

Preparation, Characterization, and X-ray Structure of the 1:1 Complex of *o*-Acetylstyrene and Carbonylbis(triphenylphosphine)ruthenium. A New Catalyst for the Copolymerization of Acetophenone and 1,3-Divinyltetramethyldisiloxane[†]

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Treatment of dihydridocarbonyltris(triphenylphosphine)ruthenium with a stoichiometric amount of styrene, followed by addition of *o*-acetylstyrene leads to a 1:1 complex of *o*-acetylstyrene and carbonylbis(triphenylphosphine)ruthenium. This species has been fully characterized and its structure determined by X-ray crystallography. This 1:1 complex is able to catalyze the copolymerization of acetophenone and 1,3-divinyltetramethyldisiloxane.

Introduction

In late 1993, Murai et al. reported that dihydridocarbonyltris(triphenylphosphine)ruthenium catalyzes the *ortho*-alkylation reaction of acetophenone with vinyl silanes.^{1,2} Similarly, we have found that acetophenones and other aromatic ketones undergo ruthenium-catalyzed step-growth copolymerization with α,ω -divinylsilanes such as 1,3-divinyltetramethyldisiloxane.^{3–6} These reactions involve ruthenium-catalyzed anti-Markovnikov addition of the *ortho* C–H bonds of acetophenones across the C–C double bonds of the vinyl silane or 1,3-divinyltetramethyldisiloxane. We have worked to define the scope and determine the mechanism of this new transition-metal-catalyzed copolymerization reaction which involves catalytic C–H activation. While the reaction is successful with a variety of aromatic ketones, such as substituted acetophenones, anthrone, fluorenone, and xanthone,⁷ the range of vinyl compounds which are successful substrates has proved to be quite limited. The C–C double bonds of vinyl silanes, vinyl siloxanes, and the vinyl group of styrene react successfully.^{2,8}

Initial ruthenium-catalyzed copolymerization reactions between acetophenone and α,ω -dienes such as 1,3-

divinyltetramethyldisiloxane gave low molecular weight polymers or oligomeric materials.³ The properties of oligomers depend greatly on their molecular weight, whereas the properties of a polymer do not change a great deal once a minimum molecular weight is achieved. For this reason, synthetic polymer chemists strive to prepare new materials of sufficient molecular weight that the properties measured do not change appreciably with small variation in polymer molecular weights. Exact stoichiometric balance is essential to obtain high molecular weight materials in step-growth polymerization. We have previously spectroscopically detected the presence of ethyl end groups bonded to silicon in the dihydridocarbonyltris(triphenylphosphine)ruthenium-catalyzed copolymerization of 1,3-divinyltetramethyldisiloxane and xanthone.⁷ To explain this observation, we have suggested that dihydridocarbonyltris(triphenylphosphine)ruthenium is capable not only of activating the C–H bonds which are *ortho* to an aromatic carbonyl group, but also of transferring its hydrogen atoms to one of the C–C double bonds of the 1,3-divinyltetramethyldisiloxane to yield 1-ethyl-3-vinyltetramethyldisiloxane. This process disrupts the stoichiometric balance by converting a difunctional monomer into a monofunctional terminating group which limits the polymer molecular weight.

In fact, we have speculated that loss of hydrogen from the ruthenium center, which creates a site of unsaturation, may be essential in activating the catalyst for the copolymerization reaction. On the basis of this analysis, we have treated dihydridocarbonyltris(triphenylphosphine)ruthenium with a stoichiometric amount of styrene for a few minutes at 120 °C. Under these conditions, the styrene is completely converted to ethylbenzene (Figure 1). Similarly, stoichiometric hydrogenation of trimethoxyvinylsilane by dihydridocarbonyltris(triphenylphosphine)ruthenium has been reported by Murai.² Subsequent addition of an equimolar mixture of acetophenone and 1,3-divinyltetramethyldisiloxane to the

[†] This paper is dedicated to a great scientist and dear friend Prof. George A. Olah on the occasion of his 70th birthday.

