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Formation and isomerization of *cis*, *cis*-Ir(H)$_2$(-≡-Ph)(CO)(PPh$_3$)$_2$ and *cis*, *cis*-Ir(H)(-≡-Ph)$_2$(CO)(PPh$_3$)$_2$ in oxidative addition of hydrogen and phenylacetylene to *trans*-Ir(CO)(-≡-Ph)(PPh$_3$)$_2$

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Abstract

Oxidative addition of H–R (H-≡-Ph and H$_2$) to *trans*-Ir(-≡-Ph)(CO)(PPh$_3$)$_2$ (**2**) gives the initial products, *cis*, *cis*-Ir(H)(-≡-Ph)$_2$(CO)(PPh$_3$)$_2$ (**3a**) and *cis*, *cis*-Ir(H)$_2$(-≡-Ph)(CO)(PPh$_3$)$_2$ (**3b**), respectively. Both *cis*-bis(PPh$_3$) complexes, **3a** and **3b** undergo isomerization to give the *trans*-bis(PPh$_3$) complexes, *trans*, *trans*-Ir(H)(-≡-Ph)$_2$(CO)(PPh$_3$)$_2$ (**4a**) and *cis*, *trans*-Ir(H)$_2$(-≡-Ph)(CO)(PPh$_3$)$_2$ (**4b**). The isomerization, **3b**→**4b** is first order with respect to **3b** with $k_1 = 6.37\times10^{-4}$ s^{-1} at 25°C under N$_2$ in CDCl$_3$. The reaction rate (k_1) seems independent of the concentration of H$_2$. A large negative entropy of activation ($\Delta S^{\neq} = -24.9\pm5.7$ cal deg^{-1} mol^{-1}) and a relatively small enthalpy of activation ($\Delta H^{\neq} = 14.5\pm3.3$ kcal mol^{-1}) were obtained in the temperature range 15~35°C for the isomerization, **3b**→**4b** under 1 atm of H$_2$.

Keywords: Iridium(I,III) complexes; Oxidative addition; *cis*-(PPh$_3$)$_2$ complexes; Isomerization; Intramolecular rearrangement

1. Introduction

The stereochemistry of oxidative addition of H–R to transition metals (M) to produce the H–M–R moiety is of interest to many chemists working in the field of homogeneous catalysis with metal complexes [1–3]. It may provide valuable information on the metal catalyzed hydrogenation, hydroformylation, hydrosilylation and polymerization of unsaturated compounds with respect to the direction of H$_2$ addition and consequently the structure of the products [4–6].

Oxidative *cis*-addition of H–R to *trans*-IrA(CO)(PPh$_3$)$_2$ (**1**) [7–22] and related complexes such as IrA(CO)(p–p) (p–p=bidentate diphosphines) [23–30] and *trans*-IrA(CO)(PMe$_3$)$_2$ [31] has been extensively studied in order to establish the reaction pathways in connection with the thermal stability of the intermediates and products. Experimental work [8,9,12–23,25–31] as well as theoretical calculations [10,11,24] have been made to characterize the intermediates observed and predicted in the oxidative reaction. *Trans* isomers (**T** and **T′**) are exclusively obtained with A being an electron withdrawing group such as a halogen [7,8,10,11], RCN [9,13] or OClO$_3$ [20,21] whereas *cis* isomers (**C** and **C′**) are observed when A is an electron donating group such as H [15,17,18], Me, Ph [14], carborane [19] or OMe [14] (Eq. (1)). The isomer, **C** seems to be a kinetic product as it readily undergoes isomerization to give the more stable **T** [18,19,31] and **C′**

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[1] The C type isomer was not observed in the reaction of trans-Ir(-≡-R)(CO)(PPh$_3$)$_2$ (**2**) with H-≡-R. The final product, *trans*, *trans*-Ir(H)(-≡-R)$_2$(CO)(PPh$_3$)$_2$ (**4a**) was incorrectly reported as *cis*, *trans*-Ir(H)(-≡-R)$_2$(CO)(PPh$_3$)$_2$ (**4a′**) [20] (see Section 3 for the characterization of **4a** and Ref. [32] which describes **4a′** in detail).

