



# Catalytic hydrogenation of C=O and C=N bonds via heterolysis of H<sub>2</sub> mediated by metal–sulfur bonds of rhodium and iridium thiolate complexes

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## ARTICLE INFO

### Article history:

Received 31 January 2009

Received in revised form 18 February 2009

Accepted 18 February 2009

Available online 28 February 2009

### Keywords:

Rhodium

Iridium

Thiolate

H<sub>2</sub> activation

Hydrogenation

## ABSTRACT

Coordinatively unsaturated rhodium and iridium complexes having a bulky thiolate, [Cp<sup>\*</sup>M(PMe<sub>3</sub>)(SDmp)](BAR<sub>4</sub><sup>F</sup>) (**1a**: M = Rh; **1b**: M = Ir; Dmp = 2,6-(mesityl)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), catalyzed the hydrogenation of benzaldehyde, *N*-benzylideneaniline, and cyclohexanone, under 1 atm of H<sub>2</sub> at low temperatures. In these catalytic reactions, the M–H/S–H complexes [Cp<sup>\*</sup>M(PMe<sub>3</sub>)(H)(HSDmp)](BAR<sub>4</sub><sup>F</sup>) (**2a**: M = Rh; **2b**: M = Ir) generated via H<sub>2</sub> heterolysis by **1a** or **1b** were suggested to transfer both M–H hydride and S–H proton to substrates. The catalytic reactions were terminated by the dissociation of H–SDmp from the metal centers of **2a** and **2b** that occurs at ambient temperature under H<sub>2</sub> atmosphere.

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## 1. Introduction

Heterolytic cleavage of H<sub>2</sub> by transition metal complexes has been useful for catalytic hydrogenation of aldehydes, ketones, and imines [1,2]. A representative class of such hydrogenation catalysts is the ruthenium–amide complexes, in which both ruthenium and amide nitrogen atoms participate in the heterolysis of H<sub>2</sub> [3]. While these complexes efficiently activate H<sub>2</sub>, biological hydrogen activation is mediated by metal–thiolate complexes in hydrogenases. The active site of [NiFe] hydrogenase consists of a thiolate-bridged (carbonyl/cyano)iron–nickel complex [4], which has been postulated to use both metal and cysteinyl sulfur atoms in the reaction with H<sub>2</sub>. The recent studies on [NiFe] hydrogenase suggested that the nickel center is a plausible binding site of H<sub>2</sub>, and that a cysteinyl sulfur bound to nickel possibly accepts a proton generated from the heterolysis of H<sub>2</sub> [5]. Thus the heterolysis of H<sub>2</sub> by [NiFe] hydrogenase may occur in a similar manner to that mediated by ruthenium–amide catalysts.

The unique function of metal–thiolate complex in [NiFe] hydrogenase prompted us to investigate into the structural and reaction models. As structural analogues of the active site of [NiFe] hydrogenase, we have synthesized a series of thiolate-bridged (CO/CN)Fe–Ni and (CO)<sub>3</sub>Fe–Ni complexes such as (PPh<sub>4</sub>)[(CN)<sub>2</sub>(CO)<sub>2</sub>Fe(μ-pdt)Ni(S<sub>2</sub>CNEt<sub>2</sub>)] (pdt = 1,3-propanedithiolate) and (CO)<sub>3</sub>-

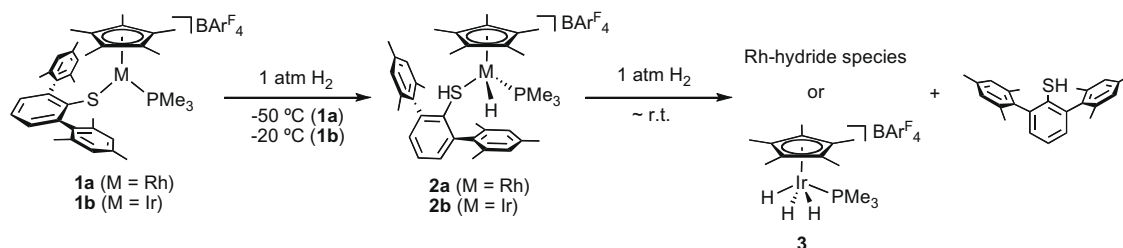
Fe(μ-S<sup>t</sup>Bu)<sub>3</sub>Ni{SC(NMe<sub>2</sub>)<sub>2</sub>}Br [6]. Also we have reported some metal–sulfur complexes as functional models, which are capable of splitting H<sub>2</sub> in a heterolytic manner [7]. For example, the half-sandwich rhodium and iridium complexes having a bulky SDmp thiolate (Dmp = 2,6-(mesityl)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [8], [Cp<sup>\*</sup>M(PMe<sub>3</sub>)(SDmp)](BAR<sub>4</sub><sup>F</sup>) (**1a**: M = Rh; **1b**: M = Ir; Ar<sup>F</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>), were found to promote the heterolysis of H<sub>2</sub> (1 atm) at low temperatures (–50 to –20 °C), giving rise to the M–H/S–H complexes [Cp<sup>\*</sup>M(PMe<sub>3</sub>)(H)(HSDmp)](BAR<sub>4</sub><sup>F</sup>) (**2a**: M = Rh; **2b**: M = Ir) (Scheme 1) [7e]. Since complexes **2a** and **2b** contain a hydride (M–H) and a proton (S–H) derived from H<sub>2</sub>, we sensed that these reactions could be applied to catalytic hydrogenation reactions. Herein we report the hydrogenation of C=O and C=N groups of benzaldehyde, *N*-benzylideneaniline, and cyclohexanone, catalyzed by **1a** and **1b** under 1 atm of H<sub>2</sub> at low temperatures.

