

# A Diruthenium $\mu$ -Methylene Complex

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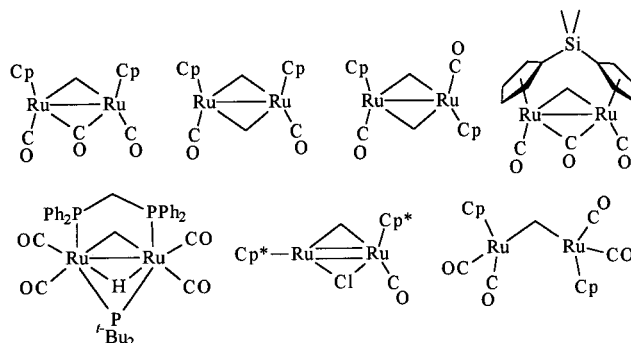
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The reaction of  $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4(\mu\text{-dppm})_2]$  (**1**;  $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ) with  $\text{CH}_2\text{N}_2$  gives the  $\mu$ -methylene complex  $[\text{Ru}_2(\mu\text{-CH}_2)(\text{CO})_4(\mu\text{-dppm})_2]$  (**2**), and complex **2** reacts with CO to regenerate complex **1** with loss of ketene. Complex **2** reacts with  $\text{HBF}_4$  or  $\text{CF}_3\text{SO}_3\text{H}$  at low temperature to form the fluxional  $\mu$ -methyl complex  $[\text{Ru}_2(\mu\text{-CH}_3)(\text{CO})_4(\mu\text{-dppm})_2]^+$  (**3**). Variable-temperature  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR studies establish that the  $\mu\text{-CH}_3$  group has an unsymmetrical coordination mode with an agostic hydrogen and is fluxional. At room temperature, the reaction of **2** with formic acid gives an equimolar mixture of complex **1** and  $[\text{Ru}_2(\mu\text{-H})(\text{H})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]$  (**4**), which is an active catalyst for the decomposition of formic acid to hydrogen and carbon dioxide, and the reaction is shown to occur via the intermediate complexes **3** and  $[\text{Ru}_2(\mu\text{-H})\{\mu\text{-C}(\text{O})\text{Me}\}(\text{HCOO})(\text{CO})_3(\mu\text{-dppm})_2]^+$  (**5**). The reaction of **2** with acetic acid at room temperature gives in sequence the complexes  $[\text{Ru}_2\{\mu\text{-C}(\text{O})\text{Me}\}(\text{OAc})(\text{CO})_3(\mu\text{-dppm})_2]$  (**6**) and  $[\text{Ru}_2(\mu\text{-H})\{\mu\text{-C}(\text{O})\text{Me}\}(\text{OAc})(\text{CO})_3(\mu\text{-dppm})_2]^+$  (**7**) before loss of methane occurs with formation of  $[\text{Ru}_2(\mu\text{-OAc})(\text{CO})_4(\mu\text{-dppm})_2]^+$  (**8**). Complex **2** reacts with methyl triflate to give ethylene and  $[\text{Ru}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_3(\mu\text{-dppm})_2]^+$  (**9**), as the triflate salt, probably via an intermediate with an ethylruthenium group. In the presence of  $\text{HBF}_4$ , complex **2** is an efficient precatalyst for the ring-opening polymerization of norbornene.

## Introduction

Transition-metal alkylidene complexes are of interest as reagents or intermediates in catalysis or as models for proposed intermediates in catalytic reactions. For example,  $\mu$ -alkylidene groups can model intermediates in the Fischer–Tropsch reaction,<sup>1</sup> and terminal alkylidene groups are important in olefin metathesis chemistry.<sup>2</sup> Ruthenium is one of the most active metals in Fischer–Tropsch catalysis,<sup>3</sup> and ruthenium alkylidene complexes are among the most versatile metathesis and cyclopropanation catalysts.<sup>4</sup> Hence, there is considerable interest in alkylidene complexes of ruthenium. This article reports the synthesis of a new ( $\mu$ -methylene)-diruthenium complex,  $[\text{Ru}_2(\mu\text{-CH}_2)(\text{CO})_4(\mu\text{-dppm})_2]$  ( $\text{dppm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$ ), and a study of its reactivity. Some related ( $\mu$ -methylene)diruthenium complexes are shown in Chart 1,<sup>5</sup> and there is also much interest in the chemistry of  $\text{Ru}_2(\mu\text{-CH}_2)$  groups that can exist on ruthenium metal surfaces.<sup>6</sup>

## Chart 1



## Results and Discussion

**Synthesis of  $[\text{Ru}_2(\mu\text{-CH}_2)(\text{CO})_4(\mu\text{-dppm})_2]$ .** Complex **2** was synthesized by reaction of  $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4(\mu\text{-dppm})_2]$  (**1**)<sup>7</sup> with diazomethane in toluene at 50 °C,

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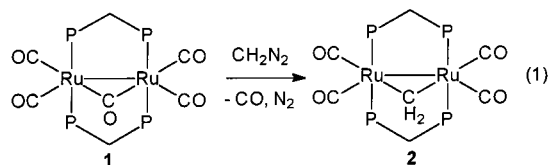
(4) (a) Kanaoka, S.; Grubbs, R. H. *Macromolecules* **1995**, 28, 4707. (b) Schwab, P.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1996**, 118, 100. (c) Dias, E. L.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1997**, 119, 3887. (d) Dias, E. L.; Grubbs, R. H. *Organometallics* **1998**, 17, 2758. (e) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: New York, 1997.

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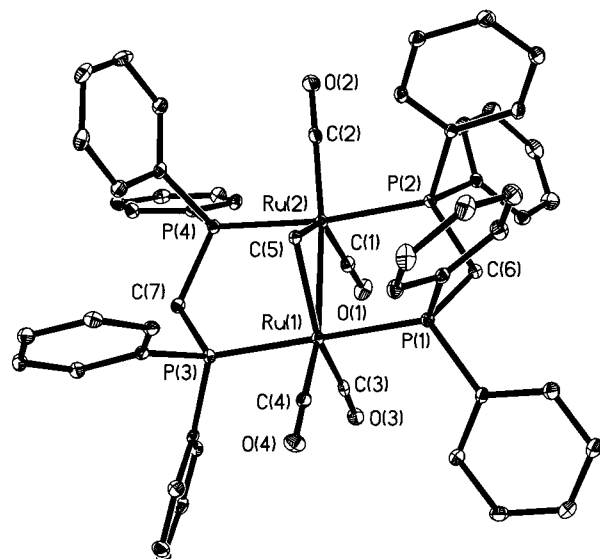
as shown in eq 1. Most syntheses of  $\mu$ -methylene



complexes from diazomethane have been carried out at lower temperatures in order to avoid decomposition of diazomethane to nitrogen and polymethylene.<sup>8,9</sup> However, complex **1** failed to react with  $\text{CH}_2\text{N}_2$  at 0 °C and, when it was warmed to room temperature, rapid decomposition of diazomethane occurred to give polymethylene. The ruthenium complex present was shown to be very largely unchanged complex **1**; therefore, the decomposition of diazomethane is catalytic. The complete conversion of **1** to **2** was successfully achieved at 50 °C, although much polymethylene was again produced by parallel decomposition of diazomethane. The polymer could be easily separated by filtration; thus, this is a reasonable synthesis of **2**, though a large excess of diazomethane is needed. Complex **2** was isolated as a yellow solid that decomposed only slowly in air at room temperature.

