

# Facile Insertion of CO<sub>2</sub> into the Ru–H Bonds of Ru(dmpe)<sub>2</sub>H<sub>2</sub> (dmpe = Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>): Identification of Three Ruthenium Formate Complexes

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The reaction of *cis*-Ru(dmpe)<sub>2</sub>H<sub>2</sub> (dmpe = Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>), **1**, with carbon dioxide has been investigated. Addition of CO<sub>2</sub> at 293 K results in the formation of two formate complexes: the major product is the *trans* formate hydride, *trans*-Ru(dmpe)<sub>2</sub>(OCHO)H, **2**, while the minor species is the bis(formate) complex, *cis*-Ru(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>, **3**. When the addition of carbon dioxide is performed at 195 K, both the bis(formate) and the *cis*-formate hydride complex, *cis*-Ru(dmpe)<sub>2</sub>(OCHO)H, **4**, are observed in larger concentrations. All three complexes have been characterized by multinuclear NMR while **2** has been isolated and characterized by X-ray crystallography. The ruthenium formate group is planar with Ru–O(1) = 2.243(4) Å. The Ru–O(1) vector is tilted away from the normal to the P<sub>4</sub> plane with resultant O(1)–Ru–P angles of 84.4(2), 88.4(1), 96.7(1), and 101.5(2)°. The C–O(2) vector of the formate group points toward the RuP<sub>4</sub> plane. The symmetric and antisymmetric OCO stretching modes in the IR spectrum of **2** were identified by reaction with <sup>13</sup>CO<sub>2</sub>.

## Introduction

The potential of CO<sub>2</sub> as an inexpensive and abundant source of carbon for use in organic synthesis has stimulated great interest in the activation of carbon dioxide by transition metal complexes.<sup>1</sup> The catalytic reduction of CO<sub>2</sub> to formic acid has been the subject of several recent studies<sup>2</sup> in homogeneous solution. In a particularly elegant extension of this work, Noyori and co-workers have demonstrated that the use of supercritical CO<sub>2</sub> (scCO<sub>2</sub>) as both reactant and solvent for the production of formic acid in the presence of hydrogen, base, and a series of ruthenium hydride catalysts results in extremely high yields (up to 7200 ton) and turnover rates (up to 1400 h<sup>-1</sup>).<sup>3</sup> These values are larger than those reported for any other catalyzed production of formic acid in conventional organic solvents. The efficiency of the scCO<sub>2</sub> system is thought to arise from the high solubility and diffusion rate of hydrogen in the supercritical fluid.

Many previous studies<sup>4</sup> have shown that the stoichiometric reaction of carbon dioxide with a metal hydride complex results in the insertion of CO<sub>2</sub> into an M–H bond to yield a metal formate complex, and indeed such

a species is postulated to be the active catalytic intermediate in the Noyori system. The problem of characterizing this active complex precisely and elucidating the sequence of steps in the mechanism of the reaction is illustrated by considering the reaction of a similarly electron-rich metal hydride complex, Mo(dmpe)<sub>2</sub>H<sub>4</sub> (dmpe = Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>), with CO<sub>2</sub>: at least six products result from the insertion of CO<sub>2</sub> into a Mo–H bond.<sup>5</sup>

Our recent interest in the thermal and photochemical reactions<sup>6</sup> of *cis*-Ru(dmpe)<sub>2</sub>H<sub>2</sub>, **1**, prompted us to study its reactivity toward CO<sub>2</sub>. The related triphenylphosphine complexes, Ru(PPh<sub>3</sub>)<sub>4</sub>H<sub>2</sub>, Ru(PPh<sub>3</sub>)<sub>3</sub>(N<sub>2</sub>)H<sub>2</sub>, and Ru(PPh<sub>3</sub>)<sub>3</sub>H<sub>4</sub>, all react with carbon dioxide to give the η<sup>2</sup>-formate complex, Ru(PPh<sub>3</sub>)<sub>3</sub>(η<sup>2</sup>-OCHO)H,<sup>7</sup> while the PMe<sub>3</sub> analogue, Ru(PMe<sub>3</sub>)<sub>4</sub>H<sub>2</sub>, has recently been shown to give the η<sup>1</sup>-formate hydride complex, *cis*-Ru(PMe<sub>3</sub>)<sub>4</sub>(η<sup>1</sup>-OCHO)H, upon bubbling with CO<sub>2</sub> at room temperature.<sup>8</sup> In the same paper, Jessop et al. have reported that *trans*-Ru(dmpe)<sub>2</sub>(H)Cl catalytically hydrogenates carbon dioxide to formic acid in scCO<sub>2</sub>, although the stoichiometric reaction with CO<sub>2</sub> has not been reported. We now demonstrate that carbon dioxide inserts into the Ru–H bond of **1** at 223 K to give an η<sup>1</sup>-formate hydride complex and that two additional formate products are formed upon warming the solution to room temperature.