## 2. Results and discussion

Coordinatively unsaturated thiolate complexes **1a** and **1b** mediate the heterolysis of H<sub>2</sub> under mild conditions. This is an advantage for catalytic reactions, because most of the precedent H<sub>2</sub> heterolysis by thiolate complexes require rigorous conditions such as high-pressure of H<sub>2</sub> and/or the presence of external protons [9], preventing their application to hydrogenation catalysts. Whereas the heterolysis of H<sub>2</sub> by **1a** or **1b** proceeds under mild conditions, the resultant M–H/S–H complexes **2a** and **2b** were found to be unstable [7e]. The metal centers of **2a** and **2b** readily liberate H–SDmp under H<sub>2</sub> atmosphere at room temperature, giving rise

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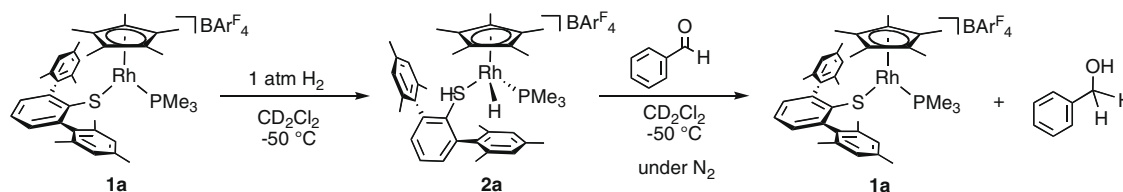
**Scheme 1.** Heterolysis of H<sub>2</sub> mediated by **1a** and **1b**.

to a complex mixture of rhodium-hydride species or a trihydride complex of iridium [Cp\*Ir(PMe<sub>3</sub>)(H)<sub>3</sub>](BARF<sub>4</sub>) (**3**) (Scheme 1) [10]. Therefore, the following hydrogenation reactions were conducted at low temperatures. Anticipating that the M–H/S–H complexes **2a** and **2b** transfer both M–H and S–H hydrogen atoms to substrates, a stoichiometric reaction between **2a** and benzaldehyde was examined. Under a nitrogen atmosphere, one equiv of benzaldehyde was added to a CD<sub>2</sub>Cl<sub>2</sub> solution of **2a** at –50 °C. The <sup>1</sup>H NMR spectrum of this reaction mixture revealed the regeneration of **1a** and the quantitative formation of benzylalcohol, completing formal turnover of the catalytic hydrogenation (Scheme 2).

Motivated by the stoichiometric reaction between **2a** and benzaldehyde, we set out the catalytic hydrogenation (Table 1). Exposure of H<sub>2</sub> (1 atm) to a CD<sub>2</sub>Cl<sub>2</sub> solution of benzaldehyde and catalytic amount of **1a** (2 mol%) at –50 °C resulted in the quantitative formation of benzylalcohol (entry 1). In contrast, a complex mixture of rhodium-hydride species, formed from **2a** and H<sub>2</sub> at room temperature, did not show any catalytic activity (entry 2), suggesting that the thermally unstable Rh–H/S–H complex **2a** is necessary for this catalytic reaction. The Rh–H/S–H hydrogen atoms in **2a** are transferred to benzaldehyde, possibly via formation of six-membered metallacycle consisting of Rh–H, S–H, and C=O groups (Scheme 3) as proposed for the hydrogenation mediated by the ruthenium–amide complexes [3]. While the rhodium