[2] It was reported that (i) the reaction of IrH(CO)(PPh$_3$)$_3$ with H-≡-R in refluxing benzene gave *cis* dihydrido complex, Ir(H)$_2$(-≡-R)(CO)(PPh$_3$)$_2$ (**A**) for which no spectral data were reported, (ii) **A** readily loses H$_2$ to give Ir(-≡-R)(CO)(PPh$_3$)$_2$ (**B**) in refluxing benzene and (iii) **B** does not react with H$_2$ at 1 atm, but reacts with H$_2$ at 50 atm and 70°C in the presence of PPh$_3$ to give IrH(CO)(PPh$_3$)$_3$ [20]. From the thorough investigation, however, we found that the reaction of Ir(-≡-Ph)(CO)(PPh$_3$)$_2$ (**2**) with H$_2$ at 1 atm and 25°C readily gives the *cis* dihydride, *cis,trans*-Ir(H)$_2$(-≡-Ph)(CO)(PPh$_3$)$_2$ (**4b**) which can be isolated in high yield (85%) (see text and Section 3 for the procedure and spectral and elemental analysis data).

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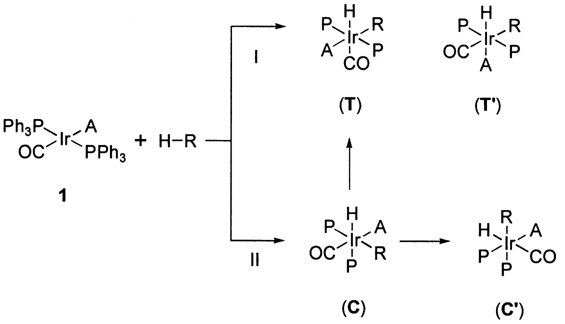
[19]. Reversible reductive elimination and oxidative addition of H–R have been suggested for the isomerization as shown in Eq. (2) [17–19,31]. To the best of our knowledge, however, no kinetic study has been reported for the isomerization of **C** to **T**.

In the course of our investigation on reactions of *trans*-Ir(-≡-Ph)(CO)$(PPh_3)_2$ (**2**), we found that **C** isomers are generated in the reactions of **1** with H_2[1] [32] and H-≡-Ph[2] and undergo isomerization to give **T** isomers at a rate appropriate for the kinetic measurements at room temperature.



(1)

$$\mathbf{C}\ \underset{\xrightarrow[-(\text{H–R})]{}}{\xleftarrow{\text{H–R}}}\ \mathbf{1}\ \underset{\xleftarrow[-(\text{H–R})]{}}{\xrightarrow{\text{H–R}}}\ \mathbf{T} \qquad (2)$$

2. Results and discussion

2.1. Formation of cis, cis-Ir(H)(-≡-Ph)$_2$(CO)(PPh$_3$)$_2$ (3a)

An intermediate is initially generated and slowly disappears during the reaction of **2** with phenylacetylene, which is unambiguously seen by the ^{1}H-NMR spectral changes (see Fig. 1). This intermediate is identified as the *cis*-$(PPh_3)_2$ species, **3a** [Eq.(3)]. The doublet of the doublet at δ −10.40 ppm strongly suggests the hydride being *trans* to one PPh_3 ($J_{P-H}=161.2$ Hz) and *cis* to the other PPh_3 ($J_{P-H}=14.7$ Hz) of **3a**. The triplet at δ −8.78 ppm clearly suggests both of PPh_3 being *cis* to the hydride ($J_{P-H}=14.7$ Hz) of the final product, **4a**. The *cis*-bis(alkynyl) structure (**3a**) is the preferred one to the *trans*-bis(alkynyl) species (**3a′**) for the following reason. The *trans* OC–Ir–A bond axis is supposed to be maintained when the **C** type isomers are formed since H–R has to approach metal with its bond axis parallel to the P–Ir–P axis of **2** to cause bending of the P–Ir–P axis only [10,18,19,24,27,28].

The characterization of *trans*, *trans*-Ir(H)(-≡-R)$_2$(CO)$(PPh_3)_2$, **4a** is straightforward according to the ^{1}H-, ^{13}C-, and ^{31}P-NMR spectral data (see also Section 3).

