

# Communications

## Acid–Base Bifunction and Umpolung of the Bridging Hydride in a Coordinatively Unsaturated Mesylimido- and Hydrido-Bridged Diiridium Complex

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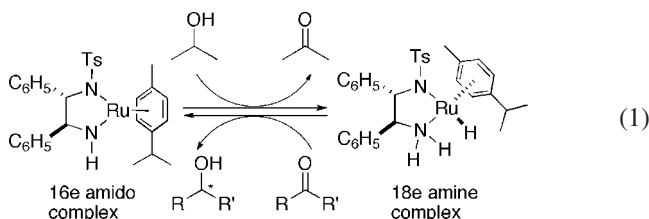
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**Summary:** The mono(mesylimido)-bridged diiridium(III) complex  $[(Cp^*IrCl)_2(\mu_2-H)(\mu_2-NHMs)]$  ( $Cp^* = \eta^5-C_5(CH_3)_5$ ,  $Ms = SO_2CH_3$ ) undergoes reversible dehydrochlorination to afford the unsaturated imido-bridged dinuclear complex  $[Cp^*Ir(\mu_2-H)(\mu_2-NMs)IrClCp^*]$  (**2**). The reaction of **2** with trimethylphosphine gives the simple adduct  $[Cp^*Ir\{P(CH_3)_3\}(\mu_2-H)(\mu_2-NMs)IrClCp^*]$ , while the reaction with CO results in sequential formation of the mono- and dicarbonyl Ir(II) complexes  $[Cp^*Ir(CO)(\mu_2-NHMs)IrClCp^*]$  and  $[(Cp^*Ir(CO))_2(\mu_2-NMs)]$  with concomitant umpolung of the bridging hydrido ligand in **2** to the amido proton.

The 16e amido complexes with  $\pi$ -stabilized unsaturation have a latently Lewis acidic metal center and Brønsted basic coordinated nitrogen atom. These adjacent functionalities allow the amido complexes to react with various pronucleophiles as well as dihydrogen in a concerted or stepwise manner, giving the 18e amine complexes with a Brønsted acidic amine proton and potentially nucleophilic ligand.<sup>1</sup> Such an “acid–base bifunction” of the metal–amido bond has now been widely used in catalytic reduction and C–C bond formation.<sup>2,3</sup> The importance of the catalyst bifunctionality in transfer hydrogenation, for example, has been validated by the isolation and interconversion of the 16e amido complex  $[Ru(Tsdpn)(p\text{-cymene})]$  and 18e amine complex  $[RuH(TsdpnH)(p\text{-cymene})]$  ( $TsdpnH = (S,S)\text{-}TsNCH(C_6H_5)CH(C_6H_5)NH_2$ ;  $Ts = SO_2C_6H_4CH_3\text{-}p$ ) as real active catalysts (eq 1).<sup>4</sup> As an extension of our continuing studies on practical molecular catalysts based on the concept of this metal/NH bifunction,<sup>3,5</sup> we have recently demonstrated that the doubly unsaturated, imido-bridged diiridium complex  $[(Cp^*Ir)_2(\mu_2-NTs)_2]$  ( $Cp^* = \eta^5-C_5(CH_3)_5$ ) behaves as both Lewis

acid and Brønsted base.<sup>6,7</sup> We report here an interconversion between a coordinatively unsaturated  $Ir_2(\mu_2-NR)$  and saturated  $Ir_2Cl(\mu_2-NHR)$  species as a dinuclear variant of the amido–amine couples in the mononuclear systems. The hydride migration to the bridging nitrogen atom, which is triggered by a  $\pi$ -acceptor coordination to the unsaturated complex, is also discussed.