Complex **2** gives a sharp singlet at  $\delta$  39.6 in the  $^{31}\text{P}$ - $\{^1\text{H}\}$  NMR spectrum, indicating a symmetrical structure. The  $^1\text{H}$  NMR spectrum of **2** displays a quintet resonance at  $\delta$  5.2, with  $^3J(\text{PH}) = 10$  Hz, and the  $^{13}\text{C}$  NMR spectrum gave a peak at  $\delta$  88. These chemical shifts are on the borderline for bridging  $\text{CH}_2$  groups in complexes containing a metal–metal bond ( $\delta(^1\text{H})$  5–11;  $\delta(^{13}\text{C})$  100–210) and those with no metal–metal bond ( $\delta(^1\text{H})$  1–5;  $\delta(^{13}\text{C})$  –37 to +65), probably as a result of the relatively long Ru–Ru distance in **2** (see below).<sup>8</sup> Two resonances characteristic of terminal carbonyls were observed in the  $^{13}\text{C}$  NMR spectrum ( $\delta$  214, 208), and four terminal carbonyl bands were observed in the IR spectrum ( $\nu_{\text{CO}}$  1970, 1926, 1902, 1878  $\text{cm}^{-1}$ ). Two resonances were observed for the  $\text{CH}^a\text{H}^b$  protons of the  $\text{CH}_2\text{P}_2$  groups. The NMR data show that complex **2** is not fluxional, unlike the parent **1**, which undergoes rapid exchange of carbonyl environments by a merry-go-round mechanism.<sup>7</sup> The  $\mu\text{-CH}_2$  group serves to lock the structure of **2**. Finally, the structure of **2** was confirmed by an X-ray diffraction study. A view of the structure is shown in Figure 1, crystal data are given in Table 1, and selected bond lengths and angles are summarized in Table 2.

As shown in Figure 1, the complex contains a *trans*- $\text{Ru}_2(\text{dppm})_2$  unit (angles  $\text{P}(2)\text{--Ru}(2)\text{--P}(4) = 172.20(3)^\circ$  and  $\text{P}(1)\text{--Ru}(1)\text{--P}(3) = 172.67(3)^\circ$ ), with each ruthenium also bound to two terminal carbonyl ligands and to the bridging methylene group. The distance  $\text{Ru}(1)\text{--Ru}(2) = 2.8704(3)$  Å indicates that there is also a metal–metal single bond. Hence, each ruthenium has an 18-electron configuration. The  $\mu\text{-CH}_2$  group symmetrically bridges the two Ru atoms, and the bond



**Figure 1.** View of the structure of  $[\text{Ru}_2(\mu\text{-CH}_2)(\text{CO})_4(\mu\text{-dppm})_2]$  (**2**) (25% thermal ellipsoids).

**Table 1. Crystal Data and Structure Refinement Details for **2****

formula, fw	$\text{C}_{55.5}\text{H}_{46}\text{ClO}_4\text{P}_4\text{Ru}_2$ , 1138.39
temp	150(2) K
wavelength	0.717 03 Å
cryst syst, space group	monoclinic, $P2_1/n$
cell dimens	$a = 16.4421(6)$ Å $b = 13.4906(5)$ Å $c = 23.3300(7)$ Å $\beta = 110.449(1)^\circ$
$V$ , $Z$	4848.8(3) Å <sup>3</sup> , 4
$d(\text{calcd})$	1.559 $\text{Mg/m}^3$
abs coeff	0.858 $\text{mm}^{-1}$
$F(000)$	2304
cryst size	$0.16 \times 0.13 \times 0.10$ mm <sup>3</sup>
$\theta$ range	$2.64\text{--}28.27^\circ$
no. of rflns, no. of indep rflns	54472, 11665
abs cor	integration
no. of data/restraints/params	11665/0/613
GOF on $F^2$	0.903
$R$ ( $I > 2\sigma(I)$ )	$R1 = 0.0378$ , $wR2 = 0.0650$
$R$ (all data)	$R1 = 0.0867$ , $wR2 = 0.0727$

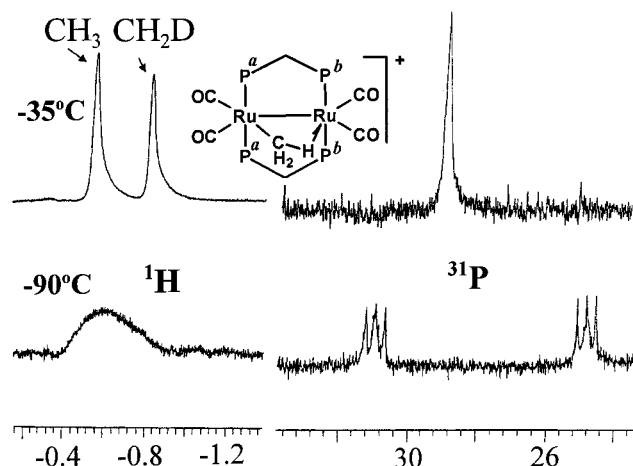
**Table 2. Selected Bond Distances (Å) and Angles (deg) in  $[\text{Ru}_2(\mu\text{-CH}_2)(\text{CO})_4(\mu\text{-dppm})_2] \cdot 0.5\text{CH}_2\text{Cl}_2$  (**2**)**

Bond Distances			
Ru(1)–Ru(2)	2.8704(3)	Ru(1)–P(1)	2.3519(8)
Ru(1)–P(3)	2.3166(8)	Ru(2)–P(2)	2.3407(8)
Ru(2)–P(4)	2.3389(8)	Ru(1)–C(5)	2.144(3)
Ru(2)–C(5)	2.150(3)	Ru(1)–C(3)	1.914(3)
Ru(1)–C(4)	1.866(3)	Ru(2)–C(2)	1.868(3)
Ru(2)–C(1)	1.918(3)	C(1)–O(1)	1.145(3)
C(2)–O(2)	1.159(3)	C(3)–O(3)	1.155(3)
C(4)–O(4)	1.164(3)		
Bond Angles			
P(2)–Ru(2)–P(4)	172.20(3)	P(1)–Ru(1)–P(3)	172.67(3)
C(5)–Ru(1)–P(1)	87.629(8)	C(5)–Ru(1)–P(3)	90.25(8)
C(5)–Ru(2)–P(2)	92.24(8)	C(5)–Ru(2)–P(4)	86.72(8)
Ru(2)–C(5)–Ru(1)	83.88(9)	C(3)–Ru(1)–C(4)	106.0(1)
C(2)–Ru(2)–C(1)	106.6(1)	C(1)–Ru(2)–C(5)	142.0(1)
C(3)–Ru(1)–C(5)	141.5(1)	C(4)–Ru(1)–C(5)	112.5(1)
C(2)–Ru(2)–C(5)	111.4(1)	C(1)–Ru(2)–P(4)	96.19(9)
C(3)–Ru(1)–P(3)	90.23(9)		

parameters are unremarkable ( $\text{Ru}(1)\text{--C}(5) = 2.144(3)$  Å,  $\text{Ru}(2)\text{--C}(5) = 2.150(3)$  Å,  $\text{Ru}(2)\text{--C}(5)\text{--Ru}(1) = 83.88(9)^\circ$ ).<sup>5,8</sup> The angle  $\text{Ru}\text{--C}\text{--Ru}$  is less acute than in most other  $\mu$ -methylene complexes with metal–metal bonds (range  $75\text{--}78^\circ$ ), as a result of the relatively long Ru–Ru bond