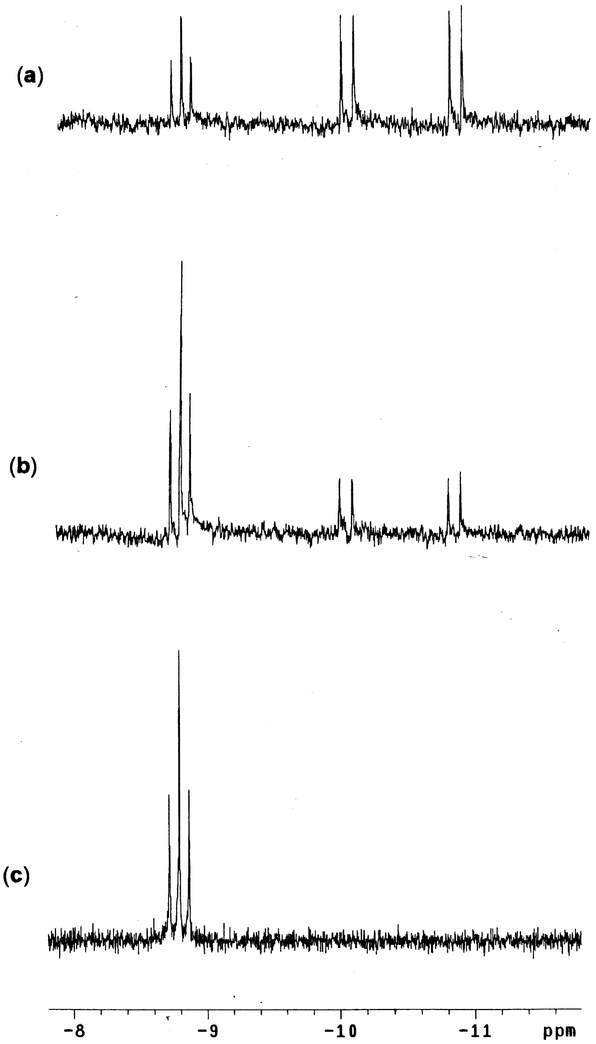
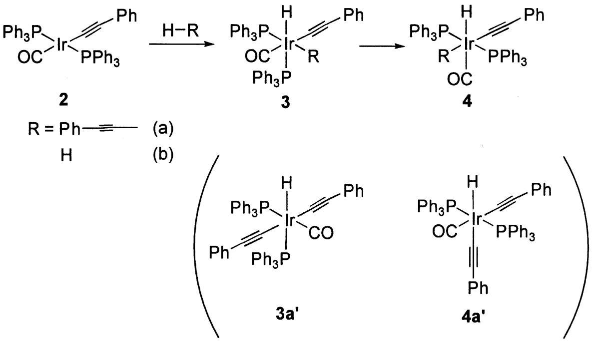


Fig. 1. ^{1}H-NMR spectral changes in the hydride region during the isomerization, *cis*, *cis*-Ir(H)(-≡-Ph)$_2$(CO)$(PPh_3)_2$ (**3a**)→*trans*, *trans*-Ir(H)(-≡-Ph)$_2$(CO)$(PPh_3)_2$ (**4a**) in $CDCl_3$ at 25°C: 2 h (a), 10 h (b) and 24 h (c) after the addition of H-≡-Ph into the solution of *trans*-Ir(-≡-Ph)(CO)$(PPh_3)_2$ (**2**).



(3)

The chemical shift of a hydride coordinated to a transition metal largely depends on the nature of the *trans* ligand and has been very useful for the characterization of iridium compounds such as *cis*, *trans*-Ir(H)$_2$(L)(CO)$(PPh_3)_2$ (L = RCN, CO, $OClO_3$, SiR_3, carborane, etc.), *trans*-Ir(H)(-≡-