## Results and Discussion

Addition of 1 atm of CO<sub>2</sub> to a toluene-*d*<sub>8</sub> solution of **1** at room temperature resulted in an immediate reaction

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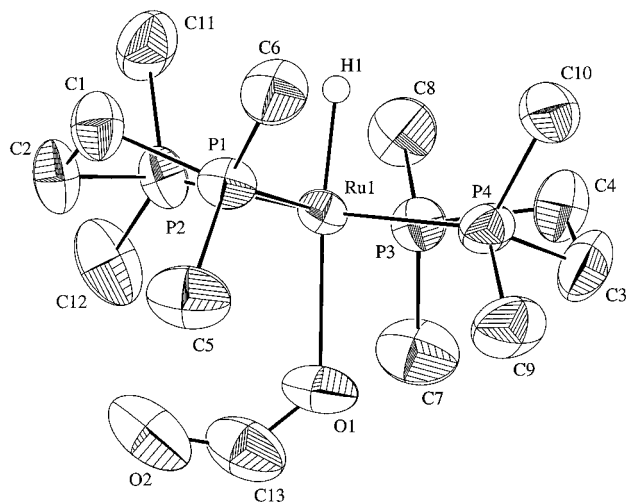
<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, November 1, 1996.

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**Figure 1.** ORTEP diagram of *trans*-Ru(dmpe)<sub>2</sub>(OCHO)H (**2**). Thermal ellipsoids are shown at the 50% level.

as shown by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy with the complete loss of starting material and the formation of two products. The major new species, **2**, appeared at δ 46.0 as a singlet, indicating a product with a *trans*-geometry. The minor product, **3**, had a *cis*-stereochemistry as demonstrated by two apparent triplet resonances at δ 54.2 and δ 38.2 (*J* = 24.3 Hz) due to sets of magnetically inequivalent phosphorus nuclei in an [AX]<sub>2</sub> pattern. Upon warming of the solution to 333 K overnight, only **2** remained. The <sup>1</sup>H NMR spectrum of this species displayed a high-field quintet resonance at δ –22.60 for a hydride coupled to four <sup>31</sup>P nuclei and a singlet at δ 8.66, suggesting the presence of a formate ligand resulting from the insertion of CO<sub>2</sub> into a Ru–H bond. The identification of this as an η<sup>1</sup>-formate group was confirmed by the appearance of two bands at 1603 and 1329 cm<sup>–1</sup> in the IR spectrum (Nujol mull), which shifted to 1564 and 1309 cm<sup>–1</sup> with <sup>13</sup>CO<sub>2</sub>, and the observation of a doublet resonance at δ 166.9 (*J*<sub>CH</sub> = 186 Hz) in the <sup>1</sup>H-coupled <sup>13</sup>C NMR spectrum of a <sup>13</sup>CO<sub>2</sub>-enriched sample. The IR and NMR data are consistent with other reported η<sup>1</sup>-formate complexes in the literature: [Rh(H<sub>2</sub>O)(PMe<sub>2</sub>Ph)<sub>2</sub>(η<sup>1</sup>-OCHO)H]<sup>+</sup> displays two bands at 1620 and 1331 cm<sup>–1</sup> in the IR spectrum<sup>2b</sup> and the <sup>1</sup>H-coupled <sup>13</sup>C NMR spectrum of Mo(dmpe)<sub>2</sub>(CO<sub>2</sub>)-(η<sup>1</sup>-OCHO)H contains a doublet resonance at δ 167.2 with *J*<sub>CH</sub> = 195 Hz.<sup>5</sup> In contrast, the ν(OCO)<sub>asym</sub> band for a bidentate formate ligand, such as found in Re-(dppe)<sub>2</sub>(η<sup>2</sup>-OCHO) (dppe = Ph<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PPh<sub>2</sub>), appears below 1600 cm<sup>–1</sup> (in this case at 1550 cm<sup>–1</sup>).<sup>9</sup> Complex **2** is therefore assigned as the formate hydride species, *trans*-Ru(dmpe)<sub>2</sub>(OCHO)H. The spectroscopic data are also very similar to the ruthenium carboxylate complex, *trans*-Ru(dmpe)<sub>2</sub>(O<sub>2</sub>C(*p*-C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>))H.<sup>10</sup>