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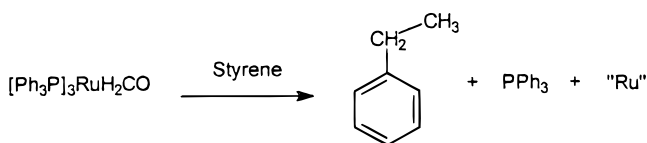


Figure 1.

activated catalyst results in a significantly higher molecular weight copolymer.⁶

Results and Discussion

We have attempted to characterize the activated ruthenium species obtained by treatment of dihydridocarbonyltris(triphenylphosphine)ruthenium with a stoichiometric amount of styrene. For reference, we have included the most salient features of the ^1H and ^{31}P NMR spectra of dihydridocarbonyltris(triphenylphosphine)ruthenium, which have not been previously reported. The ^1H NMR spectrum is characterized by two resonances at $\delta -8.18$ (dtd, 1H, $J_{\text{P-H}} = 74, 27.7$ Hz, $J_{\text{H-H}} = 6.5$ Hz) and -6.35 (tdd, 1H, $J_{\text{P-H}} = 30.2, 14.8$ Hz, $J_{\text{H-H}} = 6.5$ Hz) which are assigned to the two nonequivalent Ru-H bonds. These *cis* and *trans* $J_{\text{P-H}}$ coupling constants are similar to those reported for dihydridocarbonyltris(triphenylphosphine)osmium.⁹ Two nonequivalent phosphorus signals are observed in the ^{31}P NMR at $\delta 45.91$ (t, 1P, $J_{\text{P-P}} = 18.3$ Hz) and 58.08 (d, 2P, $J_{\text{P-P}} = 18.3$ Hz).

As expected, no resonances due to Ru-H bonds are observed in the ^1H NMR of the styrene-activated ruthenium complex. The ^{31}P NMR of this activated ruthenium species is characterized by a number of resonances. Those at $\delta -4.84$ and 25.47 are assigned to free triphenylphosphine and a small amount of triphenylphosphine oxide, respectively.¹⁰ On the basis of the integration of the ^{31}P NMR, one of the triphenylphosphine ligands has been lost from the ruthenium center.

Murai has previously examined a number of ruthenium complexes for catalytic activity in this type of reaction. While dihydridocarbonyltris(triphenylphosphine)ruthenium is most active, he has also observed that tricarbonylbis(triphenylphosphine)ruthenium is modestly effective, whereas ruthenium carbonyl $[\text{Ru}_3(\text{CO})_{12}]$ is not.² On the basis of this observation, Murai has suggested that a zerovalent ruthenium having at least two triphenylphosphine ligands is essential for catalytic activity. Neither hydrogen nor carbon monoxide are essential ligands. While it is tempting to propose that the active ruthenium species is the 14-electron system carbonylbis(triphenylphosphine)ruthenium, the ^{31}P NMR spectrum of the activated ruthenium solution shows several phosphorus signals which are not consistent with those expected for carbonylbis(triphenylphosphine)ruthenium. We suggest that dimeric and/or trimeric carbonylbis(triphenylphosphine)ruthenium species which are in equilibrium with a small amount of carbonylbis(triphenylphosphine)ruthenium may be present in solution. Attempts to crystallize such species from the solution of the activated ruthenium catalyst

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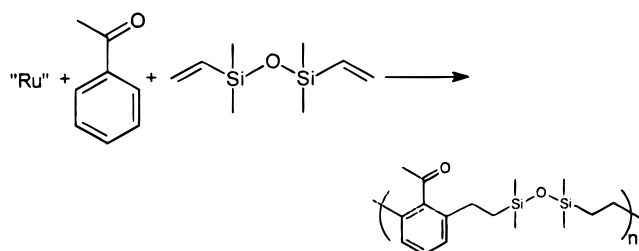


Figure 2.

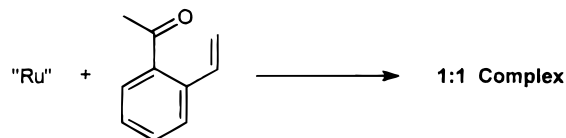


Figure 3.

have been unsuccessful. Remarkably, the solution maintains its catalytic activity at room temperature for some time. Thus, addition of an equimolar mixture of acetophenone and 1,3-divinyltetramethyldisiloxane to a solution of the active catalyst which has been stored for 24 h at room temperature results in formation of copoly(2-acetyl-1,3-diphenylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene)^{4,6} (Figure 2).

To obtain very high molecular weight polymers, we have treated *o*-acetylstyrene¹¹ with a catalytic amount of activated catalyst. This monomer was chosen because it has exactly one activated *ortho* C-H and one terminal vinyl group. Unfortunately, instead of the expected high molecular weight polymer, a small amount of a 1:1 complex between *o*-acetylstyrene and carbonylbis(triphenylphosphine)ruthenium was obtained. When a similar reaction was carried out between *o*-acetylstyrene and a stoichiometric amount of activated catalyst, an 80% yield of recrystallized 1:1 complex was obtained in addition to 1 equiv of free triphenylphosphine (Figure 3).