R)(L)(CO)(PPh_3)$_2$, (L = RCN, $OClO_3$), *cis*, *trans*-Ir(H)(-$\equiv$-R)$_2$(CO)(PPh_3)$_2$ and related compounds [8,9,13–20,32,33]. The hydride *trans* to CO is seen at relatively lower field, δ −7.0~−10.2 ppm for the related iridium compounds [8,13,16,19]. The signal due to the hydride *trans* to alkynyl group (-$\equiv$-Ph) in *cis*, *trans*-Ir(H)(-$\equiv$-Ph)$_2$(CO)(PPh_3)$_2$ (**4a**′) is observed at δ −10.01 ppm [32]. The triplet at δ −8.78 ppm is, therefore, assigned to the hydride *trans* to the CO in **4a**. The ^{13}C-NMR spectral data also support the *trans*-bis(alkynyl) moiety for **4a**. While the ^{13}C-NMR spectrum of the *cis*-bis(alkynyl) complex, **4a**′ shows a broad signal at δ 82.6 (br, Ir–$C_a\equiv$C–) and two signals at δ 108.7 (s) and 109.1 (s) (Ir–C$\equiv C_{\beta}$–) [32], the *trans*-bis(alkynyl) complex, **4a** shows only one signal for each of C_α and C_β of the two *trans* (symmetric) alkynyl groups at δ 82.0 (t, Ir–$C_\alpha\equiv$C–) and 109.5 (s, Ir–C$\equiv C_\beta$–) ppm.

2.2. Formation of cis, cis-Ir(H)$_2$(-$\equiv$-Ph)(CO)(PPh_3)$_2$ (3b)

The reaction of **2** with H_2 also produces an intermediate that is generated at the early stage of the reaction and slowly disappears to give a stable product as seen in Fig. 2. The intermediate and the final product are identified as the *cis*-(PPh_3)$_2$ complex, *cis*, *cis*-Ir(H)$_2$(-$\equiv$-Ph)(CO)(PPh_3)$_2$ (**3b**) and *trans*-(PPh_3)$_2$ complex, *cis*, *trans*-Ir(H)$_2$(-$\equiv$-Ph)(CO)(PPh_3)$_2$ (**4b**), respectively (see below).

It is evident that the multiplet-like signal centered at δ −10.30 ppm is due to the two hydrides of the intermediate, **3b**, and the two doublets of the triplet at δ −9.54 and −11.59 ppm are due to the two hydrides of the stable final product, **4b**. The Ir(H)$_2$(P)$_2$ moiety of **3b** seems to be in a same plane with the two PPh_3 being *cis* to each other and the two hydrides being also *cis* to each other. The pattern of the signal centered at δ −10.30 ppm is evidently due to the AA′XX′ spin system of the *cis*-Ir(*H*)$_2$(PPh_3)$_2$ moiety of **3b** where the two hydrides are chemically equivalent but magnetically different. The same type of pattern (AA′XX′) has been observed at δ −9.52 and −10.8 ppm for *cis*, *cis*-Ir(H)$_2$(CO)(carborane)(PPh_3)$_2$ [14] and *cis*, *cis*-Ir(H)$_2$(Me)(CO)(PPh_3)$_2$ [19], respectively, and was assigned to the two hydrides of *cis*, *cis*-Ir(*H*)$_2$(PPh_3)$_2$ moieties.

The two doublets of the triplet at δ −9.54 and −11.59 ppm for **4b** are unambiguously assigned to the hydride *trans* to CO and -$\equiv$-Ph, respectively, by comparison with the spectral data observed for related iridium hydrides [8,9,13–20,32,33]. As mentioned earlier, hydride signals in ^{1}H-NMR spectra are quite useful in characterizing related metal hydrides. The hydride *trans* to CO is usually seen at lower field (δ −7.0~−10.2 ppm) [8,9,13,16,19][3] while the hydride *trans* to alkynyl and alkenyl groups is seen at somewhat higher field (δ −10~−11 ppm) [32,33].