complex **1a** serves as a good catalyst for hydrogenation of benzaldehyde, the iridium congener **1b** was found to be less active. Complex **1b** was almost inactive at –50 °C for hydrogenation of benzaldehyde (entry 3), because the H<sub>2</sub> activation by **1b** is very slow at this temperature. At –20 °C, complex **1b** showed some catalytic activity, whereas the longer reaction time was needed (entry 4). The hydrogenation reactions of *N*-benzylideneaniline and cyclohexanone were also attempted in a similar manner (entries 5–8), and the yields of *N*-phenylbenzylamine and cyclohexanol were 66% and 53% yields, respectively, in the presence of **1a** as the catalyst (entries 5 and 7). The lower catalytic activity of **1b** was also the case for the hydrogenation of these substrates. The yield of *N*-phenylbenzylamine was 15% by using **1b** as the catalyst (entry 6), and attempts for the hydrogenation of cyclohexanone by **1b** were unsuccessful (entry 8).

The lower catalytic activity of **1b** was not only because of slow H<sub>2</sub> activation, but also due to side reactions. After the hydrogenation of cyclohexanone by **1b**, the catalytically inactive trihydride complex **3** and H–SDmp were formed. This result indicates the low reactivity of Ir–H/S–H complex **2b** toward cyclohexanone and the facile liberation of H–SDmp from **2b** in the presence of H<sub>2</sub>. The side reaction found in the hydrogenation of benzaldehyde by **1b** was different, and the NMR spectrum indicated the formation of free H–SDmp and a phenyl carbonyl complex



**Scheme 2.** Proton/hydride transfer from **2a** to benzaldehyde.

**Table 1**  
Hydrogenation reactions catalyzed by **1a** and **1b**.<sup>a</sup>

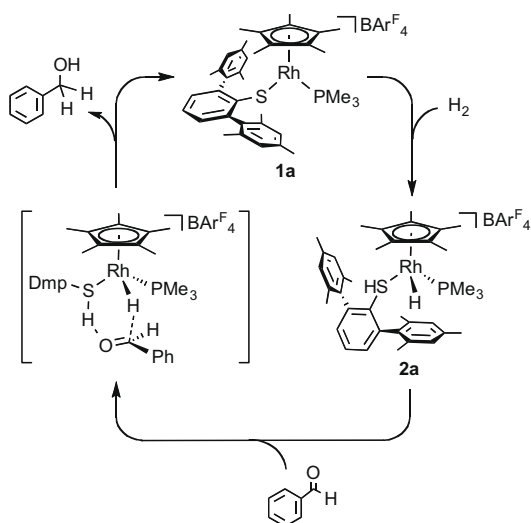
Entry	Substrate	Catalyst	Temperature (°C)	Time (h)	Yield (%) <sup>b</sup>	Product
1		<b>1a</b>	–50	24	>98	
2		Rh-hydride <sup>c</sup>	–50	24	n.d. <sup>d</sup>	
3		<b>1b</b>	–50	24	<2	
4		<b>1b</b>	–20	48	15	
5		<b>1a</b>	–50	24	66	
6		<b>1b</b>	–20	48	15	
7		<b>1a</b>	–50	24	53	
8		<b>1b</b>	–20	48	n.d. <sup>d</sup>	

<sup>a</sup> Standard conditions: 2 mol% catalysts, 1 mL CD<sub>2</sub>Cl<sub>2</sub>, 1 atm H<sub>2</sub>.

<sup>b</sup> Determined by <sup>1</sup>H NMR with reference to the internal standard ((CH<sub>3</sub>)<sub>3</sub>Si)<sub>4</sub>Si (1 wt%).

<sup>c</sup> Obtained from the reaction of **1a** with H<sub>2</sub> (1 atm) at room temperature.

<sup>d</sup> Not detected.



Scheme 3. A possible mechanism for hydrogenation.

