Organometallics **2006,** *25,* 5847−5849

A Sulfonylimido-Bridged Coordinatively Unsaturated Diiridium Complex: Intramolecular C−H Bond Activation Promoted by a Weak Acid

Koji Ishiwata, Shigeki Kuwata,* and Takao Ikariya*

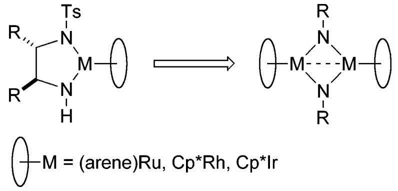
Department of Applied Chemistry, Graduate School of Science and Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

Received August 25, 2006

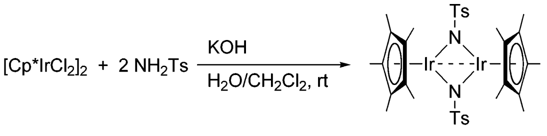
*Summary: The sulfonylimido-bridged diiridium complex [Cp*Ir(μ_2-NTs)$_2$IrCp*] (**1**; Cp* = η^5-$C_5(CH_3)_5$, Ts = $SO_2C_6H_4CH_3$-p), readily accessible from the reaction of [Cp*IrCl$_2$]$_2$ with TsNH$_2$, reacted with P(CH$_3$)$_3$ and HOTf (Tf = SO$_2$CF$_3$) to afford the adduct [Cp*Ir{P(CH$_3$)$_3$}(μ_2-NTs)$_2$IrCp*] and cationic amido−imido complex [Cp*Ir(μ_2-NHTs)(μ_2-NTs)IrCp*][OTf], respectively. On the other hand, the reaction of **1** with benzoic acid resulted in intramolecular C−H bond activation, giving the cyclometalated complex [Cp*Ir{μ_2-NHSO$_2$C$_6$H$_3$(CH$_3$)-κ^2N,C}$_2$-IrCp*].*

We have recently developed a series of mononuclear half-sandwich ruthenium, rhodium, and iridium catalysts bearing a metal/NH bifunctionality for asymmetric hydrogen transfer reduction and C−C bond formation.[1] The high efficiency of these catalysts at least partly relies on the nature of the chiral amido intermediates having both a Brønsted basic nitrogen-donor ligand[2] and the Lewis acidic, coordinatively unsaturated late metal center. We envisioned that this bifunctional effect of the amido complex would also operate in "doubly unsaturated" imido-bridged dinuclear half-sandwich complexes[3] such as [Cp*Ir(μ_2-NC$_6$H$_5$)$_2$IrCp*] (Cp* = η^5-C$_5$(CH$_3$)$_5$)[3a] because they have the same M−N structural motif (Chart 1). However, exploration into the catalysis of these complexes has been hampered by their various decomposition processes including substitution of the imido ligand and imide transfer reactions. Evidently the bridging ligand must be carefully designed to increase the stability of the dinuclear complex without losing the Lewis acid/Brønsted base bifunctionality. The electron-withdrawing sulfonyl group, which has rarely been used in the chemistry of nitrogen-bridged polynuclear complexes,[4] is an attractive candidate to stabilize the imido-bridged dinuclear platform by forming ionic and strong M−N bonds.[5] Herein we report the synthesis of the novel coordinatively unsaturated diiridium complex [Cp*Ir(μ_2-NTs)$_2$IrCp*] (**1**; Ts = SO$_2$C$_6$H$_4$-CH$_3$-*p*) with bridging sulfonylimido ligands and its Lewis acid/Brønsted base bifunctional properties.

Chart 1



The reaction of [Cp*IrCl$_2$]$_2$ with 2 equiv of *p*-toluenesulfonamide in the presence of KOH cleanly afforded the sulfonylimido-bridged diiridium complex **1**, as shown in eq 1.[6] The notable stability of **1** with respect to moisture as well as oxygen enables us to use water as a cosolvent to dissolve KOH and column chromatography under air for purification. The ^{1}H NMR spectrum of **1** indicates the presence of the Cp* and the tolyl group in a ratio of 1:1. The dinuclear structure of **1** has been confirmed by X-ray analysis (Figure 1).[7] The sulfonyl oxygen atoms in the imido ligands do not participate in coordination; consequently, the two iridium centers in **1** are coordinatively unsaturated. The metrical parameters in **1** fall in the range of those found in the related bis(imido)-bridged diiridium com-



1, 96%

(1)

---

* Corresponding authors. E-mail: skuwata@apc.titech.ac.jp; tikariya@apc.titech.ac.jp.