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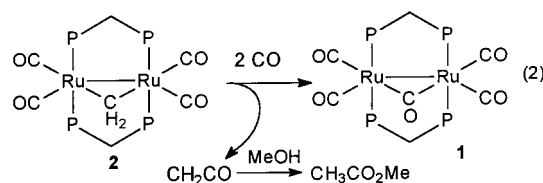


**Figure 2.** NMR spectra of the  $\mu$ -methyldiruthenium complex cation **3**, present as a mixture of the  $\text{CH}_3$  and  $\text{CH}_2\text{D}$  isotopomers, at  $-35^\circ\text{C}$  (above) and  $-90^\circ\text{C}$  (below): (left)  $^1\text{H}$  NMR spectra in the methyl region only; (right)  $^{31}\text{P}$  NMR spectra. The spectra illustrate fluxionality according to eq 4.

distance, and this angle has an important effect on the NMR parameters as discussed above.<sup>8</sup>

The formation of transition-metal  $\mu$ -methylene complexes using diazomethane is generally believed to go through an intermediate diazomethane complex.<sup>8</sup> In this study, an intermediate complex was identified at partial conversion, but it was always present along with **1** and **2** and could not be separated or identified. It was characterized only by its  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, which exhibits two multiplets at  $\delta$  31 and 36, indicating lower symmetry than in either **1** or **2**.

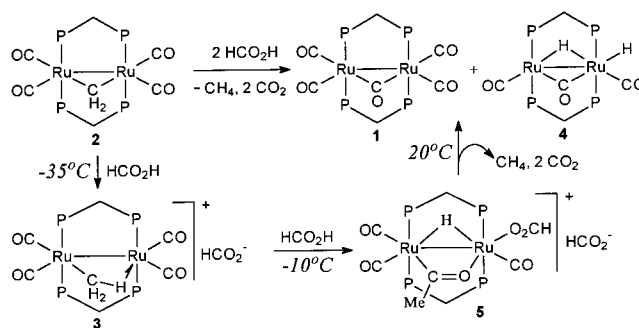
**Reaction of 2 with CO.** Complex **2** reacted easily with CO at room temperature to give complex **1** and ketene, according to eq 2. The ketene was trapped by



reaction with methanol, and the product, methyl acetate, was identified by its  $^1\text{H}$  NMR spectrum and confirmed by GC-MS. The reaction is presumed to occur by carbonyl insertion to give a bridging ketene complex,<sup>1d</sup> followed by displacement of ketene by more CO. Related diruthenium ketene complexes have been observed directly in a few cases,<sup>5h,1</sup> but none were detected in this case when the reaction was monitored by  $^1\text{H}$  NMR.

**Reaction of 2 with  $\text{HBF}_4$  or  $\text{CF}_3\text{SO}_3\text{H}$ .** At  $-10$  to  $-35^\circ\text{C}$ , the reaction of  $\text{HBF}_4$  or  $\text{CF}_3\text{SO}_3\text{H}$  with a solution of **2** in  $\text{CD}_2\text{Cl}_2$  gave the  $\mu$ -methyl complex cation  $[\text{Ru}_2(\mu\text{-CH}_3)(\text{CO})_4(\mu\text{-dppm})_2]^+$  (**3**). Complex **3** decomposed when the solution was warmed to room temperature, to give a complex mixture of products; therefore, it was characterized by NMR at low temperature. At  $-35^\circ\text{C}$ , complex **3** gave a broad singlet at  $\delta$  28.6 in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum (Figure 2), indicating the effective equivalence of all phosphorus atoms. The  $^1\text{H}$  NMR spectrum gave two broad multiplets at  $\delta$  3.10 and 3.45 due to the  $\text{CH}_2\text{P}_2$  protons of the dppm ligands and a

**Scheme 1**



broad singlet at  $\delta$   $-0.52$  which was assigned to the  $\mu$ -methyl group. These data suggest a symmetrical structure, but there is good evidence that the symmetry is lower as outlined below, with fluxionality leading to the observation of deceptively simple spectra.

The conversion of a  $\mu\text{-CH}_2$  to a  $\mu\text{-CH}_3$  group by protonation has been observed before, and methods for determining the nature of the  $\mu\text{-CH}_3$  group have been established.<sup>10,11</sup> The unsymmetrical bonding of the  $\mu\text{-CH}_3$  group in **3** (Scheme 1) was clearly established by using the NMR method introduced by Shapley.<sup>11</sup> In particular, the  $\mu\text{-CH}_2\text{D}$  group in **3-d**, obtained by reaction of **2** with  $\text{D}^+$  at  $-35^\circ\text{C}$ , gave a broad singlet in the  $^1\text{H}$  NMR spectrum at  $\delta$   $-0.80$  compared to  $\delta$   $-0.52$  for the  $\mu\text{-CH}_3$  group in **3** (Figure 2). The large chemical shift difference ( $\Delta\delta$  0.28 ppm) between  $\mu\text{-CH}_3$  and  $\mu\text{-CH}_2\text{D}$  is characteristic for a bridging methyl group with an agostic interaction between a metal and a C–H bond.<sup>10,11</sup>

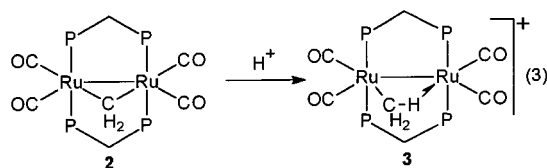
The fluxionality of complex **3** was established by recording spectra at lower temperature. At  $-90^\circ\text{C}$ , the resonances in the  $^1\text{H}$  NMR spectrum became broader, especially in the methylruthenium region (Figure 2), but no splittings were resolved. However, the single  $^{31}\text{P}$  NMR resonance at  $\delta$  28.6 at  $-35^\circ\text{C}$  had split at  $-90^\circ\text{C}$  to give two well-resolved multiplets at  $\delta$  24.6 and 31.0, indicating a less symmetrical structure for **3** (Figure 2). In the  $^{13}\text{C}$  NMR at  $-90^\circ\text{C}$  there were four CO resonances at  $\delta$  194, 197, 203, and 239. The first three resonances are assigned to terminal carbonyls, but the chemical shift of the peak at  $\delta$  239 is too high to be assigned to a terminal CO while still being a little lower than expected for a bridging carbonyl.<sup>12</sup> Hence, it is tentatively assigned to a semibridging carbonyl in **3** (eq 3). The  $^{13}\text{C}$  peaks for the carbonyl ligands broadened at higher temperatures. At  $-30^\circ\text{C}$ , only a single broad resonance at  $\delta$  198 was resolved. This peak is formed by coalescence of the peaks at  $\delta$  194 and 203, and at this temperature the peaks at  $\delta$  197 and 239 are too broad to be observed. The limiting fast exchange spectrum could not be obtained due to thermal decomposition of the sample at higher temperatures. The proposed