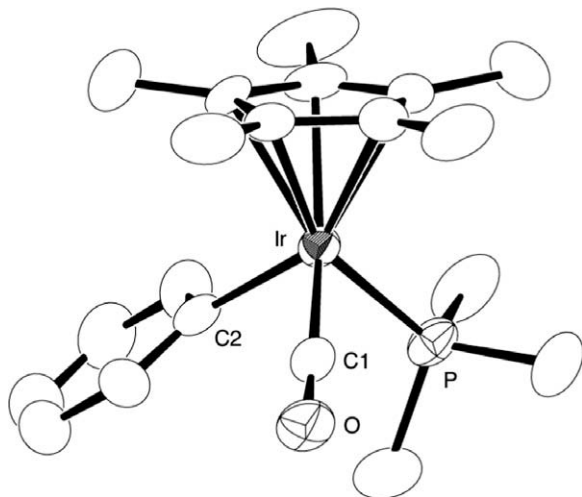


Fig. 1. Structure of the cationic part of  $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{Ph})(\text{CO})][\text{BARf}_4^+]$  (**4**) with thermal ellipsoids at the 50% probability level. All hydrogen atoms and  $\text{BARf}_4^+$  anion are omitted for clarity. Selected bond distances (Å) and angles ( $^\circ$ ): Ir–P 2.3084(18), Ir–C1 1.875(5), C1–O 1.132(6), Ir–C2 2.109(5), P–Ir–C1 89.1(2), C1–Ir–C2 89.3(2), C2–Ir–P 86.22(19).

$[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{Ph})(\text{CO})][\text{BARf}_4^+]$  (**4**), the structure of which was confirmed by an X-ray analysis (Fig. 1). The cationic part of **4** is known, and the OTf salt of **4** has been prepared from the reaction of  $\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{Me})(\text{OTf})$  with benzaldehyde [11]. Since this reaction is accompanied by the liberation of methane, benzaldehyde may be deprotonated by the Ir–Me groups to generate the Ir–C(O)Ph species. Similarly, the phenyl and carbonyl ligands in **4** are likely derived from benzaldehyde, and the formation of **4** may involve the deprotonation from benzaldehyde and the decarbonylation from the resultant Ir–C(O)Ph species. As the SDmp ligand in **1b** serves as a base for the heterolysis of  $\text{H}_2$ , this ligand may deprotonate from benzaldehyde. Other possibilities involve the liberation of H–SDmp from **2b** followed by deprotonation of benzaldehyde by Ir–H, or the protonation of the SDmp ligand in **1b** by benzylalcohol to generate an Ir-alkoxide species which may uptake a proton from benzaldehyde.

In summary, we have demonstrated the hydrogenation of benzaldehyde, *N*-benzylideneaniline, and cyclohexanone, catalyzed by

coordinatively unsaturated rhodium and iridium complexes **1a** and **1b** under 1 atm of  $\text{H}_2$  at low temperatures. These reactions involve the heterolysis of  $\text{H}_2$  to form the M–H/S–H complexes **2a** and **2b**, which may transfer both M–H hydride and S–H proton to substrates in a concerted manner as proposed for the hydrogenation mediated by ruthenium–amide complexes (Scheme 3). Whereas the yields of *N*-phenylbenzylamine and cyclohexanol were not sufficient and the catalytic activity of **1b** was low, this study may suggest a new utility of the metal–sulfur bond in thiolate complexes.

### 3. Experimental

#### 3.1. General procedures

All reactions and manipulations were performed under a nitrogen atmosphere using a glove box and standard Schlenk techniques.  $\text{CD}_2\text{Cl}_2$  was dried by  $\text{CaH}_2$  and distilled prior to use. Hexane and  $\text{CH}_2\text{Cl}_2$  were purified by the method of Grubbs and coworkers [12], where the solvents were passed over columns of activated alumina and supported copper catalyst supplied by Hansen & Co. Ltd. The  $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$ , and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were acquired on a JEOL ECA-600. The proton and carbon signals were referenced to the residual signals of  $\text{CD}_2\text{Cl}_2$ . The  $^{31}\text{P}\{^1\text{H}\}$  NMR chemical shifts are relative to the external reference of 85%  $\text{H}_3\text{PO}_4$ . Infrared spectrum was recorded on a JASCO FT/IR-410 spectrometer. ESI-MS spectrum was obtained from Micromass LCT TOF-MS spectrometer. Elemental analysis of **4** was recorded on a LECO-CHNS-932 elemental analyzer where the crystalline samples were sealed in silver capsules under nitrogen. X-ray diffraction data of **4** was collected on a Rigaku AFC8 equipped with a CCD area detector by using graphite-monochromated Mo  $\text{K}\alpha$  radiation.