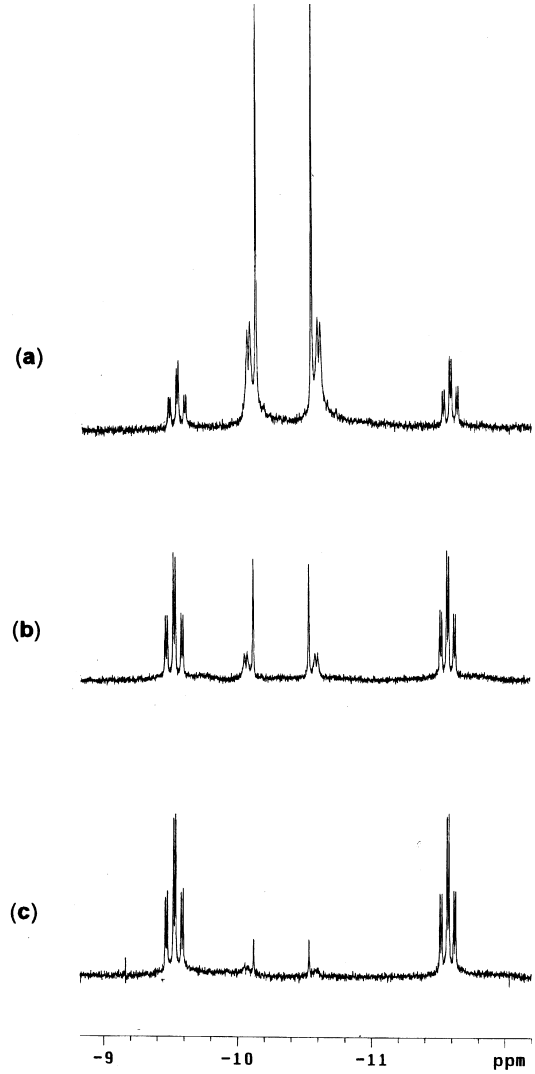


Fig. 2. ^{1}H-NMR spectral changes in the hydride region during the isomerization, *cis*, *cis*-Ir(H)$_2$(-$\equiv$-Ph)(CO)(PPh_3)$_2$ (**3b**)$\rightarrow$*cis*, *trans*-Ir(H)$_2$(-$\equiv$-Ph)(CO)(PPh_3)$_2$ (**4b**) in $CDCl_3$ at 25°C: 5 min (a), 25 min (b) and 45 min (c) after the addition of *trans*-Ir(-$\equiv$-Ph)(CO)(PPh_3)$_2$ (**2**) into the H_2 saturated $CDCl_3$ under 1 atm of H_2.

The ^{31}P-NMR spectrum ($CDCl_3$, 20°C) of the mixture of **3b** and **4b** shows only two singlets at δ 9.55 and −8.36 ppm. The singlet at δ 9.55 increases at the expense of the one at δ −8.36 ppm during the isomerization, **3b**$\rightarrow$**4b**. The fact that only one singlet is observed suggests **3b** as a **C** type isomer rather than a **C**′ type one that would be expected to show two signals in the ^{31}P NMR spectrum.

2.3. Kinetics for the isomerization of cis, cis-Ir(H)$_2$(-$\equiv$-Ph)(CO)(PPh_3)$_2$ (3b) to cis, trans-Ir(H)$_2$(-$\equiv$-Ph)(CO)(PPh_3)$_2$ (4b)

The isomerization of **3b** to **4b** was followed by measuring the decrease of the hydride signals of **3b** as well as the increase of the hydride signals of **4b** (see Fig. 2). The

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[3] The triplet at δ −8.78 ppm has been assigned to the hydride *trans* to CO in complex **4a** for the same reason (see text).

isomerization is first order with respect to **3b** as expected for a mainly unimolecular isomerization. The rate does not seem to be significantly affected by the concentration of H_2: k_1 is found to be $(6.6\pm0.1)\times10^{-4}$ s^{-1} and $(6.4\pm0.1)\times10^{-4}$ s^{-1} under H_2 (1 atm) and N_2, respectively, at 25°C in $CDCl_3$ (see Section 3 for detailed experimental conditions). A relatively large negative value of the activation entropy ($\Delta S^{\neq}=-24.9\pm5.7$ cal deg^{-1} mol^{-1}) and a relatively small activation enthalpy ($\Delta H^{\neq}=14.5\pm3.3$ kcal mol^{-1}) have been obtained from k_1 in the range 15~35°C. This observation suggests that the isomerization, **3b**→**4b** involves an intramolecular rearrangement at least in part in the temperature range 15~35°C (see below).

An intramolecular isomerization usually involves an intermediate (or transition state) formed by a trigonal twist or a rhombic twist of a fluxional octahedral complex [34–42]. The activation entropy is measured to obtaining information on the distinction between the dissociative (through a five coordinated intermediate) and non-dissociative (fluxional) mechanisms: Negative values (−54.9~−2.3 cal deg^{-1} mol^{-1}) for the activation entropy were obtained for the *cis*↔*trans* isomerization of octahedral d^6 complexes, $ML_2(CO)_4$ for which intramolecular isomerization mechanisms were suggested [35–38].