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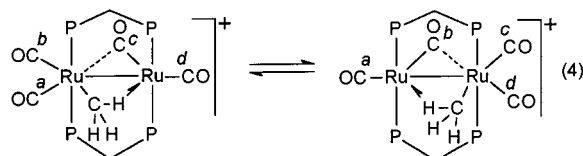
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fluxionality of **3** is shown in eq 4 and leads to equiva-



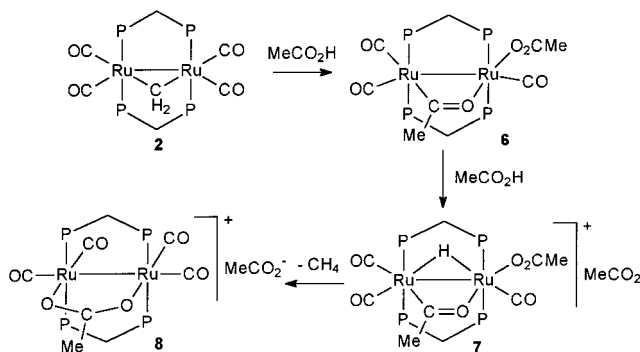
lence of the pairs of carbonyl ligands labeled *a,d* and *b,c* as well as the phosphorus atoms  $P^a$  and  $P^b$ . A second form of fluxionality involving exchange of methyl hydrogen atoms between terminal and agostic positions is clearly too fast to be frozen out even at  $-90^\circ\text{C}$  but may be responsible for the extreme broadening of the  $\text{CH}_3\text{Ru}/\text{CH}_2\text{DRu}$  resonances (no longer resolved) at  $-90^\circ\text{C}$  shown in Figure 2.

**Reaction of **2** with  $\text{HCOOH}$ .** Complex **2** is a catalyst precursor for the decomposition of formic acid to carbon dioxide and hydrogen at room temperature. It was previously shown that **1** is also an efficient catalyst for this reaction, but only in acetone solution.<sup>12</sup> At room temperature, the addition of  $\text{H}^{13}\text{COOH}$  to a solution of **2** in  $\text{CD}_2\text{Cl}_2$  caused an immediate color change from dull yellow to orange-yellow, but there was an induction period of several minutes before gas evolution was observed along with a further color change to red. The products  $^{13}\text{CO}_2$  and  $\text{H}_2$  were identified by  $^{13}\text{C}$  and  $^1\text{H}$  NMR, respectively, and  $\text{CH}_4$  was also detected by its  $^1\text{H}$  NMR spectrum. The ruthenium-containing products were an equimolar mixture of complex **1** and the coordinatively unsaturated dihydride complex  $[\text{Ru}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_2(\mu\text{-dppm})_2]^+$  (**4**), identified by their  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectra.<sup>12</sup> The overall reaction to give these products is shown in Scheme 1 (top).

The formation of equimolar amounts of **1** and **4** is clearly controlled by the amount of CO available; complex **4** is known to react rapidly with CO to give **1** and hydrogen, but there is not enough CO available to give more than 50% conversion (Scheme 1).<sup>12</sup> Complex **4** is known to be especially active in the catalytic decomposition of formic acid,<sup>12</sup> and the induction period for the catalytic reaction is therefore likely to be associated with its formation from the precursor **2**. It is noteworthy that this system based on complex **2** gives rapid catalytic decomposition of formic acid in dichloromethane solution, whereas complex **1** is inactive in this solvent and reacts only stoichiometrically to give  $[\text{Ru}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_4(\mu\text{-dppm})_2]^+[\text{HCO}_2]^-$  as the major product.<sup>12</sup> The importance of the coordinatively unsaturated complex **4** in the catalysis is thus clearly demonstrated in this study.

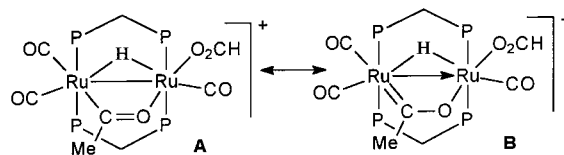
This reaction was monitored by low-temperature NMR, and several intermediates were detected. At  $-35^\circ\text{C}$ , the reaction of **2** with  $\text{HCOOH}$  occurred by simple protonation to give the  $\mu$ -methyl complex **3**, as with the stronger acids (Scheme 1). Complex **3** reacted slowly with more formic acid at  $-35^\circ\text{C}$ , and rapidly at  $-10^\circ\text{C}$ , to give the ( $\mu$ -acetyl)( $\mu$ -hydrido)diruthenium complex

Scheme 2



**5** as the only observable ruthenium complex (Scheme 2). Complex **5** was stable in the temperature range  $-10$  to  $0^\circ\text{C}$ , but at room temperature it reacted further to give the final products described above, and then the catalytic decomposition of formic acid accelerated. No intermediates were observed during the decay of **5** to give **1** and **4**. Coordination of formate is required to stabilize complex **4**, and no corresponding complex was formed in the reactions of **2** with the acids  $\text{HBF}_4$  and  $\text{CF}_3\text{SO}_3\text{H}$ , which have weakly coordinating anions.

Complex **5** was characterized by NMR spectroscopy. The  $^1\text{H}$  NMR spectrum contained two multiplets at  $\delta$  4.4 and 3.4 due to the  $\text{CH}^a\text{H}^b\text{P}_2$  protons of the dppm ligands, a singlet at  $\delta$  2.2 due to the  $\text{CH}_3$  protons of the acetyl group, and a quintet at  $\delta$   $-11.4$  due to the  $\text{Ru}_2$ -( $\mu\text{-H}$ ) group. The formate proton was obscured, but the presence of the formate group was confirmed by using  $\text{H}^{13}\text{COOH}$  in the reaction, when the formate ligand was identified by a singlet resonance at  $\delta$  171 in the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum. This assignment was further confirmed by a  $^1\text{H}^{13}\text{C}$  gHSQC (gradient heteronuclear single quantum coherence) experiment in which the formyl hydrogen was located at  $\delta$  7.5 (overlapped with the phenyl hydrogens of dppm ligands). When the reaction was carried out using  $^{13}\text{C}$ -enriched **2**, three terminal carbonyl resonances were observed in the  $^{13}\text{C}$  NMR spectrum of **5**, and a broad singlet at  $\delta$  296 was assigned to the carbonyl carbon atom of the  $\mu$ -acetyl group. The methyl carbon of the acetyl group was located at  $\delta(\text{C})$  50.0 by a  $^1\text{H}^{13}\text{C}$  HSQC experiment. The chemical shift for the acetyl carbon ( $\delta$  296) is in the range expected for bridging acetyl groups but outside the normal range of  $\delta(\text{C})$  230–260 for terminal acetyl groups.<sup>13</sup> A higher value of this chemical shift indicates a greater degree of carbene character arising from the resonance form B (rather than A) of the bridging acetyl group.<sup>13</sup>



