Structure and Reactivity of an Unusual Rhodium(I) Bis(ethylene) Complex, $RhCl(CH_2{=}CH_2)_2(PMe_3)_2$

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Received February 9, 2004

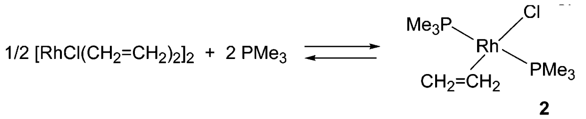
*Summary: $[RhCl(CH_2{=}CH_2)_2]_2$ reacts with PMe_3 in the presence of ethylene to give an unusual 18-electron five-coordinate Rh(I) complex, $RhCl(CH_2{=}CH_2)_2(PMe_3)_2$ (**1**). The structure of **1** was fully characterized by X-ray crystallography as well as ^1H and ^{31}P NMR. The bis(ethylene) adduct (**1**) is isolable but in equilibrium with the corresponding mono(ethylene) complex $RhCl(CH_2{=}CH_2)(PMe_3)_2$ (**2**) in solution.*

Introduction

Rh(I) complexes having weakly coordinating ligands, $RhCl(L)_n(PR_3)_2$ (L = weak ligand), are good precursors for active species in various catalytic reactions. Relevant to the olefin hydrogenation and C−H bond activation, Ford reported the transient formation of $RhCl(PMe_3)_2$ by the photolysis of $RhCl(CO)(PMe_3)_2$.[1] We and Goldman postulated the intermediacy of $RhCl(PMe_3)_2$ as an active species for alkane dehydrogenation;[2,3] for example, $RhCl(CH_2{=}CH_2)(PMe_3)_2$ works as a good catalyst precursor. The importance of similar three-coordinate 14-electron species in the rhodium-catalyzed CO_2 hydrogenation was also proposed by Leitner.[4] In addition, the intermediacy of a carbon dioxide complex was recently discussed in a stoichiometric and catalytic C−H bond activation by $RhCl(PMe_3)_3$ in the presence of excess CO_2.[5] Despite frequent references to $RhCl(L)_n(PMe_3)_2$ as stated above, coordination of alkenes to the $RhCl(PMe_3)_2$ fragment has not been fully elucidated. We report here the structure and reactivity of the unusual bis(ethylene) rhodium(I) complex $RhCl(CH_2{=}CH_2)_2(PMe_3)_2$ (**1**) and its derivatives.[6]

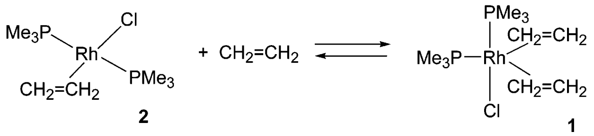
Results and Discussion

Previously, we preliminarily reported the formation of $RhCl(CH_2{=}CH_2)(PMe_3)_2$ (**2**) from $[RhCl(PMe_3)_2]_2$ and ethylene.[2b] However, the ethylene complex **2** was unstable and poorly characterized by ^{31}P NMR. We recently reinvestigated the synthesis of **2** by the reaction of $[RhCl(CH_2{=}CH_2)_2]_2$ with 2 equiv of trimethylphosphine under an atmospheric ethylene (eq 1). As seen in Figure 1, ^{31}P NMR indicated that the reaction is not as simple as expected; we observed the formation of two major phosphine complexes, which were presumably in equilibrium with each other (eq 2). One of the two complexes is assignable to a *trans*-square planar mono(ethylene) complex (**2**), which shows a doublet at δ −8.95 ppm in the ^{31}P NMR as previously reported.[2b,7] The other species seems to be a trigonal bipyramidal bis(ethylene) complex (**1**), which exhibits two double doublets at δ −23.49 and 16.79 ppm in the ^{31}P NMR. The presence of two magnetic environments and a small coupling constant between the two phosphorus atoms ($J_{(P-P)}$ = 29 Hz) suggests that the two PMe_3 ligands occupy an axial and an equatorial position. These two complexes are in equilibrium with each other because the ^{31}P NMR spectra are highly temperature dependent, and only complex **1** was observed at −80 °C. In other words, the coordination of ethylene to **2** (eq 2) seems preferable at a lower temperature.