A suitable single crystal of **2** was obtained by low-temperature crystallization from hexane and the structure determined by X-ray crystallography (Figure 1). Selected bond lengths are summarized in Table 1 and bond angles given in Table 2. The ruthenium atom is displaced from the least-squares plane P(1)–P(2)–P(3)–P(4) toward O(1) by 0.110(1) Å. The ruthenium formate

**Table 1.** Selected Intramolecular Distances (Å) for *trans*-Ru(dmpe)<sub>2</sub>(OCHO)H (**2**)

Ru–P(1)	2.295(4)	P(2)–C(12)	1.843(7)
Ru–P(2)	2.296(3)	P(3)–C(8)	1.828(7)
Ru–P(3)	2.302(4)	P(3)–C(7)	1.830(7)
Ru–P(4)	2.308(3)	P(3)–C(4)	1.848(7)
Ru–O(1)	2.243(4)	P(4)–C(9)	1.816(7)
Ru–H(1)	1.57(5)	P(4)–C(10)	1.825(7)
P(1)–C(6)	1.832(7)	P(4)–C(3)	1.848(8)
P(1)–C(1)	1.834(7)	O(1)–C(13)	1.204(9)
P(1)–C(5)	1.834(7)	O(2)–C(13)	1.226(11)
P(2)–C(2)	1.838(7)	C(1)–C(2)	1.534(9)
P(2)–C(11)	1.844(7)	C(3)–C(4)	1.520(10)

**Table 2.** Selected Intramolecular Angles (deg) for *trans*-Ru(dmpe)<sub>2</sub>(OCHO)H (**2**)

P(1)–Ru–P(2)	83.63(14)	C(11)–P(2)–C(12)	101.2(4)
P(1)–Ru–P(3)	174.91(6)	C(2)–P(2)–Ru	109.6(3)
P(1)–Ru–P(4)	96.77(14)	C(11)–P(2)–Ru	117.1(3)
P(1)–Ru–O(1)	96.68(14)	C(12)–P(2)–Ru	122.9(3)
P(1)–Ru–H(1)	87(2)	C(8)–P(3)–C(7)	101.5(4)
P(2)–Ru–P(3)	95.20(14)	C(8)–P(3)–C(4)	100.9(4)
P(2)–Ru–P(4)	174.05(6)	C(7)–P(3)–C(4)	102.7(4)
P(2)–Ru–O(1)	101.5(2)	C(8)–P(3)–Ru	122.6(3)
P(2)–Ru–H(1)	83(2)	C(7)–P(3)–Ru	117.5(3)
P(3)–Ru–P(4)	83.9(2)	C(4)–P(3)–Ru	108.8(3)
P(3)–Ru–O(1)	88.40(14)	C(9)–P(4)–C(10)	101.4(4)
P(3)–Ru–H(1)	88(2)	C(9)–P(4)–C(3)	102.7(4)
P(4)–Ru–O(1)	84.4(2)	C(10)–P(4)–C(3)	101.5(4)
P(4)–Ru–H(1)	91(2)	C(9)–P(4)–Ru	120.7(3)
O(1)–Ru–H(1)	174(2)	C(10)–P(4)–Ru	119.4(2)
C(6)–P(1)–C(1)	101.2(3)	C(3)–P(4)–Ru	108.6(3)
C(6)–P(1)–C(5)	100.7(4)	C(13)–O(1)–Ru	129.6(6)
C(1)–P(1)–C(5)	101.8(4)	C(1)–C(1)–P(1)	108.8(5)
C(6)–P(1)–Ru	121.2(3)	C(1)–C(2)–P(2)	109.2(4)
C(1)–P(1)–Ru	110.0(2)	C(4)–C(3)–P(4)	109.1(5)
C(5)–P(1)–Ru	119.0(3)	C(3)–C(4)–P(3)	108.0(5)
C(2)–P(2)–C(11)	100.5(4)	O(1)–C(13)–O(2)	131.4(9)
C(2)–P(2)–C(12)	102.3(4)		