Since no intermediates were observed during the conversion of **5** to **1** and **4**, the mechanism is uncertain. However, the steps should involve decarboxylation of

(13) (a) Shafiq, F.; Kramarz, K. W.; Eisenberg, R. *Inorg. Chim. Acta* **1993**, 213, 111. (b) Johnson, K. A.; Gladfelter, W. L. *Organometallics* **1990**, 9, 2101. (c) Jeffery, J. C.; Orpen, A. G.; Stone, F. G. A.; Went, M. J. *J. Chem. Soc., Dalton Trans.* **1986**, 173.

the formate ligand to give CO<sub>2</sub> and a second ruthenium hydride, migration of the methyl group from the acetyl group onto ruthenium to give a methyl(hydrido)ruthenium complex which can undergo reductive elimination of methane, and the further decarboxylation of formate.

**Reaction of 2 with Acetic Acid.** Since the reactions with formic acid involved catalysis, a study was made of the reactions of **2** with acetic acid, which is unlikely to undergo easy decarboxylation and so should give only stoichiometric chemistry. The results are summarized in Scheme 2.

Treatment of **2** with 1 equiv of acetic acid in CD<sub>2</sub>Cl<sub>2</sub> at room temperature gave a color change from yellow to orange-yellow, with formation of the complex [Ru<sub>2</sub>{μ-C(O)Me}(CO)<sub>3</sub>(OAc)(μ-dppm)<sub>2</sub>] (**6**). This complex was characterized by its NMR spectra. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum contained two multiplets at δ 25 and 40, and the <sup>1</sup>H NMR spectrum contained two multiplets at δ 4.2 and 3.8 due to the CH<sub>2</sub>P<sub>2</sub> protons of the dppm ligands. The <sup>1</sup>H NMR spectrum also contained singlets at δ 1.1 and 1.3 due to the methyl protons of the acetate and acetyl groups, and the corresponding <sup>13</sup>C resonances were at δ 24 and 47, respectively. In a sample prepared from <sup>13</sup>CO-labeled **2**, four resonances were observed in the <sup>13</sup>C NMR spectrum at δ 266 (μ-acetyl) and at δ 219, 209, and 196 (terminal CO).

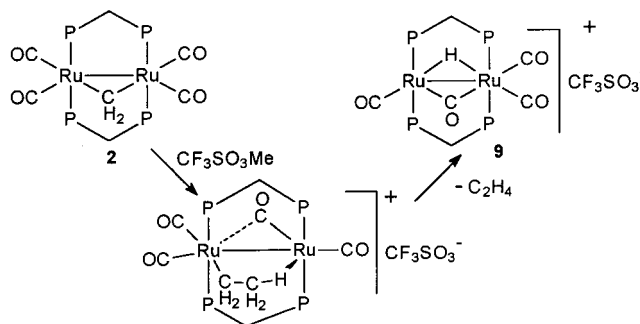
Further treatment of a solution of **6** with another 1 equiv of acetic acid gave complex **7** (Scheme 2). Now a hydride resonance was observed at δ -11.2. The spectra were otherwise similar to those of **6** (see Experimental Section), and there is also a correlation of equivalent peaks between **7** and the analogous formate derivative **5**. For example, in the <sup>13</sup>C{<sup>1</sup>H} NMR spectrum, the bridging acetyl carbonyl was found at δ 295 and three terminal carbonyl resonances were observed at δ 200, 196, and 190.

Complexes **6** and **7** were stable for hours at room temperature in solution but could not be isolated in pure form. Complex **7** decomposed slowly in solution, with elimination of methane, to give the known μ-acetate complex **8** (Scheme 2).<sup>15</sup>

**Reaction of 2 with Methyl Triflate.** Treatment of **2** in dichloromethane solution with excess MeOSO<sub>2</sub>CF<sub>3</sub> led to a color change from yellow to deep red over a period of several hours, with formation of complex **9** and ethylene (detected by <sup>1</sup>H NMR and confirmed by GC-MS) as major product. A minor ruthenium complex product was detected by its <sup>31</sup>P NMR spectrum only (δ 26) and could not be characterized further. Pure complex **9** (Scheme 3) was obtained by recrystallization and was stable to air in the solid state.

Complex **9** was characterized by its NMR spectra. The <sup>31</sup>P NMR spectrum contained two multiplets centered at δ 30.4 and 36.0, and the <sup>1</sup>H NMR spectrum in the CH<sub>2</sub>P<sub>2</sub> region displayed two multiplets at δ 3.86 and 3.42 due to the dppm ligands. The hydride was characterized by a quintet resonance at δ -8.8. The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the <sup>13</sup>CO-labeled product exhibited four multiplets for the carbonyl ligands at δ 249.4 (bridging CO) and δ 196.6, 196.4, and 195.6 (terminal

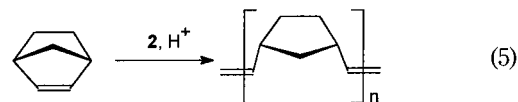
Scheme 3



CO's). Hence, structure **9** was deduced. The data are similar to those for the similar complex [Ru<sub>2</sub>(μ-H)(μ-CO)(CO)<sub>3</sub>(μ-PP)<sub>2</sub>]<sup>+</sup> (PP = (iPrO)<sub>2</sub>PNEtP(O*i*Pr)<sub>2</sub>),<sup>15</sup> and this gives support to the structural assignment. In confirmation, the IR spectrum of **9** contained three peaks at 2045, 1968, and 1926 cm<sup>-1</sup> for the three terminal carbonyls and a peak at 1685 cm<sup>-1</sup> for the bridging carbonyl ligand.

No intermediate was detected by NMR during the formation of **9** from **2**. It is likely that the slow step in the reaction sequence involves formation of a cationic ethyldiruthenium complex (shown in Scheme 3 with a β-agostic interaction, though an α-agostic interaction as in **3** is also possible) by addition of Me<sup>+</sup> to the μ-methylene group of **2**, and this is followed by rapid β-elimination of ethylene to give complex **9**, which is a new example of a coordinatively unsaturated hydridodiruthenium complex.<sup>12,15</sup>