(1) Ikariya, T.; Murata, K.; Noyori, R. *Org. Biomol. Chem.* **2006**, *4*, 393.

(2) Selected references of amido and imido complexes: (a) Fulton, J. R.; Holland, A. W.; Fox, D. J.; Bergman, R. G. *Acc. Chem. Res.* **2002**, *35*, 44. (b) Gade, L. H. *J. Organomet. Chem.* **2002**, *661*, 85. (c) Kempe, R. *Angew. Chem., Int. Ed.* **2000**, *39*, 468. (d) Li, Y.; Wong, W.-T. *Coord. Chem. Rev.* **2003**, *243*, 191. (e) Sharp, P. R. *J. Chem. Soc., Dalton Trans.* **2000**, 2647. (f) Fryzuk, M. D.; Montgomery, C. D. *Coord. Chem. Rev.* **1989**, *95*, 1.

(3) For Ir: (a) Dobbs, D. A.; Bergman, R. G. *Organometallics* **1994**, *13*, 4594. (b) Danopoulos, A. A.; Wilkinson, G.; Sweet, T. K. N.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1996**, 3771. For Ru: (c) Burrell, A. K.; Steedman, A. J. *Organometallics* **1997**, *16*, 1203. (d) Kee, T. P.; Park, L. Y.; Robbins, J.; Schrock, R. R. *J. Chem. Soc., Chem. Commun.* **1991**, 121. (e) Takemoto, S.; Kobayashi, T.; Matsuzaka, H. *J. Am. Chem. Soc.* **2004**, *126*, 10802. For Fe: (f) Takemoto, S.; Ogura, S.; Yo, H.; Hosokoshi, Y.; Kamikawa, K.; Matsuzaka, H. *Inorg. Chem.* **2006**, *45*, 4871. (g) Ohki, Y.; Takikawa, Y.; Hatanaka, T.; Tatsumi, K. *Organometallics* **2006**, *25*, 3111.

(4) Foch, I.; Párkányi, L.; Besenyei, G.; Simándi, L. I.; Kálmán, A. *J. Chem. Soc., Dalton Trans.* **1999**, 293.

(5) (a) Fujita, K.; Yamashita, M.; Puschmann, F.; Alvarez-Falcon, M. M.; Incarvito, C. D.; Hartwig, J. F. *J. Am. Chem. Soc.* **2006**, *128*, 9044. (b) Leung, W.-H.; Wu, M.-C.; Chim, J. L. C.; Wong, W.-T. *Inorg. Chem.* **1996**, *35*, 4801.

(6) Synthesis of **1**. A mixture of [Cp*IrCl$_2$]$_2$ (2.0002 g, 2.51 mmol), TsNH$_2$ (0.8749 g, 5.11 mmol), and KOH (1.1680 g, 20.8 mmol) in CH$_2$Cl$_2$/H$_2$O (20 mL/20 mL) was stirred for 8 h at room temperature. The resultant organic layer was washed with H$_2$O (10 mL × 5) and chromatographed on alumina under air. A red band eluted with CH$_2$Cl$_2$ was collected and evaporated to dryness. The resultant solid was recrystallized from CH$_2$Cl$_2$/diethyl ether (10 mL/100 mL) to yield **1** as dark red crystals (2.4022 g, 2.42 mmol, 96%). ^{1}H NMR (C$_6$D$_6$): δ 8.10, 6.85 (d, 4H each, J = 8.3 Hz, SO$_2$C$_6$$H_4CH_3$), 1.97 (s, 6H, SO$_2C_6H_4CH_3$), 1.58 (s, 30H, Cp*). Anal. Calcd for C$_{34}$H$_{44}$Ir$_2$N$_2$O$_4$S$_2$: C, 41.11; H, 4.46; N, 2.82. Found: C, 40.73; H, 4.57; N, 2.73.