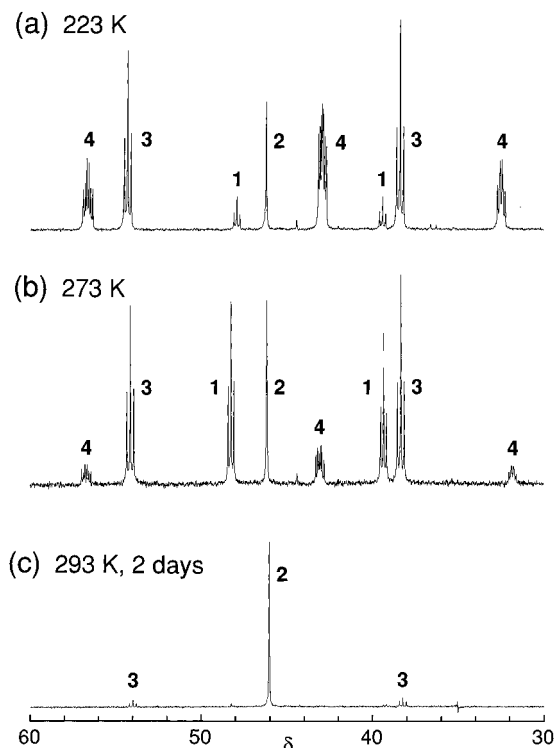
group Ru–O(1)–C(13)–O(2) unit is planar with C(13)–O(2) pointing in toward the phosphine ligands. The projection of the formate ligand onto the plane of the four phosphorus atoms lies between the chelated Ru–P bonds with torsion angles of 60.2(6)° (P(1)–Ru–O(1)–C(13)) and –24.6(6)° (P(2)–Ru–O(1)–C(13)). There is a clear distortion in the O(1)–Ru–P angles with two small angles of 84.4(2)° and 88.4(1)° and two larger angles (96.7(1)° and 101.5(2)°).

The identification of **3** as a *cis*-species was established by the addition of 1 atm of CO<sub>2</sub> to **1** at 195 K. Low-temperature <sup>31</sup>P{<sup>1</sup>H} NMR spectra recorded at 223 K showed that **3** was essentially the only species present in solution under these conditions. The <sup>1</sup>H NMR spectrum displayed no hydride resonances but did show a complex resonance in the formate region at δ 8.78, which integrated to two protons with respect to the dmpe resonances, implying the presence of two formate ligands. Selective <sup>31</sup>P decoupling of this resonance showed that it was coupled to both sets of phosphorus nuclei. The <sup>1</sup>H-coupled <sup>13</sup>C NMR spectrum, again recorded using <sup>13</sup>CO<sub>2</sub> enrichment, showed a doublet resonance at δ 167.9 (*J*<sub>CH</sub> = 193 Hz) consistent with an η<sup>1</sup>-bonding mode for both formate groups. The spectra are consistent with the formation of the bis(formate) complex, *cis*-Ru(dmpe)<sub>2</sub>(OCHO)<sub>2</sub>, resulting from the insertion of CO<sub>2</sub> into both Ru–H bonds. The related bis(benzoate) complex, *cis*-Ru(dmpe)<sub>2</sub>(O<sub>2</sub>CPh)<sub>2</sub>, has been previously reported by Hartwig et al.<sup>11</sup> We were unable

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**Figure 2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra recorded after addition of 300 Torr of  $\text{CO}_2$  to a toluene- $d_8$  solution of *cis*- $\text{Ru}(\text{dmpe})_2\text{H}_2$ , **1**, at 195 K: (a) spectrum recorded at 223 K immediately after addition; (b) spectrum recorded upon warming to 273 K; (c) spectrum recorded after 2 days at 293 K. Key: **1** = *cis*- $\text{Ru}(\text{dmpe})_2\text{H}_2$ ; **2** = *trans*- $\text{Ru}(\text{dmpe})_2(\text{OCHO})\text{H}$ ; **3** = *cis*- $\text{Ru}(\text{dmpe})_2(\text{OCHO})_2$ ; **4** = *cis*- $\text{Ru}(\text{dmpe})_2(\text{OCHO})\text{H}$ .