**Ring-Opening Polymerization of Norbornene.** Complex **2** does not react with norbornene even on heating to 75 °C. However, addition of HBF<sub>4</sub> or CF<sub>3</sub>SO<sub>3</sub>H to a CD<sub>2</sub>Cl<sub>2</sub> solution of **2** and norbornene at room temperature resulted in an immediate color change to red-yellow, and the solution slowly became viscous as polymer was formed. The ratio of *cis*- to *trans*-vinylene content in the poly(norbornene) was approximately 4:3 after 48 h, as estimated from the ratio of the corresponding singlet resonances at δ 5.3 and 5.5 in the <sup>1</sup>H NMR spectrum.<sup>16</sup> The polymerization was slow at room temperature, but the active catalyst had a long lifetime, with reaction to give polymer continuing for at least 1 week. The reaction was faster and more stereoselective when carried out at higher temperature. For example, in toluene-*d*<sub>8</sub> solution at 75 °C, polymerization was complete in 5 days, and the ratio of *cis*/*trans* alkene units in the polynorbornene was >90:10 (eq 5), as



deduced by <sup>1</sup>H and <sup>13</sup>C NMR. The polymer was isolated in high yield from such reactions. One such sample had *M<sub>n</sub>* = 46.4 × 10<sup>4</sup> and *M<sub>w</sub>* = 1.27 × 10<sup>6</sup> and thus the polydispersity *r* = 2.7, which are in the range found with some mononuclear ruthenium catalysts.<sup>17</sup>

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The reaction mechanism is not clear, but some features could be determined by low-temperature NMR studies. The bridging methyl complex **3** was the first complex observed during this catalytic reaction, being formed immediately on addition of acid to complex **2** and norbornene at  $-60^\circ\text{C}$ . At  $-40^\circ\text{C}$ , complex **3** reacted with norbornene to give a new complex, which gave a singlet resonance at  $\delta$  24 in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum but whose structure could not be deduced. When the solution was warmed to room temperature, the  $^{31}\text{P}$  NMR spectrum became very complex, indicating the formation of several complexes. In the  $^1\text{H}$  NMR spectrum, the formation of  $\text{CH}_4$  was observed at this stage and a new singlet at  $\delta$  11.0 was observed. This resonance is in the range expected for a terminal ruthenium alkylidene complex,  $\text{Ru}=\text{CHR}$ , and is at the edge of the range for bridging alkylidenes (compare  $\delta$  5.2 for complex **2**).<sup>18</sup> Hence, it is possible that the propagation step involves a terminal rather than a bridging alkylidene.

### Summary

The new diruthenium  $\mu$ -methylene complex  $[\text{Ru}_2(\mu\text{-CH}_2)(\text{CO})_4(\mu\text{-dppm})_2]$  (**2**) was synthesized by reaction of  $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4(\mu\text{-dppm})_2]$  (**1**) with diazomethane,  $\text{CH}_2\text{N}_2$ . Complex **2** has high reactivity toward electrophiles, apparently by direct reaction at a  $\text{Ru}-\text{CH}_2$  bond. The reaction with protic acids leads to formation of an asymmetric  $\text{Ru}_2(\mu\text{-CH}_3)$  group in complex **3**. The fate of the cation **3** depends on the nature of the acid and has been investigated with noncoordinating  $\text{BF}_4^-$ , coordinating  $\text{MeCO}_2^-$ , and coordinating and reactive  $\text{HCO}_2^-$ . In each case there is evidence for easy reversible migration of the  $\mu\text{-CH}_3$  group to a carbonyl ligand to give a bridging acetyl complex. Later, the methyl group is converted to methane, and this is thought to occur by migration to ruthenium followed by  $\text{C}-\text{H}$  reductive elimination. The  $\mu$ -methyl complex cation **3** is a catalyst precursor for the ring-opening polymerization of norbornene.

### Experimental Section

All manipulations were carried out under a dry nitrogen atmosphere using either standard Schlenk techniques or a glovebox and with freshly dried solvents.  $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4(\mu\text{-dppm})_2]$  (**1**) was synthesized according to the literature procedure.<sup>7</sup> NMR spectra were recorded by using Varian Inova 600 and 400 and Gemini 300 MHz spectrometers. Mass spectra were recorded using a Finnigan MAT 8200 spectrometer. Polymer molecular weights were determined in THF solution by GPC using standard polystyrene samples as references.

**Synthesis of  $[\text{Ru}_2(\mu\text{-CH}_2)(\text{CO})_4(\mu\text{-dppm})_2]$  (**2**).** To a solution of  $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_4(\mu\text{-dppm})_2]$  (**1**; 0.25 g, 0.234 mmol) in toluene (35 mL) at  $50^\circ\text{C}$  was added a solution of diazomethane in ether (prepared by distillation of ether (30 mL) containing Diazald (1 g))<sup>19</sup> over a period of 1 h. A yellow solution with a suspension of yellow polymeric material was formed. The solution was heated for a further 30 min at  $50^\circ\text{C}$ , the volume was reduced under vacuum, and the mixture was filtered to remove polymeric material. The volume of the resultant solution was reduced to 2 mL, and pentane (80 mL) was then added to precipitate the product as a yellow solid, which was

washed with pentane and dried under vacuum. Yield: 0.12 g, 48%. Anal. Calcd for  $\text{C}_{55}\text{H}_{46}\text{O}_4\text{P}_4\text{Ru}_2$ : C, 60.2; H, 4.2. Found: C, 60.0; H, 4.4. IR (Nujol,  $\text{cm}^{-1}$ ):  $\nu_{\text{CO}}$  1970, 1926, 1902, 1878. NMR in  $\text{CD}_2\text{Cl}_2$  at  $20^\circ\text{C}$ :  $\delta(^1\text{H})$  5.2 [quin, 2H,  $^3J_{\text{PH}} = 10$  Hz,  $\mu\text{-CH}_2$ ], 3.1 [m, 2H,  $\text{P}-\text{CH}-\text{P}$ ], 4.1 [m, 2H,  $\text{P}-\text{CH}-\text{P}$ ];  $\delta(^{13}\text{C})$  44 [ $\text{CH}_2\text{P}_2$ ], 88 [ $\mu\text{-CH}_2$ ]; for sample prepared from  $^{13}\text{CO}$ -labeled **2**,  $\delta(^{13}\text{C})$  214 [m, terminal CO], 208 [m, terminal CO];  $\delta(^{31}\text{P})$  39.6 [s, dppm].

**Reaction of **2** with CO.** A stream of CO was bubbled through a solution of **2** (15 mg, 0.014 mmol) in  $\text{CD}_2\text{Cl}_2$  (0.6 mL) in a septum-sealed NMR tube for 10 min, and the tube was then sealed. After 24 h, analysis by  $^1\text{H}$  and  $^{31}\text{P}$  NMR showed that most of complex **2** had reacted to give complex **1**. After addition of methanol to this solution, methyl acetate was detected by both  $^1\text{H}$  NMR and GC-MS.