When the trichloro–hydrido complex  $[(Cp^*IrCl)_2(\mu_2-H)(\mu_2-Cl)]$ <sup>8</sup> is treated with an equimolar amount of  $LiNHMs$  ( $Ms = SO_2CH_3$ ), the mono(mesylimido)- and hydrido-bridged diiridium(III) complex  $[(Cp^*IrCl)_2(\mu_2-H)(\mu_2-NHMs)]$  (**1**) is obtained in 71% yield (eq 2).<sup>9,10</sup> The <sup>1</sup>H NMR spectrum of **1** exhibits a singlet ascribed to the bridging hydrido ligand along with an NH resonance at  $\delta$  5.52, which disappears upon treatment with D<sub>2</sub>O. The presence of the NH group is also supported by the

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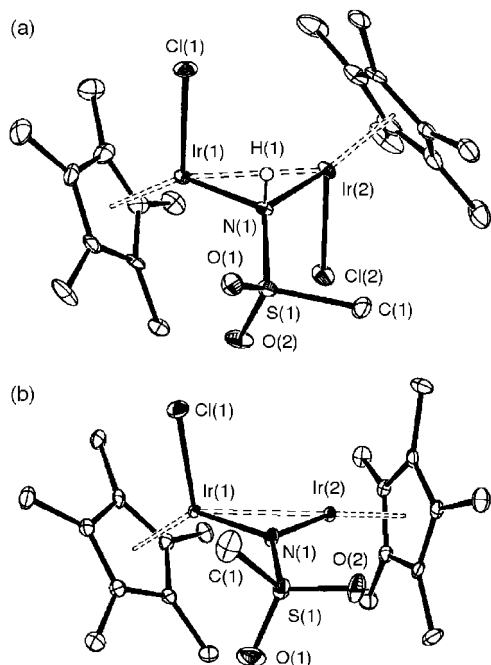
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**Figure 1.** Molecular structures of **1** (a) and **2** (b). For **1**, one of the two crystallographically independent components in the crystal is shown. Hydrogen atoms except for the amido hydrogen in **1** are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

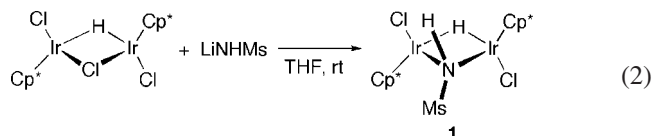
IR spectrum, showing an NH band at  $3188\text{ cm}^{-1}$ . The dinuclear structure of **1** has been confirmed by X-ray analysis, as depicted in Figure 1a.<sup>11</sup> The two Cp\* groups are situated in mutually *anti* positions with respect to the Ir<sub>2</sub>N plane, in agreement with the <sup>1</sup>H NMR spectrum showing two inequivalent Cp\* singlets. The short Ir(III)–Ir(III) distance of  $2.870\text{ \AA}$  (mean) and the geometries around the Ir atoms are consistent with a three-center–two-electron bond involving a bridging hydrido ligand (Table 1),<sup>12</sup> although the hydride as well as the amido hydrogen atom could not be located in the difference Fourier map. The amido hydrogen atom forms an intermolecular hydrogen bond with one of the sulfonyl oxygen atoms in another molecule, as suggested by the average N(1)–O(1)\* contact of  $3.04\text{ \AA}$  (Figure S1).

(9) Synthesis of **1**. To a suspension of MsNH<sub>2</sub> (124.8 mg, 1.312 mmol) in THF (50 mL) was added a hexane solution of *n*-C<sub>4</sub>H<sub>9</sub>Li (1.61 M, 815  $\mu\text{L}$ , 1.33 mmol) at room temperature, and the mixture was stirred for 1 h. The resultant white suspension was added to a solution of [(Cp\*IrCl)<sub>2</sub>( $\mu_2$ -H)( $\mu_2$ -Cl)] (1.0000 g, 1.312 mmol) in THF (50 mL) at 0 °C, and the mixture was slowly warmed to room temperature with stirring. After 20 h, the resultant orange-red solution was evaporated to dryness, and extracted with toluene–dichloromethane (40 mL/40 mL). Removal of the solvent and subsequent recrystallization from dichloromethane–hexane (5 mL/40 mL) afforded orange crystals, which were washed with acetone–hexane (10 mL/10 mL) and dried in vacuo (762.4 mg, 0.9287 mmol, 71%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  5.52 (br, 1H, NH), 3.21 (s, 3H, SO<sub>2</sub>CH<sub>3</sub>), 1.77, 1.46 (s, 15H each, Cp\*), –15.40 (s, 1H, Ir<sub>2</sub>H). IR (KBr):  $3188\text{ cm}^{-1}$  ( $\nu_{\text{NH}}$ ). Anal. Calcd for C<sub>21</sub>H<sub>35</sub>Cl<sub>2</sub>Ir<sub>2</sub>NO<sub>2</sub>S: C, 30.73, H, 4.30; N, 1.71. Found: C, 30.83; H, 4.00; N, 1.66.

