

Oxidative Addition of C–H Bonds to $\text{RhCl}(\text{PMe}_3)_3$: Relevant to the Catalytic Transformation of Hydrocarbons

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Synthetic chemists have long envisioned the direct and selective conversion of hydrocarbons under mild conditions. Transition metal complexes are a powerful tool for achieving this goal because they can activate unreactive C–H bonds of hydrocarbons.¹ Previously, we developed a $\text{RhCl}(\text{L})(\text{PMe}_3)_2-h\nu$ system ($\text{L} = \text{CO}, \text{CH}_2=\text{CH}_2, \text{PMe}_3$) that catalyzes a photopromoted C–H bond activation.^{2–5} When the reaction medium is dense CO_2 , hydrocarbons including methane and ethane are effectively functionalized.^{4,5} The generally accepted C–H bond activation pathway for the $\text{RhCl}(\text{L})(\text{PMe}_3)_2-h\nu$ system is the oxidative addition of hydrocarbons to a low valent metal center.^{6–8} To date, however, the oxidative addition products have not been isolated. In this paper, we report the isolation, full structural characterization, and reactivity of $\text{Rh}(\text{C}_6\text{H}_5)(\text{H})\text{Cl}(\text{PMe}_3)_3$ synthesized through oxidative addition of benzene to a Wilkinson-type complex, $\text{RhCl}(\text{PMe}_3)_3$ (**1**), which is an efficient catalytic precursor for carbonylation and dehydrogenation of hydrocarbons.⁴

Sixty equivalents of CO_2 (about 10 atm) was added to a benzene solution (0.4 mL) of **1** (0.014 mmol). The reaction mixture was then irradiated with a 100 W high-pressure mercury lamp at room temperature. After 24 h, **1** was selectively converted to a new complex that kept the three phosphine ligands of the starting complex as determined by ^{31}P NMR.⁹ In addition, ^1H and ^{13}C NMR spectra reveal the presence of a hydrido and a phenyl ligand on the rhodium center. The combination of various spectral data indicated the formation of *mer*- $\text{Rh}(\text{C}_6\text{H}_5)(\text{H})\text{Cl}(\text{PMe}_3)_3$ (**2**) through the oxidative addition of benzene to **1**. The complicated ^1H and ^{13}C NMR patterns in the phenyl region indicated a restricted rotation around the phenyl–rhodium bond even at room temperature. The small signals in ^1H and ^{31}P NMR are presumably attributable to the presence of the stereoisomer of **2** that is produced by exchanging the phenyl and the hydrido ligands. The large $J_{\text{P–H}}$ value (215 Hz) is consistent with the configuration having the hydrido ligand trans to phosphorus.⁹

Interestingly, the presence of CO_2 promoted the formation of **2** from **1** (Figure 1). Although the precise mechanistic discussion is premature,¹⁰ possible explanations for this effect are (i) the formation of a small amount of CO and $\text{O}=\text{PMe}_3$ from CO_2 and PMe_3 ,⁵ followed by the preferential photoreaction of $\text{RhCl}(\text{CO})(\text{PMe}_3)_2$, or (ii) the weak coordination of CO_2 to the Rh center resulting in the stabilization of productive intermediates such as $\text{RhCl}(\text{C}_6\text{H}_5)(\text{H})(\text{CO}_2)(\text{PMe}_3)_2$. The following phenomena also give some clues to the role of CO_2 : (i) Reductive elimination of benzene from **2** was not retarded by CO_2 (vide infra). (ii) Aresta reported the formation of a rhodium(I) CO_2 complex, $\text{RhCl}(\text{CO}_2)(\text{PBU}_3)_2$, from $\text{RhCl}(\text{PBU}_3)_3$ under atmospheric CO_2 . However, we have not yet detected this species by NMR or IR.¹¹

Although complex **2** is rather unstable at room temperature, single crystals of **2** were successfully obtained by recrystallization in a toluene–hexane mixture at a low temperature. The molecular structure of **2** determined by X-ray crystallography is shown in

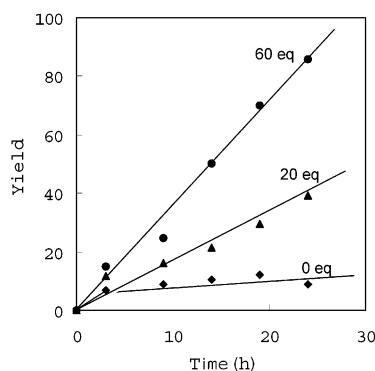


Figure 1. CO_2 concentration effect on the yield of **2** from **1**. The yield is the sum of the amount of **2** and its isomer (see ref 9).