**$[\text{Ru}_2(\mu\text{-CH}_3)(\text{CO})_4(\mu\text{-dppm})_2][\text{BF}_4]$  (**3**[ $\text{BF}_4$ ]).** To a solution of **2** (15 mg, 0.014 mmol) in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) in a septum-sealed NMR tube at  $-35^\circ\text{C}$  was added  $\text{HBF}_4\cdot\text{Et}_2\text{O}$  (3 mL, 0.021 mmol) using a microsyringe. Complex **3** was observed as the only ruthenium complex in solution. NMR in  $\text{CD}_2\text{Cl}_2$  at  $-35^\circ\text{C}$ :  $\delta(^1\text{H})$  3.1 [m, 2H,  $\text{P}-\text{CH}-\text{P}$ ], 3.45 [m, 2H,  $\text{P}-\text{CH}-\text{P}$ ],  $-0.52$  [br s, 3H,  $\mu\text{-CH}_3$ ];  $\delta(^{31}\text{P})$  28.6 [br s, dppm]; for a sample prepared by reaction of  $\text{HBF}_4$  with  $^{13}\text{CO}$ -labeled **2**,  $\delta(^{13}\text{C})$  198 [br s, terminal CO], 193 [br s, terminal CO]; for a sample prepared by reaction of  $\text{HCOOD}$  with **2** at  $-35^\circ\text{C}$ ,  $\delta(^1\text{H})$  3.1 [m, 2H,  $\text{P}-\text{CH}-\text{P}$ ], 3.4 [m, 2H,  $\text{P}-\text{CH}-\text{P}$ ],  $-0.52$  [br s,  $\mu\text{-CH}_3$ ],  $-0.80$  [br s,  $\mu\text{-CH}_2\text{D}$ ];  $\delta(^{31}\text{P})$  = 28.6 [br s, dppm]. NMR in  $\text{CD}_2\text{Cl}_2$  at  $-90^\circ\text{C}$ :  $\delta(^1\text{H})$  3.1 [br m, 2H,  $\text{P}-\text{CH}-\text{P}$ ], 3.45 [br m, 2H,  $\text{P}-\text{CH}-\text{P}$ ],  $-0.55$  [vbr s, 3H,  $\mu\text{-CH}_3$  and  $\mu\text{-CH}_2\text{D}$ ];  $\delta(^{31}\text{P})$  24.6, 31.0 [m, dppm]; for a sample prepared by reaction of  $\text{HBF}_4$  with  $^{13}\text{CO}$ -labeled **2**, at  $-80^\circ\text{C}$ ,  $\delta(^{13}\text{C})$  239 [m,  $\mu\text{-CO}$ ], 203 [m, terminal CO], 194 [m, terminal CO], 197 [m, terminal CO]. The same cation was formed by a similar reaction of **2** with  $\text{CF}_3\text{SO}_3\text{H}$  at  $-35^\circ\text{C}$ .

**NMR Studies of the Reaction of **2** with Formic Acid.** To a solution of **2** (10 mg, 0.009 mmol) in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) in a septum-sealed NMR tube at  $-35^\circ\text{C}$  was added formic acid (3  $\mu\text{L}$ , 0.06 mmol). Complexes observed and characterized during this study are as follows, as a function of temperature.

**$[\text{Ru}_2(\mu\text{-CH}_3)(\text{CO})_4(\mu\text{-dppm})_2][\text{HCOO}]$  (**3**[ $\text{HCOO}$ ]).** This compound was formed at  $-35^\circ\text{C}$ . The spectra are as described above for **3**[ $\text{BF}_4$ ].

**$[\text{Ru}_2[\mu\text{-C}(\text{O})\text{CH}_3](\text{CO})_3(\mu\text{-H})(\text{HCOO})(\mu\text{-dppm})_2][\text{HCOO}]$  (**5**[ $\text{HCOO}$ ]).** This compound was formed at  $-10^\circ\text{C}$ . NMR at  $-10^\circ\text{C}$ :  $\delta(^1\text{H})$  8.3 [s,  $\text{HCO}_2^-$ ], 7.5 [ $\text{HCO}_2\text{Ru}$ ], 4.4 [m, 2H,  $\text{P}-\text{CH}-\text{P}$ ], 3.4 [m, 2H,  $\text{P}-\text{CH}-\text{P}$ ], 2.2 [s, 3H,  $\mu\text{-C}(\text{O})\text{CH}_3$ ],  $-11.4$  [quin, 1H,  $^2J_{\text{P-H}} = 11$  Hz, RuH];  $\delta(^{31}\text{P})$  16.8 [m, dppm], 25.0 [m, dppm]; for a sample prepared from the reaction of  $\text{H}^{13}\text{COOH}$  with  $^{13}\text{CO}$ -labeled **2** in  $\text{CD}_2\text{Cl}_2$ ,  $\delta(^{13}\text{C})$  296 [br s,  $\mu\text{-COCH}_3$ ], 2006 [t,  $^2J_{\text{PC}} = 28$  Hz, terminal CO], 196 [t,  $^2J_{\text{PC}} = 28$  Hz, terminal CO], 190 [t,  $^2J_{\text{PC}} = 28$  Hz, terminal CO], 171 [s,  $\text{HCOORu}$ ], 166 [s,  $\text{HCO}_2^-$ ].

**Complex **1** and  $[\text{Ru}_2(\mu\text{-CO})(\text{CO})_3(\mu\text{-H})(\text{H})(\mu\text{-dppm})_2]$  (**4**).** These compounds were present at  $22^\circ\text{C}$  in equimolar amounts and were characterized by comparison of spectra with authentic samples.<sup>12</sup> Formic acid (and formate) was completely decomposed after 1 h at  $22^\circ\text{C}$ , and  $\text{CH}_4$ ,  $\text{CO}_2$ , and  $\text{H}_2$  were detected by NMR.

**Studies of the Reaction of **2** with Acetic Acid.  $[\text{Ru}_2[\mu\text{-C}(\text{O})\text{CH}_3](\text{CO})_3(\text{CH}_3\text{COO})(\mu\text{-dppm})_2]$  (**6**).** To a solution of **2** (10 mg, 0.009 mmol) in  $\text{CD}_2\text{Cl}_2$  (0.5 mL) at room temperature was added acetic acid (0.5  $\mu\text{L}$ , 0.009 mmol). Complex **6** was the only product observed. NMR in  $\text{CD}_2\text{Cl}_2$  at  $20^\circ\text{C}$ :  $\delta(^1\text{H})$  4.2 [m, 2H,  $\text{P}-\text{CH}-\text{P}$ ], 3.8 [m, 2H,  $\text{P}-\text{CH}-\text{P}$ ], 1.3 [s, 3H,  $\text{C}(\text{O})\text{-CH}_3$ ], 1.1 [s, 3H,  $\text{CH}_3\text{COO}$ ];  $\delta(^{31}\text{P})$  25.5 [m, dppm], 39.6 [m, dppm]; for sample prepared from the reaction of  $\text{CH}_3\text{COOH}$  with  $^{13}\text{CO}$ -labeled **2** in  $\text{CD}_2\text{Cl}_2$ ,  $\delta(^{13}\text{C})$  266 [br s,  $\text{C}(\text{O})\text{CH}_3$ ], 219 [t,  $^2J_{\text{PC}} = 66$  Hz, terminal CO], 209 [t,  $^2J_{\text{PC}} = 61$  Hz, terminal CO], 196 [t,  $^2J_{\text{PC}} = 61$  Hz, terminal CO]. The complex decomposed on attempted isolation.