The 1:1 complex of *o*-acetylstyrene with carbonylbis(triphenylphosphine)ruthenium is structurally most interesting (Figure 4). The X-ray structure and crystallographic data clearly show a strong bond between the carbonyl oxygen and the ruthenium center in the solid state. This interaction persists in solution, as shown by the phosphorus-carbon coupling which is observed in the ^{13}C NMR resonances assigned to the acetyl carbonyl group. The C-C double bond of *o*-acetylstyrene is strongly π -coordinated to the ruthenium center in the solid state. Specifically the C-C bond length is 1.43 Å, which is approximately intermediate between a C-C single bond and a C-C double bond length. Both the Ru-C bond lengths and the C-C bond length are comparable to those reported for the 16-electron system bis(styrene)bis(triphenylphosphine)ruthenium(0) by Wilkinson¹² and for other similar ruthenium π complexes¹³ such as the *o*-styrenyldiphenylphosphine complex of ruthenium tricarbonyl.¹⁴ This ruthenium π -co-

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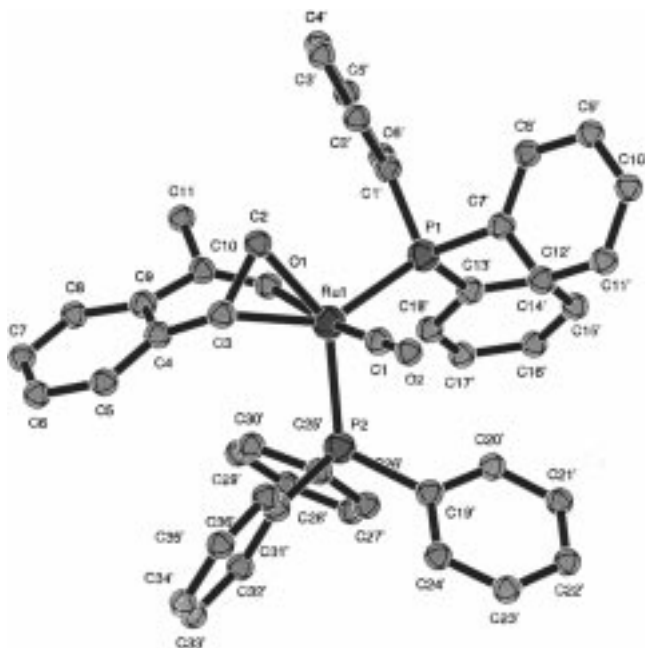


Figure 4. X-ray structure of the 1:1 complex of *o*-acetylstyrene and carbonylbis(triphenylphosphine)ruthenium.

ordinated structure persists in solution, as shown by the phosphorus–carbon coupling in the ^{13}C NMR resonances which are assigned to the π -coordinated C–C double bond.

A similar 1:1 complex between *o*-propionylstyrene¹⁵ and carbonylbis(triphenyl phosphine)ruthenium has been prepared and fully characterized. Finally, it should be noted that the 1:1 complex of *o*-acetylstyrene and carbonylbis(triphenylphosphine)ruthenium and the analogous 1:1 complex of *o*-propionylstyrene are able to catalyze the copolymerization of acetophenone and 1,3-divinyltetramethyldisiloxane.⁶ This may involve dissociation of these 1:1 complexes to yield catalytically active carbonylbis(triphenylphosphine)ruthenium or related oligomeric polynuclear ruthenium complexes (Figure 5).

Experimental Section

^1H , ^{13}C , and ^{31}P NMR spectra were obtained on a Bruker AC-250, AM-360, or AMX 500 spectrometer operating in the FT mode. Ten percent w/v solutions in chloroform-*d* or benzene-*d*₆ were used to obtain the NMR spectra. ^{13}C NMR spectra were run with broad-band proton decoupling. Residual benzene or chloroform were used as internal standards for the ^1H and ^{13}C NMR spectra. ^{31}P NMR spectra were run with broad-band proton decoupling and were externally referenced to 85% phosphoric acid. IR spectra of thin films on sodium chloride plates were recorded on a Perkin-Elmer 2000 FT-IR spectrometer. UV spectra of cyclohexane solutions were acquired on a Shimadzu UV-260 UV–vis spectrometer.

GPC analysis of the molecular weight distribution of the polymeric materials was performed on a Waters system composed of a U6K injector, a 510 HPLC solvent delivery system, a R401 refractive index detector, and a model 820 Maxima control system. Two linear Waters Styragel 7.8 mm \times 30 cm columns HR1 and HR4 in series packed with $<5\ \mu\text{m}$ particles of monodisperse cross-linked styrene divinylbenzene copolymer were used for the analysis. HPLC-grade THF was

used as the eluting solvent at a flow rate of 0.8 mL/min. The retention times were calibrated against those of known monodisperse polystyrene standards: M_w 929 000, 212 400, 47 500, 13 700, and 794 whose M_w/M_n are less than 1.09.