#### 3.2. Reaction of **2a** with 1 equiv. of benzaldehyde

A Schlenk tube with a stirring bar was charged with **1a** (30.4 mg, 0.02 mmol) and  $\text{CD}_2\text{Cl}_2$  (0.6 mL with 1 wt%  $\{(\text{CH}_3)_3\text{Si}\}_4\text{Si}$  as the internal standard). After freeze–pump–thaw cycles, the tube was filled with 1 atm of  $\text{H}_2$  at  $-80^\circ\text{C}$ , and the tube was kept at  $-50^\circ\text{C}$  with stirring. The color of solution changed from purple to green, indicating the dominant formation of **2a** (the yield of **2a** was 89% under a similar condition [7e]). The Schlenk tube was filled with  $\text{N}_2$  after freeze–pump–thaw cycles, and one equiv of benzaldehyde (25  $\mu\text{L}$  of 0.8 M  $\text{CD}_2\text{Cl}_2$  solution, 0.02 mmol) was added to this solution at  $-50^\circ\text{C}$ . The solution was stirred for 6 h under a  $\text{N}_2$  atmosphere. The color of the reaction mixture turned to purple, and the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR revealed the conversion of benzaldehyde to benzylalcohol (>98%), regeneration of **1a** (86%), and the formation of decomposed rhodium-hydride species (14%) and H–SDmp (14%).

#### 3.3. General procedure for the catalytic hydrogenation

In a glove box, a Schlenk tube with a stirring bar was charged with **1a** or **1b** (0.02 mmol) and  $\text{CD}_2\text{Cl}_2$  (0.5 mL, with  $\{(\text{CH}_3)_3\text{Si}\}_4\text{Si}$  as the internal standard). After freeze–pump–thaw cycles, the tube was filled with 1 atm of  $\text{H}_2$  at  $-80^\circ\text{C}$  (**1a**) or  $-40^\circ\text{C}$  (**1b**), and substrate (1 mmol in 0.5 mL  $\text{CD}_2\text{Cl}_2$ ) was added under  $\text{H}_2$  atmosphere. The reaction mixture was stirred at  $-50^\circ\text{C}$  (**1a**) or  $-20^\circ\text{C}$  (**1b**) under  $\text{H}_2$ , and was warmed to room temperature after catalysis. The yields of the catalytic products were determined by the  $^1\text{H}$  NMR.

The rhodium-hydride species used in Table 1.entry 2, was generated from the reaction of a  $\text{CD}_2\text{Cl}_2$  (0.5 mL with  $\{(\text{CH}_3)_3\text{Si}\}_4\text{Si}$ ) of **1a** (0.02 mmol) with 1 atm of  $\text{H}_2$  at room temperature for 24 hrs. The color of the solution turned from purple to dark green, and the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR showed the conversion of **1a** to uncharac-

terizable rhodium-hydride species and H-SDmp [7e,13]. This mixture was cooled and used for the catalytic reaction.

### 3.4. Characterization of $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{Ph})(\text{CO})](\text{BAR}_4^{\text{F}})$ (**4**) obtained from the reaction in Table 1, entry 4

According to Table 1, entry 4, complex **1b** was treated with benzaldehyde and  $\text{H}_2$  (1 atm) at  $-20^\circ\text{C}$ . After 48 h, the  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of the reaction mixture exhibited the signals for  $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{Ph})(\text{CO})](\text{BAR}_4^{\text{F}})$  (**4**, 37% based on the internal standard  $\{(\text{CH}_3)_3\text{Si}\}_4\text{Si}$ ), H-SDmp (37%), and **2b** (63%). Single crystals of **4** suitable for X-ray diffraction and elemental analysis were obtained by diffusing this solution into hexane at room temperature under a nitrogen atmosphere.  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  7.71 (bs, 8H, *o*-H of  $\text{Ar}^{\text{F}}$ ), 7.56 (bs, 4H, *p*-H of  $\text{Ar}^{\text{F}}$ ), 7.13 (m, 5H, Ph), 1.95 (d,  $J_{\text{PH}} = 2.0$  Hz, 15H,  $\text{Cp}^*$ ), 1.63 (d,  $J_{\text{PH}} = 10.6$  Hz, 9H,  $\text{PMe}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$   $-35.6$  (s,  $\text{PMe}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  167.5 (d,  $J_{\text{PC}} = 11.6$  Hz, CO), 162.3 (q,  $J_{\text{BC}} = 50.2$  Hz, *ipso*-C of  $\text{Ar}^{\text{F}}$ ), 139.8, 131.0 (s, *o*-C of Ph), 135.4 (s, *o*-C of  $\text{Ar}^{\text{F}}$ ), 129.4 (q,  $J_{\text{FC}} = 34.7$  Hz, *m*-C of  $\text{Ar}^{\text{F}}$ ), 126.3 (s, *m*-C of Ph), 125.2 (q,  $J_{\text{FC}} = 274.1$  Hz,  $\text{CF}_3$ ), 122.2 (d,  $J_{\text{PC}} = 9.7$  Hz, *ipso*-C of Ph), 118.0 (s, *p*-C of  $\text{Ar}^{\text{F}}$ ), 104.2 (s,  $\text{C}_5(\text{CH}_3)_5$ ), 16.3 (d,  $J_{\text{PC}} = 42.5$  Hz,  $\text{PMe}_3$ ), 9.7 (s,  $\text{C}_5(\text{CH}_3)_5$ ). ESI-MS ( $\text{CH}_2\text{Cl}_2$ ):  $m/z = 509.1$  ( $4^+$ ). IR (KBr pellet):  $2042$  ( $\nu_{\text{CO}}$ )  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{C}_{52}\text{H}_{42}\text{PF}_{24}\text{OBlr}$ : C, 45.49; H, 3.08. Found: C, 45.49; H, 3.22%.