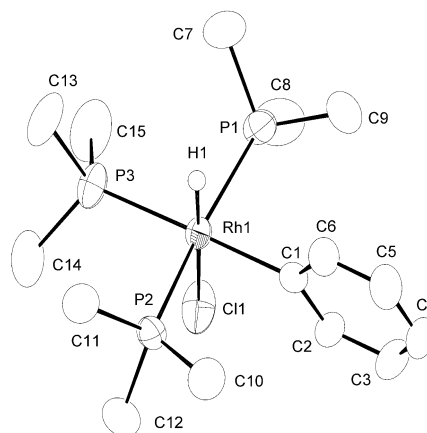
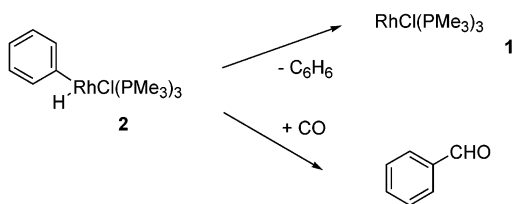


Figure 2. X-ray crystal structure of **2**. Selected bond distances (Å) and angles (deg): Rh1–H1 1.33(7), Rh1–C1 2.102(5), Rh1–C11 2.500(1), Rh1–P1 2.312(1), Rh1–P2 2.320(1), Rh1–P3 2.363(1), C1–Rh1–H1 92(2), Cl1–Rh1–C1 94.2(1), P1–Rh1–P2 165.71(6), C1–Rh1–P1 85.7(1), C1–Rh1–P2 85.6(1).

Figure 2.¹² The structure is consistent with the solution structure speculated by NMR and IR. The coordination sphere around the rhodium center corresponds to an octahedron with H1 and C1 in the cis positions. Although various molecules such as dihydrogen, hydrogen halides, halogens, alkyl halides, acyl halides, silyl hydrides, and aldehydes are known to oxidatively add to $\text{RhCl}(\text{PR}_3)_3$,^{13,14} examples of intermolecular oxidative addition of hydrocarbons to $\text{RhCl}(\text{PR}_3)_3$ have not been reported.

The reactivity of the phenyl(hydrido) complex **2** is summarized in Scheme 1. Although **2** was produced in the presence of excessive CO_2 , insertion of CO_2 into the Rh–H or Rh–Ph bond was not observed. Complex **2** was unstable in solution at room temperature under nitrogen. Benzene and **1** were gradually regenerated via reductive elimination. The rate of the reaction was measured using ^1H and ^{31}P NMR spectroscopy to follow the disappearance of **2** at

Scheme 1



25 °C in THF- d_8 . The reaction is first-order in [2] with a rate constant of $3.8 \times 10^{-5} \text{ s}^{-1}$. The presence of CO_2 (60 equiv) did not significantly alter the reaction. The treatment of 2 with atmospheric CO at 25 °C in THF- d_8 resulted in 80% conversion in 1 h as judged by 1H NMR. GC-MS analysis after 5 h revealed the formation of benzaldehyde (6%) along with the reductive elimination product, benzene (74%). For the catalytic C–H bond carbonylation by the $RhCl(CO)(PMe_3)_2$ - $h\nu$ system, $Rh(C_6H_5)(H)Cl(PMe_3)_2$ and $Rh(C_6H_5)(H)Cl(CO)(PMe_3)_2$ were postulated as catalytic intermediates.⁷ The benzaldehyde formation from 2 shown in Scheme 1 possibly proceeds through these intermediates.

On the other hand, the prolonged photoreaction of 1 with benzene under CO_2 produced a small amount of colorless crystals of a phenyl(carbonato) complex, *mer*- $Rh(C_6H_5)(CO_3)(PMe_3)_3$ (3), revealing the activation of the C–H bond and CO_2 . The structure was determined by X-ray crystallography.¹⁵ The fluxional behavior of the *ortho*-protons in 1H NMR revealed that in 3 the phenyl–rhodium bond rotates more easily due to wider phenyl–Rh–P angles than in 2. Complex 3 was presumably formed via 2 because both possess a phenyl group and three trimethylphosphine ligands. The addition of 1 equiv of water to the system did not promote the formation of 3. A possible explanation for the origin of the carbonate ligand is the disproportionation of CO_2 to CO_3^{2-} and CO, although the participation of adventitious water is not denied.¹⁶ The small amount of benzophenone detected in the reaction mixture supports the CO_2 disproportionation mechanism.

In conclusion, we have revealed that $RhCl(PMe_3)_3$ can break the C–H bond of benzene under irradiation to give $Rh(C_6H_5)(H)Cl(PMe_3)_3$ in a high yield. The structure and the reactivities were elucidated. It is noteworthy that $RhCl(PMe_3)_3$ is an active catalyst for the photopromoted C–H bond activations.

