** within hours at room temperature (eq 1). This exchange is faster than the conversion of **2** to **3**.

(1)
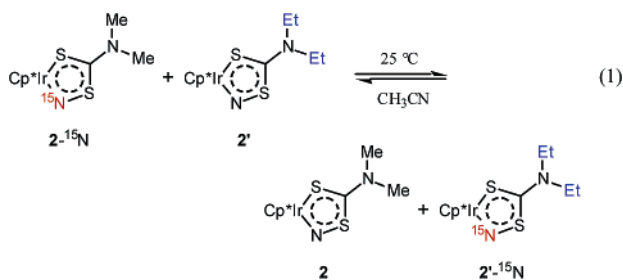
In sum, remarkably facile nitrogen atom transfer reactions are observed in this system. A nitrogen atom originally in an azide ligand is photolytically inserted into an Ir^III—S bond, forming **2**. Labeling studies show that this nitrogen atom exchanges between molecules of **2** at room temperature. Complex **2** also rearranges at room temperature to insert the nitrogen atom into a C—S bond of the dithiocarbamate, forming a new C—N bond. Studies into the mechanisms and generality of these and related transformations are in progress.

Supporting Information Available: Experimental procedures, spectra, and X-ray crystallographic information for **1**, **2**, and **4** (CIF/PDF format). This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Full experimental details are in the Supporting Information. ¹H NMR (CD₃CN) **1′**: δ 1.22 (NCH₂CH₃), 1.73 (Cp*), 3.51 (NCH₂CH₃); **2′**: δ 1.21 (NCH₂CH₃), 2.05 (Cp*), 3.81 (NCH₂CH₃); **3′**: δ 1.11 (NCH₂CH₃), 2.10 (Cp*), 3.76 (NCH₂CH₃).
(8) Crystallographic data: For **2**: C₁₃H₂₁IrN₂S₂, M = 461.64, monoclinic, P2₁/c, a = 9.7290(3) Å, b = 11.2510(4) Å, c = 14.1330(6) Å, β = 101.808(1)°, V = 1514.3(1) Å³, Z = 4, ρ_c = 2.025 Mg m⁻³, μ(Mo Kα) = 9.078 mm⁻¹, T = 130(2) K, 5827 reflns collected, 3575 unique (R_int = 0.049), R1{I > 2σ(I)} = 0.038, wR2(all data) = 0.078. For **4**: C₂₆H₄₂-Ir₂N₄S₄, M = 923.28, triclinic, P1̄, a = 10.4540(4) Å, b = 11.1600(6) Å, c = 14.133(1) Å, α = 84.117(2)°, β = 87.457(2)°, γ = 66.235(4)°, V = 1501.1(2) Å³, Z = 2, ρ_c = 2.043 Mg m⁻³, μ(Mo Kα) = 9.158 mm⁻¹, T = 130(2) K, 7062 reflns collected, 4658 unique (R_int = 0.061), R1{I > 2σ(I)} = 0.051, wR2(all data) = 0.123.
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(14) From singly labeled NaN₃-¹⁵N. ¹⁵N NMR (CD₃CN, 25 °C, δ vs CD₃NO₂): **1**, −238.4 and −346.2; **1′**, −236.7 and −344.7; **2** (−20 °C), −13.1; **2′** (−20 °C), −13.5; **3**, −144.1; **3′**, −153.3; N₂, −71.9 (Martin, G. J.; Martin, M. L.; Gouesnard, J.-P. *¹⁵N-NMR Spectroscopy*; Springer-Verlag: Berlin, 1981.)
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