### 3.5. Degradation of **1a** in the presence of excess benzaldehyde at room temperature

The reaction of **1a** (30.4 mg, 0.02 mmol) with benzaldehyde (106.2 mg, 1 mmol) in  $\text{CD}_2\text{Cl}_2$  at room temperature gave a brown solution. The  $^1\text{H}$  and  $^{31}\text{P}\{^1\text{H}\}$  NMR showed the formation of free H-SDmp and an uncharacterizable rhodium species having  $\text{Cp}^*$  and  $\text{PMe}_3$ .  $^1\text{H}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  1.72 (d,  $J_{\text{PH}} = 3.1$  Hz,  $\text{Cp}^*$ ), 1.50 (d,  $J_{\text{PH}} = 11.0$  Hz,  $\text{PMe}_3$ ).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CD}_2\text{Cl}_2$ ):  $\delta$  3.29 (d,  $J_{\text{RHP}} = 157.9$  Hz,  $\text{PMe}_3$ ). After the catalytic hydrogenation of benzaldehyde (Table 1, entry 1), the same rhodium species was detected as the degradation product at room temperature.

### 3.6. X-ray structural determination

Crystal data and refinement parameters of **4** are summarized in Table 2. Single crystals were coated with oil (Immersion Oil, type B: Code 1248, Cargill Laboratories Inc.) and mounted on loop. Diffraction data were collected at  $-100^\circ\text{C}$  under a cold nitrogen stream on a Rigaku AFC8 equipped with Mercury CCD detector equipped with a graphite-monochromated Mo  $K\alpha$  source ( $\lambda = 0.71070$  Å). Six preliminary data frames were measured at  $0.5^\circ$  increments of  $\omega$ , to assess the crystal quality and preliminary unit cell parameters. The intensity images were also measured at  $0.5^\circ$  intervals of  $\omega$ . The frame data were integrated using Rigaku/MS CrystalClear program package, and the data sets were corrected for absorption using REQAB program. The calculation was performed with SHELX-97. Structure was solved by a Patterson method and refined by full-matrix least-square procedures on  $F^2$ . Anisotropic refinement was applied to all non-hydrogen atoms except for disordered  $\text{CF}_3$  groups of  $\text{BAR}_4^{\text{F}}$ . All of the hydrogen atoms were placed at calculated positions. Five of  $\text{CF}_3$  groups are disordered over two positions. The atom coordinates are available as a CIF file.

### Acknowledgment

This research was financially supported by Grant-in-Aids for Scientific Research (Nos. 18GS0207 and 18064009) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. M.S. thanks the IRTG program (International Research Training

**Table 2**

Crystal data and structure refinement for  $[\text{Cp}^*\text{Ir}(\text{PMe}_3)(\text{Ph})(\text{CO})](\text{BAR}_4^{\text{F}})$  (**4**).

	<b>4</b>
Formula	$\text{C}_{52}\text{H}_{41}\text{OIrF}_{24}$ PB
Formula weight	1371.86
Crystal color, habit	colorless, block
Crystal dimensions (mm)	$0.30 \times 0.10 \times 0.05$
Crystal system	Monoclinic
Space group	$P2_1/c$ (No. 13)
<i>a</i> (Å)	18.611(3)
<i>b</i> (Å)	12.612(2)
<i>c</i> (Å)	23.741(4)
$\beta$ ( $^\circ$ )	107.041(2)
<i>V</i> (Å <sup>3</sup> )	5327.8(16)
<i>Z</i>	4
$D_{\text{calc}}$ ( $\text{g cm}^{-3}$ )	1.71
$\mu$ (Mo $K\alpha$ ) ( $\text{cm}^{-1}$ )	26.65
Max $2\theta$ ( $^\circ$ )	55.0
Number of reflections measured	Total: 41317 Unique: 12168 ( $R_{\text{int}} = 0.069$ )
Number of observations (all reflections)	12168
Number of variables	707
Reflection/parameter ratio	17.21
$R_1$ ( $I > 2\sigma(I)$ ) <sup>a</sup>	0.0538
$wR_2$ (all reflections) <sup>b</sup>	0.143
GOF on $F^2$ <sup>c</sup>	1.069

<sup>a</sup>  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  ( $I > 2\sigma(I)$ ).