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Supporting Information Available: NMR and crystallographic data of 2 and 3, 1H and ^{31}P NMR data and a kinetic data for the decomposition of 2 to 1, and the result of the PMe_3 addition experiment (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- Analytical data of 2: 1H NMR (400 MHz in C_6D_6 at 25 °C) δ –18.26 (ddt, 1H, RhH, $J(RhH) = 19$ Hz, $J(PH) = 28$, $J(PH) = 15$ Hz), 0.98 (apparent triplet due to virtual coupling, 18H, $P(CH_3)_3$), 1.09 (d, 9H, $P(CH_3)_3$, $J(PH) = 6$ Hz), 7.10 (m, 2H, Ph), 7.27 (m, 1H, Ph), 7.49 (t, 1H, Ph, $J(HH) = 6$ Hz), 8.92 (t, 1H, Ph, $J(HH) = 7$ Hz). $^{31}P\{^1H\}$ NMR (160 MHz in C_6D_6 at 25 °C) δ –20.81 (dt, $J(RhP) = 79$ Hz, $J(PP) = 29$ Hz), –7.37 (dd, $J(RhP) = 103$ Hz, $J(PP) = 29$ Hz). $^{13}C\{^1H\}$ NMR (100 MHz in CD_2Cl_2 at –50 °C) δ 17.43 (apparent triplet due to virtual coupling, $P(CH_3)_3$), 19.58 (d, $P(CH_3)_3$, $J(PC) = 22$ Hz), 120.98, 125.07, 125.71, 128.82, 139.05, 145.64 (Ph). NMR data of the isomer: 1H NMR (400 MHz in C_6D_6 at 25 °C) δ –9.70 (ddt, 1H, RhH, $J(RhH) = 17$ Hz, $J(PH) = 215$ Hz, $J(PH) = 15$ Hz), 8.61 (t, 1H, Ph, $J(HH) = 8$ Hz). $^{31}P\{^1H\}$ NMR (160 MHz in CD_2Cl_2 at –50 °C) δ –22.93 (dt, $J(RhP) = 74$ Hz, $J(PP) = 26$ Hz), –9.10 (dd, $J(RhP) = 95$ Hz, $J(PP) = 26$ Hz). IR (KBr) ν 2036 cm^{-1} (Rh–H). Anal. Calcd for $C_{15}H_{33}ClP_3Rh$: C, 40.51; H, 7.48; Cl, 7.97. Found: C, 40.72; H, 7.49; Cl, 8.09.
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- Recrystallized from toluene–hexane at –40 °C. Crystal data for 2: A single crystal (0.20 × 0.30 × 0.40 mm) was sealed in a capillary glass tube. The diffraction data were collected at 193 K on a Rigaku AFC-7R automated four-cycle diffractometer by using graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å) and the ω -2 method. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms except for the Rh–H hydrogen were located by assuming ideal positions ($d = 0.95$) and were included in the structure calculation without further refinement of the parameters. Crystal data: $C_{15}H_{33}ClP_3Rh$, $Mr = 444.71$, monoclinic, space group $P2_1/n$ (No. 14), $a = 9.787(3)$, $b = 11.944(5)$, $c = 17.892(4)$, $\beta = 94.14(2)$, $V = 2085(1)$, $Z = 4$, $D_{calc} = 1.416$ g cm^{-3} , 2θ max = 55, GOF = 1.97. The final R factor was 0.048 ($R_w = 0.077$) for 3929 reflections with $I_o > 2\sigma(I_o)$.
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- Recrystallized from CH_2Cl_2 – Et_2O at room temperature. Crystal data for 3: A single crystal (0.20 × 0.30 × 0.40 mm) was sealed in a capillary glass tube for the data collection, and diffraction data were collected at 296 K. Crystal data: $C_{16}H_{32}O_3P_3Rh$, $Mr = 468.25$, tetragonal, space group $P4/n$ (No. 85), $a = 22.597(3)$, $c = 8.705(4)$, $V = 4445(2)$, $Z = 8$, $D_{calc} = 1.399$ g cm^{-3} , 2θ max = 55, GOF = 1.71. The final R factor was 0.049 ($R_w = 0.078$) for 3929 reflections with $I_o > 2\sigma(I_o)$. Analytical data of 3: 1H NMR (400 MHz in CD_2Cl_2 at 25 °C) δ 1.18 (apparent triplet due to virtual coupling, 18H, $P(CH_3)_3$), 1.61 (d, 9H, $P(CH_3)_3$, $J(PH) = 10$ Hz), 6.94 (m, 3H, Ph), 7.13 (br, 2H, Ph). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 12.31 (apparent triplet due to virtual coupling, $P(CH_3)_3$), 17.46 (d, $P(CH_3)_3$, $J(PC) = 31$ Hz), 122.13, 126.89, 135.51, 145.07 (Ph), 166.24 (CO_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ –3.64 (dd, $J(RhP) = 99$ Hz, $J(PP) = 36$ Hz), 1.51 (dt, $J(RhP) = 126$ Hz, $J(PP) = 36$ Hz). 1H NMR (400 MHz in CD_2Cl_2 at –80 °C) δ 1.08 (apparent triplet due to virtual coupling, 18H, $P(CH_3)_3$), 1.54 (d, 9H, $P(CH_3)_3$, $J(PH) = 10$ Hz), 6.72 (d, 1H, Ph, $J(HH) = 7$ Hz), 6.87 (m, 3H, Ph), 7.37 (d, 1H, Ph, $J(HH) = 7$ Hz). IR (KBr) ν 1552 cm^{-1} (CO_3). Anal. Calcd for $C_{16}H_{32}O_3P_3Rh$: C, 41.04; H, 6.89; O, 10.25. Found: C, 40.95; H, 7.21; O, 10.35. HRMS(EI): calcd for $C_{16}H_{31}O_3P_3Rh$, 467.0540; found, 467.0545 ($M^+ - H$).
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