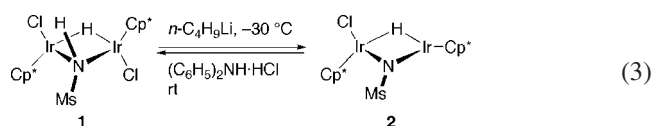
(10) The analogous reaction using TsNH<sub>2</sub> resulted in cyclometalation of the tolyl group: Arita, H.; Ishiwata, K.; Kuwata, S.; Ikariya, T., unpublished result.

(11) Crystal data for **1**: triclinic,  $P\bar{1}$ ,  $a = 12.244(5)\text{ \AA}$ ,  $b = 14.843(7)\text{ \AA}$ ,  $c = 15.510(7)\text{ \AA}$ ,  $\alpha = 114.224(7)^\circ$ ,  $\beta = 91.944(4)^\circ$ ,  $\gamma = 92.901(4)^\circ$ ,  $V = 2562.7(19)\text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calc}} = 2.128\text{ g cm}^{-3}$ , 11 559 unique reflections ( $2\theta < 55^\circ$ ), 591 parameters,  $R1 = 0.051$  [ $I > 2\sigma(I)$ ],  $wR2 = 0.135$  (all data), GOF = 1.009.

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Notably, as observed in the mononuclear amine–chloro complexes,<sup>4</sup> dehydrochlorination of the amido-bridged dinuclear complex **1** with a base provides the imido-bridged coordinatively unsaturated complex [(Cp\*Ir( $\mu_2$ -H)( $\mu_2$ -NMs)IrCl)Cp\*] (**2**) as thermally unstable dark red crystals in moderate yield (eq 3).<sup>13</sup> The X-ray analysis has revealed the detailed structure of **2** as shown in Figure 1b.<sup>14</sup> The chloro ligand is terminally bound to the Ir(1) atom, whereas the Ir(2) center is obviously unsaturated with the short Ir–N distance ( $1.911(4)\text{ \AA}$ ) in comparison with the Ir(1)–N(1) distance of  $2.063(5)\text{ \AA}$ .<sup>15</sup> The angle sum around the N(1) atom,  $355.3^\circ$ , is consistent with the sp<sup>2</sup>-hybridization of the bridging imido nitrogen. The N–S distance of  $1.599(4)\text{ \AA}$  is almost equal to those in the related imido-bridged complex [(Cp\*Ir)<sub>2</sub>( $\mu_2$ -NTs)<sub>2</sub>] ( $1.599\text{ \AA}$ , mean)<sup>6</sup> and slightly shorter than that in the amido complex **1** ( $1.644\text{ \AA}$ , mean). A high-field resonance at  $\delta -8.02$  in the <sup>1</sup>H NMR spectrum is ascribed to the hydrido ligand, which seems to bridge the two Ir atoms judging from the configurations of the metals and the Ir(III)–Ir(III) distance in **2**. Despite the unsymmetrical solid-state structure, the two Cp\* groups in **2** appear to be equivalent in the <sup>1</sup>H NMR spectrum even at  $-80\text{ }^\circ\text{C}$ , suggesting a dynamic exchange of the chloro ligand between the two Ir atoms. An alternative explanation is that the solution structure of **2** is different from the solid-state structure and is a more symmetrical one such as a  $\mu_2$ -chloro structure.