(7) Crystal data for **1**: monoclinic, $P2_1/c$, a = 14.195(9) Å, b = 14.417(8) Å, c = 17.929(11) Å, β = 113.210(8)°, V = 3372.4(35) Å^3, Z = 4, ρ_{calc} = 1.956 g cm^{-3}, 7690 unique reflections ($2\theta < 55°$), 442 parameters, $R1$ = 0.040 [$I > 2\sigma(I)$], w$R2$ = 0.105 (all data), GOF = 1.008.

10.1021/om060777m CCC: $33.50

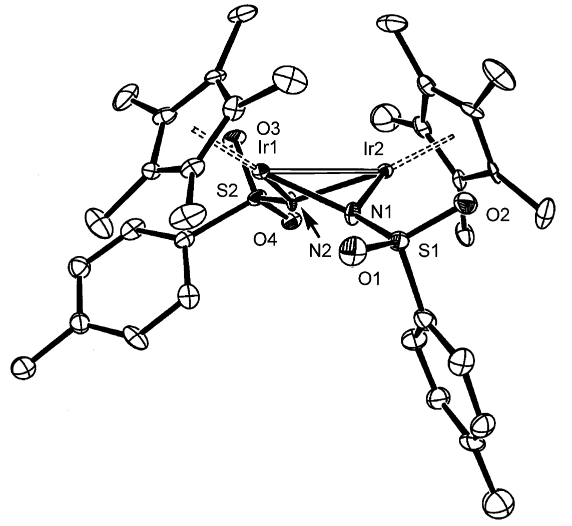


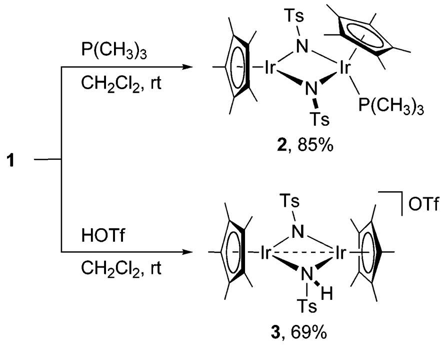
Figure 1. Crystal structure of **1**. Hydrogen atoms are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond distances (Å): Ir1−N1, 2.007(8); Ir1−N2, 2.004(6); Ir2−N1, 2.021(7); Ir2−N2, 2.016(7).

Table 1. Selected Interatomic Distances (Å) and Angles (deg) for Imido-Bridged Diiridium Complexes $[Cp^*Ir(\mu_2\text{-}NR)_2IrCp^*]$

R	c-C_5H_{11}	C_6H_5	2,6-$(CH_3)_2C_6H_3$	CN	Ts
Ir−Ir (Å)	2.6133(5)	2.778(1)	2.894(1)	2.8179(9)	2.8343(4)
Ir−N (Å)[a]	2.034 2.046(8)	1.986	1.973	2.01	2.012
sum of the bond angles around N (deg)	339.8 351.8	338[a]	354[a]	332[a]	343.8 353.5
ref	3b	3a	3a	9	this work

[a] Mean values.

Scheme 1



plexes, as summarized in Table 1. Table 1 also shows that slight steric modification in the imido substituents, e.g., from phenyl to 2,6-xylyl, renders the geometry at the nitrogen atoms much closer to planarity.

Owing to the coordinatively unsaturated nature, the sulfonylimido-bridged diiridium complex **1** reacted with trimethylphosphine at room temperature to give the phosphine adduct $[Cp^*Ir\{P(CH_3)_3\}(\mu_2\text{-}NTs)_2IrCp^*]$ (**2**) as shown in Scheme 1. Complex **2** has been characterized by ^1H and $^{31}P\{^1H\}$ NMR spectroscopy along with a preliminary X-ray analysis.[8] Imide transfer to give phosphine imide, which is known for the corresponding phenylimido complex,[3a] did not occur even in the presence of an excess of the phosphine and at elevated temperatures, suggesting the robustness of the bis(imido)-bridged dinuclear core in **1**. The reactions of the cyanamido-bridged diiridium complex $[Cp^*Ir(\mu_2\text{-}NCN)_2IrCp^*]$ with phosphines are also known to end in the simple Lewis acid−base reaction without rupture of the M_2N_2 core.[9] Apparently, the electron-withdrawing sulfonyl groups in **1** increase the strength of the Ir−N bonds.