<sup>b</sup>  $wR_2 = [(\sum (w(|F_o| - |F_c|)^2) / \sum wF_o^2)]^{1/2}$  (all reflections).

<sup>c</sup>  $\text{GOF} = [\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2}$  (where  $N_o$  = number of observations,  $N_v$  = number of variables).

Group "Complex Functional Systems in Chemistry" Münster-Nagoya) for a graduate externship.

### Appendix A. Supplementary material

CCDC 715530 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2009.02.018](https://doi.org/10.1016/j.jorganchem.2009.02.018).

### References

- [1] E.T. Papish, M.P. Magee, J.R. Norton, in: M. Peruzzini, R. Poli (Eds.), *Recent Advances in Hydride Chemistry*, Elsevier, Amsterdam, 2001 (Chapter 2).
- [2] G.J. Kubas, *Metal Dihydrogen and  $\sigma$ -Bond Complexes*, Kluwer Academic/Plenum Publishers, New York, 2001.
- [3] (a) For example: R. Noyori, T. Ohkuma, *Angew. Chem., Int. Ed.* **40** (2001) 40–73;  
(b) R. Noyori, M. Yamakawa, S. Hashiguchi, *J. Org. Chem.* **66** (2001) 7931–7944;  
(c) R. Noyori, M. Kitamura, T. Ohkuma, *Proc. Natl. Acad. Sci. USA* **101** (2004) 5356–5362;  
(d) R. Noyori, C.A. Sandoval, K. Muñiz, T. Ohkuma, *Philos. Trans. R. Soc. A* **363** (2005) 901–912;  
(e) K. Muñiz, *Angew. Chem., Int. Ed.* **44** (2005) 6622–6627;  
(f) S. Gladiali, E. Alberico, *Chem. Soc. Rev.* **35** (2006) 226–236;  
(g) J.S.M. Samec, J.E. Bäckvall, P.G. Andersson, P. Brandt, *Chem. Soc. Rev.* **35** (2006) 237–248;  
(h) T. Ikariya, A.J. Blacker, *Acc. Chem. Res.* **40** (2007) 1300–1308;  
(i) M. Ito, T. Ikariya, *J. Chem. Soc., Chem. Commun.* (2007) 5134–5142.
- [4] (a) For example: V. Nivière, C. Hatchikian, C. Cambillau, M. Frey, *J. Mol. Biol.* **195** (1987) 969–971;  
(b) A. Volbeda, M.-H. Charon, C. Piras, E.C. Hatchikian, M. Frey, *J.C. Fontecilla-Camps, Nature* **373** (1995) 580–587;  
(c) A. Volbeda, E. Garcin, C. Piras, A.L. de Lacey, V.M. Fernandez, E.C. Hatchikian, M. Frey, *J.C. Fontecilla-Camps, J. Am. Chem. Soc.* **118** (1996) 12989–12996;  
(d) Y. Higuchi, T. Yagi, N. Yasuoka, *Structure* **5** (1997) 1671–1680;  
(e) E. Garcin, X. Vernede, E.C. Hatchikian, A. Volbeda, M. Frey, *J.C. Fontecilla-Camps, Structure* **7** (1999) 557–566;  
(f) H. Ogata, Y. Mizoguchi, N. Mizuno, K. Miki, S. Adachi, N. Yasuoka, T. Yagi, O. Yamauchi, S. Hirota, Y. Higuchi, *J. Am. Chem. Soc.* **124** (2002) 11628–11635.
- [5] (a) Recent reviews M.Y. Darensbourg, E.J. Lyon, X. Zhao, I.P. Georgakaki, *Proc. Natl. Acad. Sci. USA* **100** (2003) 3683–3688;