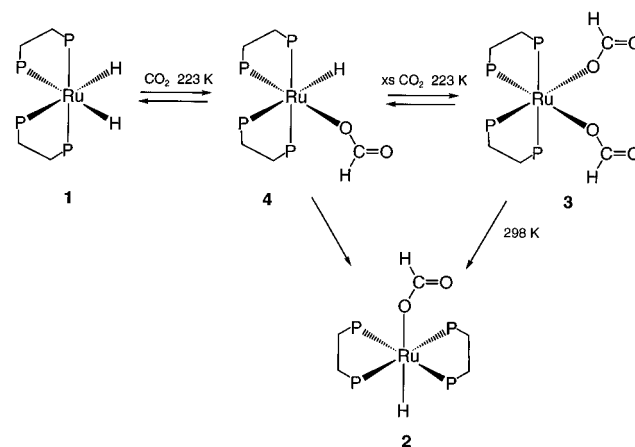
to isolate **3** as it converted very slowly to **2** even at 223 K under 1 atm  $\text{CO}_2$  and more rapidly upon warming the solution to room temperature.

The expected precursor to **3** would be the *cis* mono(formate) hydride complex, *cis*- $\text{Ru}(\text{dmpe})_2(\text{OCHO})\text{H}$ , **4**. We have been able to characterize this species spectroscopically upon addition of <1 atm  $\text{CO}_2$  to a toluene- $d_8$  solution of **1** at 195 K. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum recorded at 223 K showed the presence of **3** and **4**, together with smaller amounts of **1** and **2** (Figure 2a). An ABMX pattern was observed for **4** with resonances for the mutually *trans*  $^{31}\text{P}$  nuclei close to coincidence. The hydride resonance appeared as a doublet of quartets at  $\delta -7.35$  in the  $^1\text{H}$  spectrum, while the formate resonance appeared close to that for **3** at  $\delta 8.91$ .

Allowing the solution to warm to 273 K resulted in the depletion of the hydride resonance of **4** and growth in the hydride signal due to **1**, indicating that the insertion of  $\text{CO}_2$  into the Ru–H bond was reversible (Figure 2b). A small decrease in the concentration of **3** is also seen, suggesting that the pathway from **4** to **3** may also be reversible. Very little change was observed in the amount of **2** at this point. When the solution was brought to room temperature, a small increase was recorded in the concentration of **2** at the expense of **4**. After 2 days, **2** and **3** were the only species left in solution (Figure 2c) in a ratio of 5:1. Although the pathway of interconversion of **2**, **3**, and **4** is not completely understood, a probable relationship is shown in Scheme 1.

These experiments demonstrate the facile interconversion of  $\text{Ru}(\text{dmpe})_2\text{H}_2$  and three  $\text{CO}_2$ -insertion prod-

### Scheme 1. Solution Chemistry of *cis*- $\text{Ru}(\text{dmpe})_2\text{H}_2$ , **1**, with Carbon Dioxide



ucts. The low barrier to  $\text{CO}_2$  insertion is suggestive of a concerted mechanism.<sup>12</sup> There is no evidence that partial dissociation of a dmpe ligand is required.<sup>8</sup> Under the conditions of our experiments, the *cis*-formate hydride complex, **4**, is the kinetic product but is extremely unstable with respect to the *trans* isomer, **2**. The bis(formate) complex, **3**, is formed with quite modest concentrations of  $\text{CO}_2$  (<0.1 mol  $\text{dm}^{-3}$ ). The corresponding room-temperature reaction of  $\text{Ru}(\text{PMe}_3)_4\text{H}_2$  with  $\text{CO}_2$  in  $\text{C}_6\text{D}_6$  gave only a *cis*-formate hydride complex.<sup>8</sup> Under the catalytic conditions employed by Jessop et al. with  $\text{Ru}(\text{PMe}_3)_4\text{H}_2$  dissolved in  $\text{scCO}_2$  at 50  $^\circ\text{C}$ ,<sup>8</sup> analogues of each of the species **2**–**4** could be present and play a role in the catalytic hydrogenation.

### Experimental Section

**General Methods and Materials.** All reactions were carried out using standard Schlenk, high-vacuum, and glove-box techniques. Toluene- $d_8$  was dried over potassium/benzophenone and vacuum distilled. Carbon dioxide (Messer Griesheim, 99.999%) and  $^{13}\text{CO}_2$  (Aldrich, 99.5%) were used as received. NMR spectra were recorded using a Bruker MSL 300 spectrometer and referenced as follows:  $^1\text{H}$  (residual toluene- $d_7$  at  $\delta 2.1$  ppm),  $^{31}\text{P}$  (externally to  $\text{H}_3\text{PO}_4$  at 0 ppm) and  $^{13}\text{C}$  (toluene- $d_8$  at  $\delta 21.5$ ). IR spectra were recorded as Nujol mulls on a Mattson Research Series FTIR spectrometer. Elemental analysis was performed by Elemental Microanalysis Limited, Okehampton, Devon, U.K. (Only complex **2** was sufficiently stable for microanalysis.)