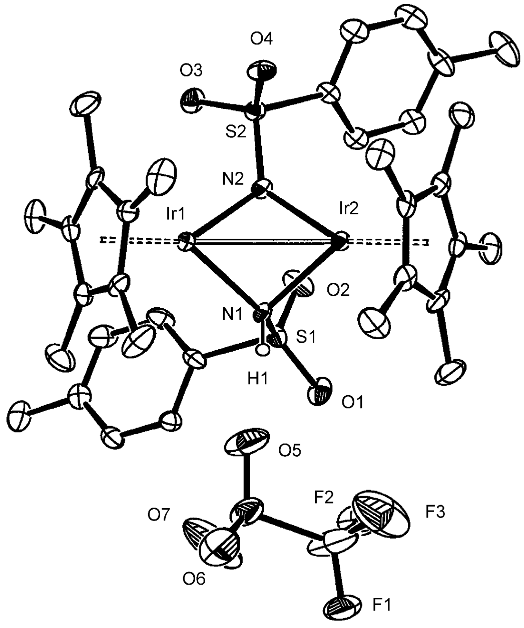


Figure 2. Crystal structure of **3**. One of the two crystallographically independent units is shown, and hydrogen atoms except for the amido hydrogen are omitted for clarity. Thermal ellipsoids are drawn at 30% probability. Selected bond distances (Å): Ir1−Ir2, 2.8345(4); Ir1−N1, 2.114(6); Ir1−N2, 1.969(6); Ir2−N1, 2.131(6); Ir2−N2, 1.989(7); Ir3−Ir4, 2.8408(3); Ir3−N3, 2.125(5); Ir3−N4, 1.970(6); Ir4−N3, 2.109(6); Ir4−N4, 1.970(6).

Electron-withdrawing groups on the imido nitrogen should make the imido ligand less nucleophilic. Nevertheless, the sulfonylimido-bridged diiridium complex **1** did undergo facile N-protonation with an equimolar amount of triflic acid to afford the amido- and imido-bridged cationic complex $[Cp^*Ir(\mu_2\text{-}NHTs)(\mu_2\text{-}NTs)IrCp^*][OTf]$ (**3**; Tf = SO_2CF_3).[10] The ^1H NMR spectrum of **3** shows two sets of signals for the tolyl groups in the amido and imido ligands along with one Cp* singlet; the amido proton is observed at δ 10.11. The protonation of the imido nitrogen atom is also evident from the IR spectrum, which exhibits a ν_{NH} band at 3108 cm^{-1}. The single-crystal X-ray analysis of **3** has confirmed its detailed structure (Figure 2).[11] The close contact (3.05 Å, mean of the two crystallographically independent units) between the N(1) atom and the triflate oxygen strongly suggests the presence of a hydrogen bond between the NHTs ligand and the triflate ion, although the amido hydrogen

---

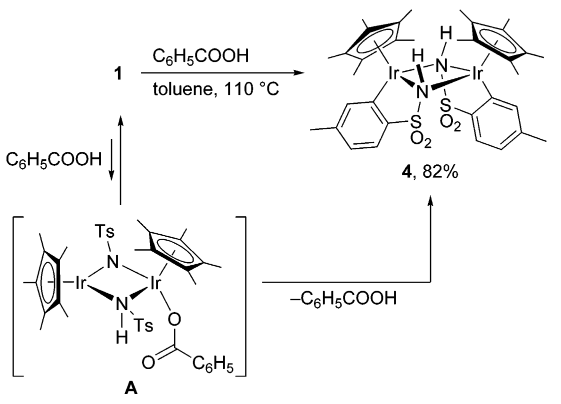
(8) See Supporting Information.