- (b) D.J. Evans, C.J. Pickett, *Chem. Soc. Rev.* 32 (2003) 268–275;  
(c) P.M. Vignais, B. Billoud, *Chem. Rev.* 107 (2007) 4206–4272;  
(d) J.C. Fontecilla-Camps, A. Volbeda, C. Cavazza, Y. Nicolet, *Chem. Rev.* 107 (2007) 4273–4303;  
(e) A.L. De Lacey, V.M. Fernández, M. Rousset, R. Cammack, *Chem. Rev.* 107 (2007) 4304–4330;  
(f) W. Lubiz, E. Reijerse, M. van Gestel, *Chem. Rev.* 107 (2007) 4331–4365.
- [6] (a) Z. Li, Y. Ohki, K. Tatsumi, *J. Am. Chem. Soc.* 127 (2005) 8950–8951;  
(b) Y. Ohki, K. Yasumura, K. Kuge, S. Tanino, M. Ando, Z. Li, K. Tatsumi, *Proc. Natl. Acad. Sci. USA* 105 (2008) 7652–7657;  
(c) S. Pal, Y. Ohki, I. Yoshikawa, K. Kuge, K. Tatsumi, *Chem. Asian J.* (2009), doi:10.1002/asia.200800434;  
(d) S. Tanino, Z. Li, Y. Ohki, K. Tatsumi, *Inorg. Chem.* 48 (2009) 2358–2360.
- [7] (a) Y. Ohki, N. Matsuura, T. Marumoto, H. Kawaguchi, K. Tatsumi, *J. Am. Chem. Soc.* 125 (2003) 7978–7988;  
(b) T. Matsumoto, Y. Nakaya, K. Tatsumi, *Angew. Chem., Int. Ed.* 47 (2008) 1913–1915;  
(c) T. Matsumoto, Y. Nakaya, N. Itakura, K. Tatsumi, *J. Am. Chem. Soc.* 130 (2008) 2458–2459;  
(d) Y. Ohki, Y. Takikawa, H. Sadohara, C. Kesenheimer, B. Engendahl, E. Kapatina, K. Tatsumi, *Chem. Asian J.* 3 (2008) 1625–1635;  
(e) Y. Ohki, M. Sakamoto, K. Tatsumi, *J. Am. Chem. Soc.* 130 (2008) 11610–11611.
- [8] (a) J.J. Ellison, K. Rhuland-Senge, P.P. Power, *Angew. Chem., Int. Ed.* 33 (1994) 1178–1180;  
(b) Y. Ohki, H. Sadohara, Y. Takikawa, K. Tatsumi, *Angew. Chem., Int. Ed.* 43 (2004) 2290–2293;  
(c) S. Ohta, Y. Ohki, Y. Ikagawa, R. Suizu, K. Tatsumi, *J. Organomet. Chem.* 692 (2007) 4792–4799;  
(d) Y. Ohki, Y. Ikagawa, K. Tatsumi, *J. Am. Chem. Soc.* 129 (2007) 10457–10465;  
(e) M. Ito, T. Matsumoto, K. Tatsumi, *Inorg. Chem.* 48 (2009) 2215–2223.
- [9] (a) J.C.V. Laurie, L. Duncan, R.C. Haltiwanger, R.T. Weberg, M. Rakowski DuBois, *J. Am. Chem. Soc.* 108 (1986) 6234–6241;  
(b) P.G. Jessop, R.H. Morris, *Inorg. Chem.* 32 (1993) 2236–2237;  
(c) M. Schlaf, A.J. Lough, R.H. Morris, *Organometallics* 15 (1996) 4423–4436;  
(d) D. Sellmann, G.H. Rackelmann, F.W. Heinemann, *Chem. Eur. J.* 3 (1997) 2071–2080;  
(e) D. Sellmann, T. Gottschalk-Gaudig, F.W. Heinemann, *Inorg. Chem.* 37 (1998) 3982–3988;  
(f) D. Sellmann, A. Fürsattel, *Angew. Chem., Int. Ed.* 38 (1999) 2023–2026;  
(g) D. Sellmann, F. Geipel, M. Moll, *Angew. Chem., Int. Ed.* 39 (2000) 561–563;  
(h) D. Sellmann, R. Prakash, F.W. Heinemann, M. Moll, M. Klimowicz, *Angew. Chem., Int. Ed.* 43 (2004) 1877–1880.
- [10] The complex cation  $[\text{Cp Ir}(\text{PMe}_3)(\text{H})_3]^+$  is known: T.M. Gilbert, R.G. Bergman, *J. Am. Chem. Soc.* 107 (1985) 3502–3507.
- [11] P.J. Alaimo, B.A. Arudtsen, R.G. Bergman, *Organometallics* 19 (2000) 2130–2143.
- [12] A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, *Organometallics* 15 (1996) 1518–1520.
- [13] A known hydride complex  $[\text{Cp}^* \text{Rh}(\text{PMe}_3)(\text{H}_2)\text{H}]^+$  was observed as a thermally unstable species: F.L. Taw, H. Mellows, P.S. White, F.J. Hollander, R.G. Bergman, M. Brookhart, D.M. Deinekey, *J. Am. Chem. Soc.* 124 (2002) 5100–5108.