2

(1)



2 **1**

(2)

As seen in Figure 2, the above assignment is also supported by ^1H NMR. At room temperature, three $P{-}CH_3$ signals were observed at δ 1−2 ppm assignable to the mono(ethylene) and bis(ethylene) complexes. The

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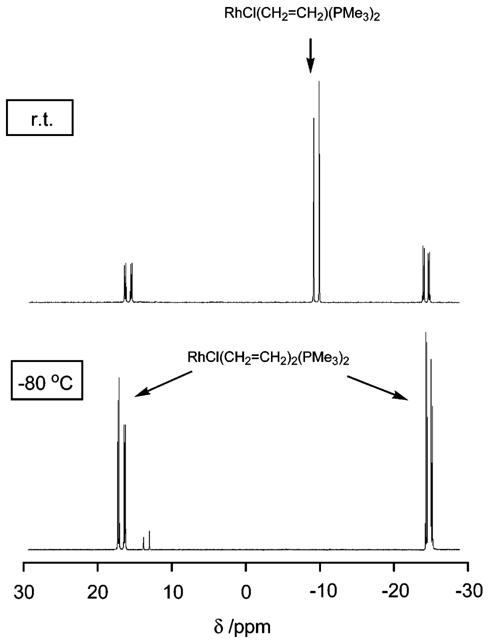

Figure 1. $^{31}P\{^1H\}$ NMR of $RhCl(CH_2{=}CH_2)_2(PMe_3)_2$ under ethylene (THF-d_8, 20 °C (upper) and −80 °C (lower)).

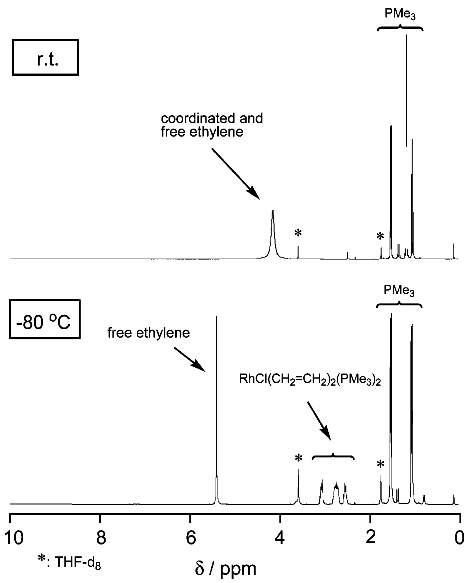

Figure 2. ^1H NMR of $RhCl(CH_2{=}CH_2)_2(PMe_3)_2$ under ethylene (THF-d_8, 20 °C (upper) and −80 °C (lower)).

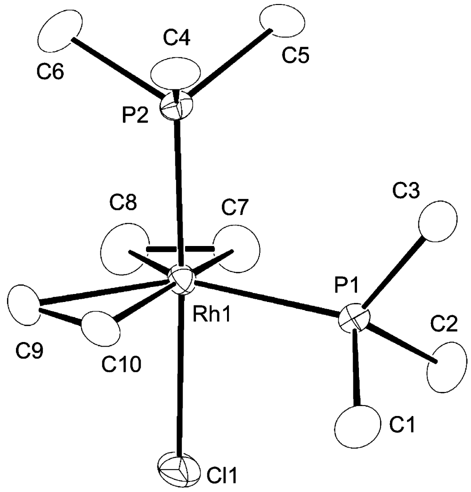

Figure 3. X-ray structure of $RhCl(CH_2{=}CH_2)_2(PMe_3)_2$. Selected bond distances (Å) and angles (deg): Rh1−Cl 2.4600(6), Rh1−P1 2.3710(6), Rh1−P2 2.2360(6), Rh1−C7 2.161(2) Rh1−C8 2.156(3), C7−C8 1.389(5), Cl−Rh1−P2 177.20(2), Cl−Rh1−C7 86.02(8), Cl−Rh1−C8 85.46(10), Cl−Rh1−P1 84.89(2), P1−Rh1−C7 95.10(9), P1−Rh1−C8 132.21(10), C7−Rh1−C9 133.3(1).