(9) Kajitani, H.; Tanabe, Y.; Kuwata, S.; Iwasaki, M.; Ishii, Y. *Organometallics* **2005**, *24*, 2251.

(10) Synthesis of **3**. To a solution of **1** (99.7 mg, 0.100 mmol) in CH_2Cl_2 (5 mL) was added TfOH (11 μL, 0.12 mmol), and the mixture was stirred for 1 h at room temperature. The resultant dark reddish-brown solution was concentrated to ca. 1 mL. Addition of diethyl ether (10 mL) gave **3** as dark reddish-brown crystals (79.6 mg, 0.070 mmol, 69%). ^1H NMR (C_6D_6): δ 10.11 (s, 1H, NH), 8.40, 8.30, 7.09, 6.83 (d, 2H each, J = 7.8 Hz, $SO_2C_6H_4CH_3$), 1.93, 1.90 (s, 3H each, $SO_2C_6H_4CH_3$), 1.42 (s, 30H, Cp*). Anal. Calcd for $C_{35}H_{45}F_3Ir_2N_2O_7S_3$: C, 36.77; H, 3.97; N, 2.45. Found: C, 36.64; H, 3.90; N, 2.34.

(11) Crystal data for **3**: triclinic, $P\bar{1}$, a = 15.028(3) Å, b = 15.560(3) Å, c = 18.069(3) Å, α = 69.227(5)°, β = 86.128(7)°, γ = 83.760(7)°, V = 3925.0(12) $Å^3$, Z = 4, ρ_{calc} = 1.935 g cm^{-3}, 17 194 unique reflections ($2\theta < 55°$), 1027 parameters, $R1$ = 0.043 [$I > 2\sigma(I)$], $wR2$ = 0.119 (all data), GOF = 1.001.

Scheme 2



could not be located on the difference Fourier map. The tetrahedral configuration of the N(1) atom is also indicated by the sum of the Ir−N−Ir and two Ir−N−S angles (323.3°, mean). In contrast, the corresponding angle sum for the N(2) atom (345.9°, mean) is consistent with the sp^2-hybridized imido nitrogens. The $Ir-N_{amido}$ bonds of 2.120 Å (mean) are significantly longer than the $Ir-N_{imido}$ bonds (1.975 Å, mean), as observed in the *N*-cyclohexyl congener [Cp*Ir(μ_2-NHCy)(μ_2-NCy)IrCp*]Cl (Cy = cyclohexyl).[3b]

Notably, protonation of **1** with a weaker acid led to a totally different result. When **1** was treated with benzoic acid in refluxing toluene, intramolecular C−H activation of the tosylimido ligands occurred to afford the doubly cyclometalated diiridium complex [Cp*Ir{μ_2-$NHSO_2C_6H_3(CH_3)$-$\kappa^2 N,C$}$_2$IrCp*] (**4**) in 82% yield (Scheme 2).[12,13] Use of benzoic acid proved to be essential because no thermal reaction took place without benzoic acid. The ^1H NMR spectrum of **4** features singlets at δ 7.81 and 4.39 ascribed to the cyclometalated tolyl groups and the amido protons, respectively. The presence of the NH protons is also suggested by the ν_{NH} band at 3256 cm^{-1} in the IR spectrum. The dimeric structure of **4** with the two Cp* ligands sitting in mutually *syn* position with respect to the Ir_2N_2 ring has been revealed by single-crystal X-ray analysis, although the structural refinement was unable to be completed due to severe disorder.[8,14] We have recently reported acidic alcohol or phenol-assisted cyclometalation of the coordinatively unsaturated mononuclear amido complexes [LM(Tsdpen)] (LM = (*p*-cymene)Ru, Cp*Ir; TsdpenH = $TsNHCH(C_6H_5)CH(C_6H_5)NH_2$).[15] In these reactions, the intermediary alkoxo−amine complexes such as [LM(OCH_2CF_3)(TsdpenH)] are observed (for Ru) and even isolated (for Ir), although the details of the subsequent reaction pathway leading to the cyclometalation products remain somewhat obscure. Based on these results as well as the acid−base bifunctionality of **1** substantiated by the above experiments, it seems plausible that the first step in the acid-promoted cyclometalation of **1** involves an equilibrium between **1** and the amido−imido−benzoato complex **A** as in the corresponding mononuclear systems.[15,16]