**Synthesis.** The preparation of *cis*- $\text{Ru}(\text{dmpe})_2\text{H}_2$ , **1**, has been described elsewhere.<sup>6a</sup>

***trans*- $\text{Ru}(\text{dmpe})_2(\text{OCHO})\text{H}$  (**2**).** A 1 atm  $\text{CO}_2$  pressure (95 mmol  $\text{dm}^{-3}$ )<sup>13</sup> was added at room temperature to a Young's NMR tube containing a solution of **1** (34 mg, 0.085 mmol) in toluene- $d_8$  (0.6 mL). The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum showed a mixture of **2** and *cis*- $\text{Ru}(\text{dmpe})_2(\text{OCHO})_2$ , **3**. When the spectrum was rerun following overnight heating of the sample in a graphite bath to 333 K, only **2** remained. Removal of the solvent and recrystallization of the white solid from hexane at 253 K gave **2** in analytically pure form. Anal. Calcd for  $\text{C}_{13}\text{H}_{34}\text{O}_2\text{P}_4\text{Ru}$ : C, 34.89; H, 7.67. Found: C, 34.88; H, 7.26. Spectroscopic data for **2**:  $^1\text{H}$  NMR (toluene- $d_8$ , 300 MHz, 293 K)  $\delta -22.60$  (quin,  $J_{\text{PH}} = 21.3$  Hz, 1H, Ru–H), 1.14 (s, 12H, 4  $\times$   $\text{PCH}_3$ ), 1.31 (m, 4H, 2  $\times$   $\text{PCH}_2$ ), 1.37 (m, 4H, 2  $\times$   $\text{CH}_2$ ), 1.37

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(s, 12H, 4 × PCH<sub>3</sub>), 8.66 (s, 1H, O<sub>2</sub>CH). <sup>31</sup>P{<sup>1</sup>H}: δ 46.0 (s). <sup>13</sup>C–<sup>1</sup>H coupled: δ 166.9 (d, J<sub>HC</sub> = 186 Hz). IR (Nujol, cm<sup>-1</sup>) 1925 (ν(Ru–H)), 1603 (ν(O<sup>12</sup>CO<sub>asym</sub>)), 1329 (ν(O<sup>12</sup>CO<sub>sym</sub>)); 1564 (ν(O<sup>13</sup>CO<sub>asym</sub>)), 1309 (ν(O<sup>13</sup>CO<sub>sym</sub>)). Mass spec. EI *m/z* 402 (M – HCO<sub>2</sub>H)<sup>+</sup>.

**cis-Ru(dmpe)<sub>2</sub>(OCHO)<sub>2</sub> (3).** Addition of 1 atm of CO<sub>2</sub> (95 mmol dm<sup>-3</sup>) to a toluene-*d*<sub>8</sub> solution of **1** (10 mg, 0.025 mmol) at 195 K resulted in the formation of just **3**. Spectroscopic data for **3**: <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 300 MHz, 273 K) δ 0.71 (d, J<sub>PH</sub> = 7.6 Hz, 6H, 2 × PCH<sub>3</sub>), 0.97 (d, J<sub>PH</sub> = 9.5 Hz, 6H, 2 × PCH<sub>3</sub>), 1.21–1.43 (br m, PCH<sub>2</sub>), 1.57 (t, J<sub>PH</sub> = 3.2 Hz, 6H, 2 × PCH<sub>3</sub>), 1.86 (t, J<sub>PH</sub> = 3.8 Hz, 6H, 2 × PCH<sub>3</sub>), 8.78 (m, 2H, OCHO). <sup>31</sup>P{<sup>1</sup>H}: δ 38.2 (pseudo t, splitting = 24.3 Hz), 54.2 (pseudo t, splitting = 24.3 Hz). <sup>13</sup>C–<sup>1</sup>H coupled: δ 167.9 (d, J<sub>HC</sub> = 193 Hz). IR (Nujol, cm<sup>-1</sup>) 1613 (ν(OCO<sub>asym</sub>)), 1317 (ν(OCO<sub>sym</sub>)).