interconversion between **1** and **2** is slow by the NMR time scale because we can clearly differentiate the two species in ^{31}P and ^1H NMR spectroscopy. On the other hand, ^1H NMR showed a broad ethylene signal around δ 4.1 ppm at room temperature assignable to overlapping of **1**, **2**, and free ethylene. Although the precise mechanism of the fluxional behavior of ethylene signals is not clear at the moment, four distinctly resolved ethylene signals at δ 5.40 (s), 3.04 (m), 2.73 (m), and 2.53 (m) ppm were observed at −80 °C. The integral ratio of the coordinated ethylene signals versus PMe_3 was also consistent with the bis(ethylene) complex structure **1**. The rotation of the ethylene ligands around the ethylene−rhodium bond should be slow at a low temperature, below −50 °C, because we can distinguish each proton in ethylene by ^1H NMR.

Rh(I) alkene complexes having two phosphine ligands usually have a 16-electron square planar structure;[7,8] an 18-electron five-coordinate arrangement as seen in **1** is unprecedented except the complexes with an anchored alkene.[9] The five-coordinate structure was further unambiguously confirmed by single-crystal X-ray analysis. The solid structure of **1** with typical bond lengths and angles is shown in Figure 3. The molecular structure of **1** has a trigonal bipyramidal coordination around the Rh center with the two ethylene groups lying on the equatorial plane and two mutually *cis* PMe_3 groups. The configuration is consistent with the structure expected from ^{31}P and ^1H NMR. The P(2)−Rh(1)−Cl(1) [177.20(2)°] bond angle is only slightly less than 180°. A much longer bond between Rh(1)−P(1) [2.3710(6) Å] than the bond distance of Rh(1)−P(2) [2.2360(6) Å] is probably due to the influence of the two ethylene ligands situated on the equatorial plane. The bond distance of Rh(1)−Cl(1) [2.4600(6) Å] is quite normal. The C=C bond distances [1.384(4) and 1.389(5) Å] of **1** are slightly shorter than the corresponding mean [1.4120(12) Å] reported for the C=C bond of $IrCl(CH_2{=}CH_2)_2(Et_3P)_2$.[6]

The temperature dependence of the equilibrium constant between **1** and **2** estimated from the ^{31}P NMR afforded the thermodynamic data for equation 2: $\Delta H = -51$ kJ/mol, $\Delta S = -157$ J/mol/K, $\Delta G_{298} = -4.1$ kJ/mol. The present rhodium bis(ethylene) complex is less stable than the similar iridium complex having PEt_3 ligands.[6]

Relevant to the C−H bond activation in CO_2 by the $RhCl(PMe_3)_2$ fragment, the formation of a carbon dioxide complex was discussed.[5,10] This prompted us to briefly investigate the reaction of **1** with CO_2 because ethylene is expected to dissociate easily. Even under excess CO_2 (0.2 MPa, 25 °C), ^{31}P NMR revealed a strong doublet

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assignable to $RhCl(CH_2{=}CH_2)(PMe_3)_2$ as the dominant species along with three small doublets at δ 3.44, 4.28, and 12.64. On the other hand, $^{13}C\{^1H\}$ NMR exhibited a weak broad singlet at δ 170.2 assignable to coordinated CO_2.[11] A higher CO_2 pressure (3 MPa) resulted in the deposition of solid, due to the decrease of solvent polarity.

In summary, an unusual 18-electron, five-coordinate Rh(I) ethylene complex, $RhCl(CH_2{=}CH_2)_2(PMe_3)_2$, was isolated, and the molecular structure was unambiguously elucidated. A temperature-dependent equilibrium between the bis(ethylene) and mono(ethylene) complex was observed.

Experimental Section

All manipulations were carried out under a purified argon atmosphere using standard Schlenk and glovebox techniques. Solvents were purified by conventional means and were distilled immediately prior to use. The ^1H, $^{13}C\{^1H\}$, and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL-LA400WB superconducting high-resolution spectrometer (400 MHz for ^1H). $^{31}P\{^1H\}$ NMR spectra were referenced to external 85% phosphoric acid. IR spectra were recorded on a Shimadzu FTIR-8500 spectrometer. The elemental analyses were carried out using a CE-EA 1110 automatic elemental analyzer.