The present study clearly demonstrates that the electron-withdrawing sulfonyl group adjusts the balance of the Brønsted basicity of the bridging imido ligands and the stability of the bis(imido)-bridged coordinatively unsaturated dinuclear complex **1**. The cyclometalation of **1** promoted by benzoic acid is particularly noteworthy because it opens the possibility of cooperative catalysis, using nitrogen-bridged dinuclear complexes based on the basic nitrogen ligand and adjacent coordinatively unsaturated metal center, as in the corresponding mononuclear amido complexes.[1,17] Further elucidation of the mechanism of the cyclometalation and development of new catalysis using sulfonylimido-bridged multimetallic complexes are the focus of our ongoing work.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (Nos. 14078209 and 18065007) from the Ministry of Education, Culture, Sports, Science and Technology, Japan (T.I.) and Asahi Glass Foundation (S.K.).

Supporting Information Available: Text giving details of the syntheses and X-ray studies of **1**−**4**, and CIF files giving X-ray crystallographic data for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM060777M

---

(12) Synthesis of **4**. A mixture of **1** (926.0 mg, 0.932 mmol) and C_6H_5COOH (113.8 mg, 0.932 mmol) in toluene (50 mL) was allowed to reflux for 48 h. After removal of the solvent, the resultant solid was dissolved in CH_2Cl_2 (10 mL) and chromatographed on alumina under air. A yellow band eluted with CH_2Cl_2 was collected and dried in vacuo to yield **4** as a yellow powder (760.5 mg, 0.766 mmol, 82%). ^1H NMR (C_6D_6): δ 7.81 (s, 2H, $SO_2C_6H_3CH_3$), 6.33 (d, 2H, J = 8.2 Hz, $SO_2C_6H_3CH_3$), 4.39 (s, 2H, NH), 2.17 (s, 6H, $SO_2C_6H_3CH_3$), 1.35 (s, 30H, Cp*). The signal for the rest aryl proton is overlapped with the solvent signal. Anal. Calcd for $C_{34}H_{44}Ir_2N_2O_4S_2$: C, 41.11; H, 4.46; N, 2.82. Found: C, 41.08; H, 4.43; N, 2.72.

(13) We could not observe any intermediates in this reaction, even at room temperature. On the other hand, the amido−imido complex **3** in toluene started to decompose at 80 °C to give *p*-toluenesulfonamide without formation of **4**.

(14) The dimeric structure of **4** was also supported by the ESI-MS measurement, showing the $[M + Na]^+$ peak at *m*/*z* 1017.5.

(15) Koike, T.; Ikariya, T. *Organometallics* **2005**, *24*, 724.

(16) (a) Davies, D. L.; Donald, S. M. A.; Al-Duaij, O.; Macgregor, S. A.; Pölleth, M. *J. Am. Chem. Soc.* **2006**, *128*, 4210. (b) Davies, D. L.; Al-Duaij, O.; Fawcett, F.; Giardiello, M.; Hilton, S. T.; Russell, D. R. *Dalton Trans.* **2003**, 4132. (c) Arita, S.; Koike, T.; Ikariya, T., manuscript in preparation.

(17) (a) Ohkuma, T.; Utsumi, N.; Tsutsumi, K.; Murata, K.; Sandoval, C.; Noyori, R. *J. Am. Chem. Soc.* **2006**, *128*, 8724. (b) Clarke, Z. E.; Maragh, P. T.; Dasgupta, T. P.; Gusev, D. G.; Lough, A. J.; Abdur-Rashid, K. *Organometallics* **2006**, *25*, 4113. (c) Morris, D. J.; Hayes, A. M.; Wills, M. *J. Org. Chem.* **2006**, *71*, 7035.