The amido-bridged chloro complex **1** is regenerated by the reaction of the imido-bridged unsaturated complex **2** with diphenylamine hydrochloride. Addition of pronucleophiles and dihydrogen across the metal–( $\mu$ -NR) bonds in this mode would be a key step to realize dinuclear acid–base bifunctional catalysis. As related reactions, Dobbs and Bergman demonstrated that the bis(imido)-bridged diiridium complex [(Cp\*Ir)<sub>2</sub>( $\mu_2$ -NC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>] reacts with H<sub>2</sub> to afford the cyclometalated complex [(Cp\*Ir( $\mu_2$ -H)<sub>2</sub>( $\mu_2$ -NHC<sub>6</sub>H<sub>4</sub>- $\kappa^2$ N,C)Ir)Cp\*] with a loss of aniline; initial hydrogenation of the Ir–N bonds followed by intramolecular C–H cleavage has been proposed in this reaction.<sup>7i</sup> More recently, an equilibrium between the imido-bridged diruthenium complex [(Cp\*Ru)<sub>2</sub>( $\mu_2$ -NC<sub>6</sub>H<sub>5</sub>)( $\mu_2$ -CO)], aniline, and the bis(amido)-bridged complex [(Cp\*Ru)<sub>2</sub>( $\mu_2$ -NHC<sub>6</sub>H<sub>5</sub>)<sub>2</sub>( $\mu_2$ -CO)] was

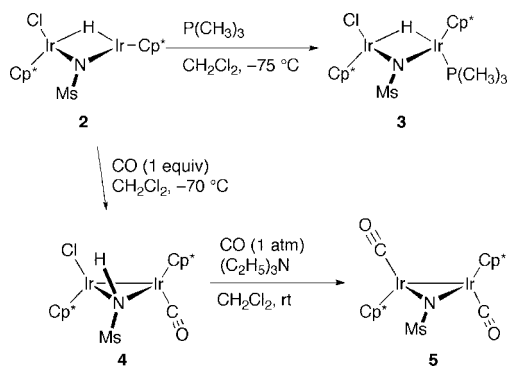
(13) Synthesis of **2**. To a solution of **1** (82.2 mg, 0.100 mmol) in THF (10 mL) was added a hexane solution of *n*-C<sub>4</sub>H<sub>9</sub>Li (1.61 M, 62.0  $\mu\text{L}$ , 0.100 mmol) at  $-30\text{ }^\circ\text{C}$ , and the mixture was stirred for 30 min at this temperature. The resultant deep red solution was evaporated to dryness and extracted with cold toluene (10 mL). Removal of the solvent and subsequent recrystallization from toluene–hexane (2 mL/10 mL) at  $-30\text{ }^\circ\text{C}$  afforded **2** as deep red crystals (55.5 mg, 0.0708 mmol, 71%). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.15 (s, 3H, SO<sub>2</sub>CH<sub>3</sub>), 1.68 (s, 30H, Cp\*),  $-8.02$  (s, 1H, Ir<sub>2</sub>H). Anal. Calcd for C<sub>21</sub>H<sub>34</sub>ClIr<sub>2</sub>NO<sub>2</sub>S: C, 32.15; H, 4.37; N, 1.79. Found: C, 32.24; H, 4.51; N, 1.76.

(14) Crystal data for **2**: monoclinic,  $P2_1/c$ ,  $a = 14.283(3)\text{ \AA}$ ,  $b = 11.501(3)\text{ \AA}$ ,  $c = 14.714(4)\text{ \AA}$ ,  $\beta = 103.945(3)^\circ$ ,  $V = 2345.7(10)\text{ \AA}^3$ ,  $Z = 4$ ,  $\rho_{\text{calc}} = 2.221\text{ g cm}^{-3}$ , 5336 unique reflections ( $2\theta < 55^\circ$ ), 286 parameters,  $R1 = 0.024$  [ $I > 2\sigma(I)$ ],  $wR2 = 0.086$  (all data), GOF = 1.005.

(15) In contrast, the Ir–Cp\* distances for the two Ir centers exhibit no significant difference (Ir(1)–C:  $2.178\text{ \AA}$ , Ir(2)–C:  $2.184\text{ \AA}$  (mean)).