Synthesis of $RhCl(CH_2{=}CH_2)_2(PMe_3)_2$ (1). To a solution of $[RhCl(CH_2{=}CH_2)_2]_2$ (0.87 g, 2.25 mmol) in toluene (15 mL) was added trimethylphosphine (0.68 g, 8.87 mmol) under ethylene atmosphere. After stirring for 3 h at 0 °C, further cooling of the reaction mixture resulted in the formation of yellow single crystals of **1** (1.22 g, 78% yield). The product was recrystallized from toluene at −40 °C for X-ray analysis. ^1H NMR (400 MHz in THF-d_8 at −80 °C): δ 1.04 (d, 9H, $P(CH_3)_3$, $J(PH) = 10$ Hz), 1.51 (d, 9H, $P(CH_3)_3$, $J(PH) = 8$ Hz), 2.53 (m, 2H, $CH_2{=}CH_2$) 2.73 (m, 4H, $CH_2{=}CH_2$), 3.04 (m, 2H, $CH_2{=}CH_2$). $^{31}P\{^1H\}$ NMR: δ −23.49 (dd, $J(RhP) = 118$ Hz, $J(PP) = 29$ Hz), 16.79 (dd, $J(RhP) = 133$ Hz, $J(PP) = 29$ Hz). Anal. Calcd for $C_{10}H_{26}ClP_2Rh$: C, 34.65; H, 7.56; Cl, 10.23. Found: C, 33.75; H, 7.25; Cl, 10.11; a little lower carbon content than the theoretical value is attributable to the decomposition of **1** to **2**. Crystal data for **1**: monoclinic $P2_1/n$ (no. 14), colorless, $a = 9.296(2)$ Å, $b = 12.836(3)$ Å, $c = 13.264(2)$ Å, $\beta = 100.68(1)°$, $V = 1555.5(4)$ Å^3, $Z = 4$, $D_c = 1.480$ g cm^{-3}, $6 < 2\theta < 55$, $R = 0.024$, $R_w = 0.045$, GOF = 1.86 for all independent data (3567) and 128 parameters.

NMR Data of 2. ^1H NMR (400 MHz in THF-d_8 at 25 °C): 1.16 (apparent triplet due to virtual coupling, 18H, $P(CH_3)_3$), 4.15 (br, $CH_2{=}CH_2$). $^{31}P\{^1H\}$ NMR: δ −8.95 (d, $J(RhP) = 118$ Hz).

Thermodynamic Data. A 0.067 M THF-d_8 solution of **1** was prepared at room temperature under nitrogen. The equilibrium constants between **1** and **2** were evaluated on the basis of the area ratio of the $^{31}P\{^1H\}$ NMR peaks at five different temperatures (253, 263, 273, 283, and 298 K). A linear van't Hoff plot obtained by the least squares method ($R^2 = 0.9942$) gave thermodynamic parameters of the reaction.

Reaction of 1 with $^{13}CO_2$. In a 5 mm NMR tube, THF-d_8 (0.4 mL) was vacuum transferred onto **1** (15 mg, 0.04 mmol), followed by pressurization by $^{13}CO_2$ (0.2 MPa). $^{31}P\{^1H\}$ NMR showed a strong doublet at δ −9.11 (d, $J(RhP) = 118$ Hz), which is assignable to **2**, along with three small doublets at δ 3.44, 4.28, and 12.64. $^{13}C\{^1H\}$ NMR exhibited a weak singlet at δ 170.2 (br s) assignable to coordinated CO_2 along with the signals in the P−Me region. $RhCl(^{13}CO)(PMe_3)_2$ (^{13}C NMR: δ 189.3, dt, $J = 26$ and 17 Hz) was not observed in the reaction mixture as judged by ^{31}P and ^{13}C NMR.[10]

Acknowledgment. This research was supported in part by a grant from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

Supporting Information Available: ^1H NMR and crystallographic data of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0400144

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