It is still possible that a part of **3b** undergoes isomerization through the reaction pathway involving the reversible reductive elimination and oxidative addition of H_2 as seen in Eq. (2). Although no evidence has been obtained for the reaction of **2** with H_2 directly (not via **3b**) to give **4b**, we found that **4b** very slowly loses H_2 to give **2**: Less than 5% of **4b** loses H_2 in 5 h at 35°C under N_2 in $CDCl_3$.

Further investigation seems to be needed to elucidate the detailed mechanism of the isomerization, **3**→**4** when better experimental methods become available.

It should be mentioned that kinetic measurements have not been carried out for the reaction of **2** with H-≡-Ph as it is inappropriate for kinetic measurements. The reaction is much slower than the reaction of **2** with H_2. The initial step, the formation of **3a** (**2**→**3a**) is so slow that the rate measurements of the following isomerization, **3a**→**4a**, could not be made in the absence of **2**. A significant amount of unreacted **2** is observed even at the latest stage of the isomerization, **3a**→**4a**. Reductive elimination of H-≡-Ph from **4a** is not observed at 25°C while a small amount of H-≡-Ph has been detected in $CDCl_3$ solution of **4a** after 1 h of refluxing.

3. Experimental section

Reactions were carried out under N_2 with the use of standard Schlenk techniques. NMR spectra were recorded on either Varian Gemini 200 or 300 spectrometers (^{1}H, 200/300 MHz; ^{13}C, 50.3, 75.5 MHz; ^{31}P, 121.7 MHz). IR spectra were obtained on a Shimadzu IR-440 spectrophotometer. Elemental analyses were carried out at the Organic Chemistry Reaction Center, Sogang University.

3.1. Syntheses

*3.1.1. Ir(-C≡C-Ph)(CO)(PPh$_3$)$_2$ (**2**)*

This compound was previously prepared from the reaction of $Ir(\eta^3\text{-}C_3H_5)(CO)(PPh_3)_2$ with H-≡-Ph [20]. In this study, it was synthesized by a new method as described below. To a yellow solution of $[Ir(NCCH_3)(CO)(PPh_3)_2]ClO_4$ [3 g] (0.178 mg, 0.2 mmol) and NEt_3 (0.031 ml, 0.22 mmol) in $CHCl_3$ (10 ml), H-≡-Ph (0.024 ml, 0.22 mmol) was added under N_2 and the resulting dark brown solution was stirred for 8 min. Hexane (70 ml) was added to the reaction mixture and the precipitate of $HNEt_3^+ClO_4^-$ was removed by filtration. Yellow solid **2** was obtained by vacuum distillation of the filtrate and recrystallized by using $CHCl_3$ and hexane. The yield was 0.134 mg (80% based on **2**). ^{1}H NMR ($CDCl_3$, 25°C): δ 6.37 (m). ^{13}C NMR ($CDCl_3$, 25°C): δ 67.7 (t, $J_{P-C}=12.5$ Hz, Ir-*C*≡C-Ph), 109.5 (s, Ir-*C*≡C-Ph), 167.4 (t, $J_{P-C}=8.7$ Hz, Ir–CO). ^{31}P NMR ($CDCl_3$, 25°C): δ 7.57 (s). IR (KBr, cm^{-1}): ν(CO) 1993 (s), ν(C≡C) 2104 (m). Anal. Calcd for $IrP_2C_{45}H_{35}O$: C, 63.89; H, 4.17. Found: C, 64.06; H, 4.21.