**cis-Ru(dmpe)<sub>2</sub>(OCHO)H (4).** Spectroscopic evidence for the formation of **4** was obtained upon addition of 300 Torr (37.5 mmol dm<sup>-3</sup>) CO<sub>2</sub> to a toluene-*d*<sub>8</sub> solution of **1** (20 mg, 0.05 mmol) at 195 K. NMR data for **4**: <sup>1</sup>H NMR (toluene-*d*<sub>8</sub>, 300 MHz, 223 K) δ -7.35 (dq, J<sub>PH</sub> = 99.5 Hz, J<sub>PH</sub> = 23.5 Hz, 1H, Ru–H), 0.56 (d, J<sub>PH</sub> = 7.6 Hz, 3H, PCH<sub>3</sub>), 0.87 (d, J<sub>PH</sub> = 5.1 Hz, 3H, PCH<sub>3</sub>), 0.97 (s, 3H, PCH<sub>3</sub>), 1.0–1.4 (br m, CH<sub>2</sub>), 1.11 (s, 3H, PCH<sub>3</sub>), 1.18 (d, J<sub>PH</sub> = 7.0 Hz, 3H, PCH<sub>3</sub>), 1.38 (s, 3H, PCH<sub>3</sub>), 1.55 (d, J<sub>PH</sub> = 6.1 Hz, 3H, PCH<sub>3</sub>), 1.84 (d, J<sub>PH</sub> = 5.1 Hz, 3H, PCH<sub>3</sub>), 8.91 (m, 1H, OCHO). <sup>31</sup>P{<sup>1</sup>H}: δ 57.0 (t d, J<sub>PP</sub> = 25.8 Hz, J<sub>PP</sub> = 14.1 Hz), 43.3 (m), 32.9 (m). <sup>13</sup>C–<sup>1</sup>H coupled: δ 169.7 (d, J<sub>HC</sub> = 189 Hz).

**X-ray Structure of trans-Ru(dmpe)<sub>2</sub>(OCHO)H (2).** Crystals of **2** suitable for X-ray diffraction were obtained by recrystallization from hexane at 253 K. A summary of crystal data is shown in Table 3. A single crystal was mounted on a glass fibre in epoxy cement. Data were collected on a Rigaku AFC6S diffractometer. Data reduction, and Lorentz, polarization, and 2θ-dependent absorption corrections were applied with the TEXSAN system.<sup>14</sup> The structure was solved by direct methods with full-matrix least-squares refinement carried out using the TEXSAN software package.<sup>14</sup> The hydride was located on a difference map and refined isotropically. The remaining hydrogen atoms were included at calculated sites and refined with the “riding” model. Final refinement was carried out using SHELXL 93.<sup>15</sup>

**Table 3. Crystal Parameters for trans-Ru(dmpe)<sub>2</sub>(OCHO)H (2)**

formula	C <sub>13</sub> H <sub>34</sub> O <sub>2</sub> P <sub>4</sub> Ru
fw	447.35
cryst system	monoclinic
space group	P2 <sub>1</sub> /n
<i>a</i> , Å	9.30(2)
<i>b</i> , Å	16.163(7)
<i>c</i> , Å	14.204(13)
β, deg	93.27(11)
<i>V</i> , Å <sup>3</sup>	2132(5)
<i>Z</i>	4
size, mm	0.5 × 0.4 × 0.3
color	colorless
<i>d</i> (calc), Mg m <sup>-3</sup>	1.394
λ(Mo Kα), Å	0.710 69
<i>T</i> , K	293
μ(calc), cm <sup>-1</sup>	10.35
2θ range, deg	5–50
<i>F</i> (000), electrons	928
index range	0 ≤ <i>h</i> ≤ 11, 0 ≤ <i>k</i> ≤ 19, –16 ≤ <i>l</i> ≤ 16
reflcs measd	4148
indepdt reflcs	3746
no. of params	185
<i>R</i> <sub>F</sub> [ <i>I</i> > 2σ( <i>I</i> )]	0.0418
<i>wR</i> <sub>i</sub>	0.1106
GOF	0.851
largest diff peak, e Å <sup>-3</sup>	0.511
smallest diff peak, e Å <sup>-3</sup>	–0.357

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**Supporting Information Available:** Tables of crystallographic data for **2** including atomic coordinates, anisotropic displacement parameters, hydrogen coordinates, selected torsion angles, and least-squares planes (5 pages). Ordering information is given on any current masthead page.

OM960588B

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