**Table 1.** Selected Interatomic Distances (Å) and Angles (deg) for **1**, **2**, **4**, and **5**

	<b>1</b>		<b>2</b>	<b>4</b>	<b>5</b>
	molecule A	molecule B			
Ir(1)–Ir(2)	2.8666(6)	2.8729(5)	2.7583(2)	2.7316(6)	2.6827(2)
Ir(1)–N(1)	2.142(7)	2.128(8)	2.063(5)	2.099(9)	2.064(4)
Ir(2)–N(1)	2.153(8)	2.154(8)	1.911(4)	2.095(9)	2.028(6)
Ir(1)–Cl(1)	2.405(3)	2.400(3)	2.425(1)	2.402(3)	
Ir(2)–Cl(2)	2.402(4)	2.405(4)			
N(1)–S(1)	1.643(9)	1.645(10)	1.599(4)	1.64(1)	1.598(5)
Ir(1)–N(1)–Ir(2)	83.7(2)	84.3(2)	87.8(2)	81.3(3)	81.9(2)
Ir(1)–N(1)–S(1)	123.0(6)	121.2(6)	135.4(2)	123.6(5)	124.0(2)
Ir(2)–N(1)–S(1)	128.8(5)	129.5(5)	132.1(3)	124.6(5)	123.4(2)

**Scheme 1**

observed by Matsuzaka and co-workers.<sup>7e</sup> In these transformations, however, the amido-bridged complexes were not isolated.<sup>16</sup>

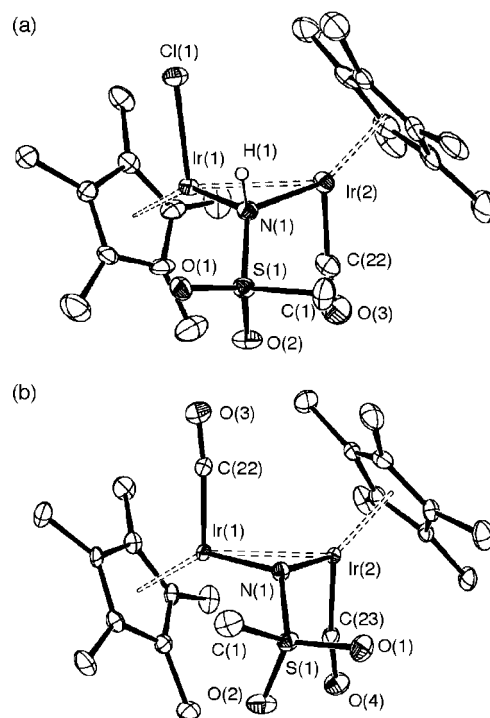
The coordinatively unsaturated complex **2** reacts with two-electron donors as shown in Scheme 1. The reaction with trimethylphosphine affords the corresponding 18e adduct [Cp\*Ir{P(CH<sub>3</sub>)<sub>3</sub>}(μ<sub>2</sub>-H)(μ<sub>2</sub>-NMs)IrClCp\*] (**3**), which is characterized by <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy.<sup>17</sup> In marked contrast, the reaction with 1 equiv of CO leads to the formation of the amido-bridged monocarbonyl complex [Cp\*Ir(CO)(μ<sub>2</sub>-NHMs)-IrClCp\*] (**4**) without a hydrido ligand.<sup>18</sup> A characteristic singlet due to the NH proton at δ 4.66 in the <sup>1</sup>H NMR and an ν<sub>NH</sub> band at 3176 cm<sup>-1</sup> in the IR spectrum confirmed the presence of the amido ligand in **4**. An X-ray analysis has disclosed the tetrahedral configuration of the bridging nitrogen atom and the intermolecular hydrogen bond between the amido proton and one of the sulfonyl oxygen atoms as in the crystal of **1** (Figures 2a and S2).<sup>19</sup> The formal umpolung of the bridging hydrido ligand in **2** to the amido proton in **4** can be rationalized by the