*3.1.2. IrH(-C≡C-Ph)$_2$(CO)(PPh$_3$)$_2$ (**4a**)*

A yellow solution of **2** (85 mg, 0.1 mmol) in CH_2C1_2 (10 ml) was stirred in the presence of H-C≡C-Ph (11 mg, 0.11 mmol) under N_2 at 25°C for 10 h, during which time the solution turned pale yellow. Cold hexane (25 ml) was added to the solution in a dry-ice/acetone bath to precipitate pale yellow microcrystals of **4a**, which were collected by filtration, washed with cold hexane (2×10 ml), and dried under vacuum. The yield was 81 mg (85%). ^{1}H NMR ($CDCl_3$, 25°C): δ −8.78 (t, 1H, $J_{P-H}=14.7$ Hz, Ir–H), 6.37 (m, 4H, *ortho* protons of -C≡C-Ph). ^{13}C NMR ($CDCl_3$, 25°C): δ 82.0 (t, $J_{P-C}=12.65$ Hz, Ir-C≡C-Ph), 109.5 (s, Ir-C≡C-Ph), 167.4 (t, $J_{P-C}=8.1$ Hz, Ir–CO). ^{31}P NMR ($CDCl_3$, 25°C): δ 1.56 (s). IR (KBr, cm^{-1}): ν(CO) 2020 (s), ν(C≡C) 2107 (m). Anal. Calcd for $IrP_2C_{53}H_{41}O$: C, 66.65; H, 4.33. Found: C, 66.66; H, 4.41.

*3.1.3. Ir(H)$_2$(-C≡C-Ph)(CO)(PPh$_3$)$_2$ (**4b**)*

A yellow solution of **2** (85 mg, 0.1 mmol) in CH_2Cl_2 (10 ml) was stirred under H_2 (1 atm) at 25°C for 5 min, during which time the solution turned pale yellow. Cold hexane (25 ml) was added to the CH_2Cl_2 solution in a dry ice/acetone bath to precipitate pale yellow microcrystals of **4b**, which were collected by filtration, washed with cold hexane (2×10 ml), and dried under vacuum. The yield was 75 mg (85%). ^{1}H NMR ($CDCl_3$, 25°C): δ −9.54 (td, 1 H, $J_{P-H\alpha}=17.25$ Hz, $J_{H\alpha-H\beta}=4.12$ Hz, Ir–H_α), −11.59

(td, 1 H, $J_{P-H\beta}=15.63$ Hz, Ir–H_{β}), 6.32 (m, 2 H, *ortho* protons of -C≡C-Ph). ^{13}C NMR ($CDCl_3$, 25°C): δ 88.16 (t, $J_{P-C}=12.34$ Hz, Ir-C≡CPh), 113.87 (s, Ir-C≡CPh), 174.69 (t, $J_{P-C}=6.34$ Hz, Ir–CO). ^{31}P NMR ($CDCl_3$, 25°C): δ 9.55 (s). IR (KBr, cm^{-1}): ν(CO) 1968.5 (s), ν(C≡C) 2064.0 (w). Anal. Calcd for $IrP_2C_{45}H_{37}O$: C, 63.74; H, 4.40. Found: C, 63.73; H, 4.24.

*3.1.4. Kinetic measurements for the isomerization of cis, cis-Ir(H)$_2$(-≡-Ph)(CO)(PPh$_3$)$_2$ (**3b**) to cis, trans-Ir(H)$_2$(-≡-Ph)(CO)(PPh$_3$)$_2$ (**4b**)*

The reaction was followed by measuring the hydride signals of **3b** and/or **4b** (see Fig. 2) under H_2 and N_2 in the temperature region 15~35°C in $CDCl_3$. An automatic acquisition program (installed on Varian Gemini 300 MHz spectrometer; acquisition time, 1.997 s; repetition delay, 3.0 s; scan, 6) was used to collect the kinetic data by measuring the spectra in the hydride region (δ −9.0~−12.0) at intervals of 30 s. The reactions were monitored for 30 min. (i) Under H_2 (1 atm): a 50 mg of **2** was dissolved in $CDCl_3$ (0.5 ml) in an NMR tube under H_2 (1 atm) at 25°C and the reaction mixture was put in the cell compartment of a Varian Gemini 300 MHz spectrometer maintained at 25°C. Compound **2** completely underwent H_2 addition to give **3b** within 2 min according to ^{1}H NMR measurements. During these two min, the color of the solution changed from yellow to pale yellow. Disappearance of **3b** and appearance of **4b** were measured by following the signals at δ −10.10 (**3b**) and −9.54 (**4b**) ppm. (ii) Under N_2: N_2 was thoroughly bubbled for 1 min into a CDC1$_3$ solution containing **3b** and a small amount of **4b** and ^{1}H NMR spectral changes were measured to follow the isomerization, **3b**→**4b**, in the same manner as described above.

Acknowledgements

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