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**[Ru<sub>2</sub>(μ-C(O)CH<sub>3</sub>)(CO)<sub>3</sub>(μ-H)(OAc)(μ-dppm)<sub>2</sub>][OAc] (7[OAc]).** To a solution of **2** (10 mg, 0.009 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) at room temperature was added acetic acid (1 μL, 0.018 mmol). Complex **7** was the only observed ruthenium product. NMR in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C: δ(<sup>1</sup>H) 4.5 [m, 2H, P-CH-P], 3.6 [m, 2H, P-CH-P], 2.3 [s, 3H, C(O)CH<sub>3</sub>], 2.0 [s, MeCO<sub>2</sub><sup>-</sup>], 1.1 [s, 3H, CH<sub>3</sub>COORu], -11.2 [quin, 1H, <sup>2</sup>J<sub>PH</sub> = 11 Hz, RuH]; δ(<sup>31</sup>P) 17.8 [m, dppm], 24.3 [m, dppm]; for sample prepared from the reaction of CH<sub>3</sub>COOH with <sup>13</sup>CO-labeled **2** in CD<sub>2</sub>Cl<sub>2</sub>, δ(<sup>13</sup>C) 295 [br s, C(O)CH<sub>3</sub>], 200 [m, terminal CO], 196 [m, terminal CO], 190 [m, terminal CO]. The complex decomposed on attempted isolation.

**[Ru<sub>2</sub>(CO)<sub>4</sub>(μ-OAc)(μ-dppm)<sub>2</sub>][OAc] (8[OAc]).** To a solution of **2** (10 mg, 0.009 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) at room temperature was added acetic acid (4 μL, 0.072 mmol). After 4 days, complex **8** was observed as the major ruthenium product by NMR. Methane was also detected. Complex **8** was characterized by its known NMR spectra.<sup>14</sup>

**[Ru<sub>2</sub>(μ-H)(CO)<sub>3</sub>(μ-CO)(μ-dppm)<sub>2</sub>][OTf] (9[OTf]).** To a solution of **2** (25 mg, 0.023 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (0.5 mL) in an NMR tube was added excess MeOSO<sub>2</sub>CF<sub>3</sub> (4 mL, 0.035 mmol) by microsyringe. The color of the solution turned from yellow to deep red in 4 h. Ether (2 mL) was carefully layered over the solution, and orange needles of the product formed after 24 h. The crystals were washed with pentane and dried under vacuum. Yield: 15 mg (52%). Anal. Calcd for C<sub>55</sub>H<sub>45</sub>F<sub>3</sub>Ru<sub>2</sub>O<sub>7</sub>P<sub>4</sub>S: C, 53.6; H, 3.7. Found: C, 53.0; H, 3.9. IR (Nujol, cm<sup>-1</sup>): 2045 [terminal CO], 1968 [terminal CO], 1926 [terminal CO], 1685 [μ-CO]. NMR in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C: δ(<sup>1</sup>H) 3.86 [m, 2H, P-CH-P], 3.42 [m, 2H, P-CH-P], -8.8 [quin, 1H, <sup>2</sup>J<sub>PH</sub> = 10 Hz, μ-H]; δ(<sup>31</sup>P) 30.4 [m, dppm], 36 [m, dppm]; for sample prepared from the reaction of MeOTf with <sup>13</sup>CO-labeled **2** in CD<sub>2</sub>Cl<sub>2</sub>, δ(<sup>13</sup>C) 249 [m, μ-CO], 197 [m, terminal CO], 196 [m, terminal CO], 195.6 [m, terminal CO].

**Polymerization of Norbornene. (A) Characterization of the Polymerization Product.** To a solution of complex **2** (10 mg, 0.009 mmol) and norbornene (60 mg, 0.636 mmol) in toluene-*d*<sub>8</sub> (0.5 mL) in a septum-sealed NMR tube at 0 °C was added HBF<sub>4</sub> (1.5 mL, 0.01 mmol) using a microsyringe. The NMR tube was then heated to 75 °C, at which point the mixture slowly became viscous. The monomer (δ(=CH) 6.05) decayed over 4 days, with formation of predominantly *cis*-polynorbornene. The ratio of *cis*/*trans* linkages in the polynorbornene was 95:5, as determined by integration of the respective resonances at δ 5.3 and 5.5; in agreement, the <sup>13</sup>C NMR spectrum showed very largely *ccc* triads (δ 134.1 with only very minor resonances at δ 133.2, 133.4, and 134.2 due to *tcc* and *ctc* triads.<sup>4e,16</sup> When reaction was complete, the polymer precipitated as a white solid by addition of methanol (2 mL).

**(B) Synthesis of *cis*-Polynorbornene.** To a solution of norbornene (0.13 g, 1.38 mmol) and **2** (40 mg, 0.036 mmol) in toluene (30 mL) at 0 °C was added HBF<sub>4</sub> (6 mL, 0.042 mmol) by microsyringe. The solution was stirred and heated to 75 °C for 5 days. Methanol (50 mL) was then added to the viscous solution to precipitate *cis*-polynorbornene as a white solid. Yield: 0.09 g (69%).

**(C) NMR Studies of the Formation of Polynorbornene.** To a solution of **2** (20 mg, 0.018 mmol) and norbornene (10 mg, 0.106 mmol) in CD<sub>2</sub>Cl<sub>2</sub> (0.5 mL) in a septum-sealed NMR tube at -60 °C was added HBF<sub>4</sub> (3 mL, 0.021 mmol). The tube was then placed into the NMR probe at -90 °C. After 20 min, the first spectra were recorded and further spectra were recorded as the temperature was raised. Only complex **3** was present in the temperature range from -90 to -60 °C. NMR in CD<sub>2</sub>Cl<sub>2</sub> at -40 °C: δ(<sup>31</sup>P) 29 [br s, dppm, due to **3**], 24 [s, dppm]; δ(<sup>1</sup>H) 11 [s]. NMR in CD<sub>2</sub>Cl<sub>2</sub> at 20 °C: δ(<sup>31</sup>P) 33 [s], 31 [s], 30.6 [s], 29 [s], 28.7 [s], 28.3 [s], 27.2 [s], 25.2 [s], 23.6 [dd]; δ(<sup>1</sup>H) 10.5 [br s], 0.2 [s, CH<sub>4</sub>].

**Structure Determination of **2**.** Crystals of [Ru<sub>2</sub>(μ-CH<sub>2</sub>)(CO)<sub>4</sub>(μ-dppm)<sub>2</sub>]<sup>1/2</sup>CH<sub>2</sub>Cl<sub>2</sub> were grown by slow diffusion of pentane into a dichloromethane solution. A yellow block was mounted on a glass fiber. Data were collected at low temperature (150 K) using a Nonius Kappa-CCD diffractometer with COLLECT (Nonius, 1998) software. The unit cell parameters were calculated and refined from the full data set. Crystal cell refinement and data reduction were carried out using the Nonius DENZO package. The data were scaled using SCALEPACK (Nonius, 1998), and no other absorption corrections were applied. The crystal data and refinement parameters are listed in Table 1.

The SHELXTL 5.1 (G. M. Sheldrick, Madison, WI) program package was used to solve the structure by direct methods, followed by successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were calculated geometrically and were riding on their respective carbon atoms. The solvent molecule was refined anisotropically without hydrogen atoms in the model. It was near a center of symmetry and was refined at half-occupancy.

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**Supporting Information Available:** Tables of complete X-ray data for complex **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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