stronger π-accepting character of CO, which increases the acidity of the hydride. The hydride migration leads to the formal reduction of the diiridium(III) center to Ir(II)<sub>2</sub>, which is stabilized by the formation of an Ir–Ir single bond of 2.7316(6) Å.<sup>20</sup> For comparison, the reaction of the mononuclear amido–hydrido complex [Cp\*IrH(NHC<sub>6</sub>H<sub>5</sub>){P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}] with CO is known to result in reductive elimination of aniline to give the Ir(I) carbonyl complex [Cp\*Ir(CO){P(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>}]<sup>21</sup> When **2** is treated with an excess of CO in the presence of a base, the imido-bridged bis(carbonyl) complex [(Cp\*Ir(CO))<sub>2</sub>(μ<sub>2</sub>-NMs)] (**5**) is obtained.<sup>22</sup> The IR and <sup>1</sup>H NMR spectra of **5** suggest the absence of an NH group. The CO stretching frequency at 1942 cm<sup>-1</sup> is comparable to that of the isoelectronic sulfido-bridged diiridium(II) complex [(Cp\*Ir(CO))<sub>2</sub>(μ<sub>2</sub>-S)] (1929 cm<sup>-1</sup>).<sup>23</sup> Figure 2b depicts the crystal structure of **5**.<sup>24</sup> The two carbonyl ligands lie in mutually *anti* positions with respect to the Ir<sub>2</sub>N plane. In contrast to **2**, the configuration of the bridging imido nitrogen deviates far from the planarity with the angle sum around the N(1) atom of 329.3°, possibly because of the coordinative saturation of the Ir atoms without π-donation of the imido nitrogen atom. The Ir(II)–Ir(II), Ir<sub>saturated</sub>–N, and N–S distances

(16) Hydrogenation of a saturated Ru–(μ<sub>3</sub>-NH) bond to an Ru–H and Ru–(μ<sub>2</sub>-NH<sub>2</sub>) moieties in a triruthenium complex was reported recently: (a) Nakajima, Y.; Kameo, H.; Suzuki, H. *Angew. Chem., Int. Ed.* **2006**, *45*, 950. (b) Kameo, H.; Nakajima, Y.; Suzuki, H. *Eur. J. Inorg. Chem.* **2007**, 1793.

(17) Complex **3** has eluded isolation due to its thermal instability. Spectral data of **3**. <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ 3.10 (s, 3H, SO<sub>2</sub>CH<sub>3</sub>), 2.07 (d, 15H, <sup>4</sup>J<sub>PH</sub> = 2.3 Hz, Cp\*), 1.95 (s, 15H, Cp\*), 1.47 (d, 9H, <sup>2</sup>J<sub>PH</sub> = 11.5 Hz, P(CH<sub>3</sub>)<sub>3</sub>), –11.20 (d, 1H, <sup>2</sup>J<sub>PH</sub> = 16.0 Hz, Ir<sub>2</sub>H). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>): δ –30.5 (s).

(18) Synthesis of **4**. To a solution of **1** (45.5 mg, 0.0554 mmol) in THF (7 mL) was added a hexane solution of *n*-C<sub>4</sub>H<sub>9</sub>Li (1.58 M, 35 μL, 0.055 mmol) at –30 °C, and the mixture was stirred for 40 min at this temperature. The resultant deep red solution of **2** was evaporated to dryness and extracted with cold dichloromethane (10 mL). To the extract was added CO (1.35 mL at 24 °C, 0.0554 mmol) by a syringe at –70 °C, and the mixture was stirred for 2 h at this temperature. After removal of the solvent in vacuo, recrystallization from dichloromethane–diethyl ether (2 mL/10 mL) afforded **4** as orange crystals (13.6 mg, 0.0167 mmol, 30% based on **1**). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 4.66 (br, 1H, NH), 2.63 (s, 3H, SO<sub>2</sub>CH<sub>3</sub>), 1.78, 1.76 (s, 15H each Cp\*). IR (KBr): 3176 cm<sup>-1</sup> (ν<sub>NH</sub>), 1950 cm<sup>-1</sup> (ν<sub>CO</sub>). Anal. Calcd for C<sub>22</sub>H<sub>34</sub>ClIr<sub>2</sub>NO<sub>3</sub>S: C, 32.52; H, 4.22; N, 1.72. Found: C, 32.33; H, 4.38; N, 1.68.



**Figure 2.** Molecular structures of **4** (a) and **5** (b). Hydrogen atoms except for the amido hydrogen in **4** are omitted for clarity. Thermal ellipsoids are drawn at the 30% probability level.

are comparable with those in the imido-bridged complex **2**, respectively.

In summary, we have demonstrated that the reversible addition of hydrogen chloride across the unsaturated M–N bond

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(19) Crystal data for **4**: orthorhombic, *Pbca*,  $a = 16.469(7)$  Å,  $b = 15.342(7)$  Å,  $c = 20.655(9)$  Å,  $V = 5219(4)$  Å<sup>3</sup>,  $Z = 8$ ,  $\rho_{\text{calc}} = 2.068$  g cm<sup>-3</sup>, 5989 unique reflections ( $2\theta < 55^\circ$ ), 305 parameters,  $R1 = 0.041$  [ $I > 2\sigma(I)$ ],  $wR2 = 0.146$  (all data), GOF = 1.003.

(20) (a) For nitrogen-bridged diiridium(II) complexes, see: Jiménez, M. V.; Sola, E.; López, J. A.; Lahoz, F. J.; Oro, L. A. *Chem.–Eur. J.* **1998**, *4*, 1398. (b) Matsuzaka, H.; Ariga, K.; Kase, H.; Kamura, T.; Kondo, M.; Kitagawa, S.; Yamasaki, M. *Organometallics* **1997**, *16*, 4514. (c) Kolel-Veetil, M. K.; Curley, J. F.; Yadav, P. R.; Ahmed, K. J. *Polyhedron* **1994**, *13*, 919.

(21) Glueck, D. S.; Newman-Winslow, L. J.; Bergman, R. G. *Organometallics* **1991**, *10*, 1462.

(22) Synthesis of **5**. To a solution of **1** (40.0 mg, 0.0487 mmol) in THF (5 mL) was added a hexane solution of *n*-C<sub>4</sub>H<sub>9</sub>Li (1.61 M, 30.5 μL, 0.0491 mmol) at –30 °C, and the mixture was stirred for 40 min at this temperature. To the resultant deep red solution of **2** was added triethylamine (7.0 μL, 0.050 mmol) and then bubbled CO, and the mixture was stirred for 1 h at room temperature. After removal of the solvent in vacuo, the residue was dissolved in dichloromethane and subjected to chromatography on alumina. An orange band eluted with dichloromethane was recrystallized from toluene–hexane (1 mL/15 mL) to give **5** as orange crystals (32.5 mg, 0.0404 mmol, 83% based on **1**). <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>): δ 3.01 (s, 3H, SO<sub>2</sub>CH<sub>3</sub>), 1.83 (s, 15H each Cp\*). IR (KBr): 1942 cm<sup>-1</sup> (ν<sub>CO</sub>). Anal. Calcd for C<sub>23</sub>H<sub>33</sub>Ir<sub>2</sub>NO<sub>4</sub>S: C, 34.36; H, 4.14; N, 1.74. Found: C, 34.13; H, 4.02; N, 1.72.

(23) Jones, W. D.; Chin, R. M. *J. Am. Chem. Soc.* **1994**, *116*, 198.

is also operative in an imido-bridged dinuclear system. Coordination of a π-acceptor to the unsaturated complex **2** increases the acidity of the bridging hydrido ligand, leading to the migration of the hydride to the bridging nitrogen and formal reduction to Ir(II)<sub>2</sub>. Further study will be directed to the development of the catalysis based on this acid–base bifunction and umpolung of the hydride in the nitrogen-bridged dinuclear complexes.

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**Supporting Information Available:** Text giving experimental details and CIF file giving X-ray crystallographic data for **1**, **2**, **4**, and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(24) Crystal data for **5**: monoclinic, *P2<sub>1</sub>/c*,  $a = 8.504(4)$  Å,  $b = 17.302(8)$  Å,  $c = 17.943(9)$  Å,  $\beta = 106.364(5)^\circ$ ,  $V = 2533(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_{\text{calc}} = 2.108$  g cm<sup>-3</sup>, 5730 unique reflections ( $2\theta < 55^\circ$ ), 313 parameters,  $R1 = 0.028$  [ $I > 2\sigma(I)$ ],  $wR2 = 0.096$  (all data), GOF = 1.004.