X-ray Structure Analysis. A crystal of dimensions $0.65 \times 0.48 \times 0.23\ \text{mm}^3$ was mounted on a glass fiber with oil and placed in a Siemens P₄/RA diffractometer for data collection at $-120\ ^\circ\text{C}$. The angular settings of 26 well-centered reflections indicated a monoclinic unit cell whose dimensions are given in Table 1. Four monitor reflections indicated no significant decrease in intensity during data collection, which was carried out with Cu K α radiation up to a 2θ maximum of 90° . The position of the Ru atom and the six atoms attached to it were obtained from a Patterson map with the crystallographic package SHELX-86.¹⁶ The rest of the non-hydrogen atoms were subsequently located from a series of structure factor/difference-Fourier calculations.¹⁷ The vinyl group was found to coordinate to the Ru atom in a π fashion, forming a three-membered ring. The important bond lengths and angles in the 1:1 complex are given in Table 2. The X-ray analysis was completed with several cycles of full-matrix least-squares refinements, with anisotropic thermal parameters assigned to all atoms. The final agreement factor was $R(F) = 6.4\%$ for 2761 nonzero reflections with $F > 4\sigma(F)$.

Elemental analysis was performed by Oneida Research Services, Whitesboro, NY. All reactions were run in flame-dried glassware under an inert atmosphere of argon.

Reagents. Dihydridocarbonyltris(triphenylphosphine)ruthenium was prepared from ruthenium trichloride trihydrate.¹⁸

o-Acetylstyrene was prepared following a literature procedure¹¹ from *N*-acetyl 2-phenylethylamine. The final step in this synthesis involves the sequential base-induced fragmentation of 3,4-dihydro-1,2-dimethylisoquinolinium bisulfate to yield the *N*-methyl imine of *o*-acetylstyrene, which undergoes hydrolysis to yield *o*-acetylstyrene. In this reaction, *o*-propionylstyrene is formed as a byproduct. The yield of *o*-acetylstyrene was 54%, while *o*-propionylstyrene was obtained in 6% yield. These compounds were separated by column chromatography on a silica gel column. *o*-Acetylstyrene was eluted first with a mixed solvent system of ethyl acetate (2.5%) and pentane (97.5%). Subsequently, *o*-propionylstyrene was eluted with a mixture of ethyl acetate (8%) and pentane (92%).

o-Acetylstyrene has the following spectral properties: ^1H NMR δ 2.58 (s, 3H), 5.35 (dd, 1H, $J = 10$ and 1.5 Hz), 5.65 (dd, 1H, $J = 17.5$ and 1.5 Hz), 7.22 (dd, 1H, $J = 17.5$ and 10 Hz), 7.33 (dt, 1H, $J = 7.5$ and 1.25 Hz), 7.46 (dt, 1H, $J = 7.5$ and 1.25 Hz), 7.57 (dd, 1H, $J = 7.5$ and 1.25 Hz), 7.64 (dd, 1H, $J = 7.5$ and 1.25 Hz); ^{13}C NMR δ 29.61, 116.42, 127.30, 127.35, 128.56, 131.44, 135.75, 137.20, 137.48, 201.74.

o-Propionylstyrene¹⁵ has the following spectral properties: ^1H NMR δ 1.07 (t, 3H, $J = 7.5$ Hz), 2.78 (q, 2H, $J = 7.5$ Hz), 5.21 (dd, 1H, $J = 11$ and 1.5 Hz), 5.51 (dd, 1H, $J = 17.5$ and 1.5 Hz), 6.98 (dd, 1H, $J = 17.5$ and 11 Hz), 7.20 (dt, 1H, $J = 7.5$ and 1.5 Hz), 7.31 (dt, 1H, $J = 7.5$ and 1.5 Hz), 7.44 (td, 2H, $J = 7.5$ and 1.5 Hz); ^{13}C NMR δ 8.17, 35.08, 116.35, 127.12, 127.63, 130.00, 130.92, 135.48, 136.97, 137.81, 205.45.

Preparation of the 1:1 Complex of *o*-Acetylstyrene and Carbonylbis(triphenylphosphine)ruthenium. In a 25 mL three-necked flask equipped with a reflux condenser and two rubber septa was placed dihydridocarbonyltris(triphenylphosphine)ruthenium (459 mg, 0.5 mmol), which had been purified by column chromatography on an alumina column

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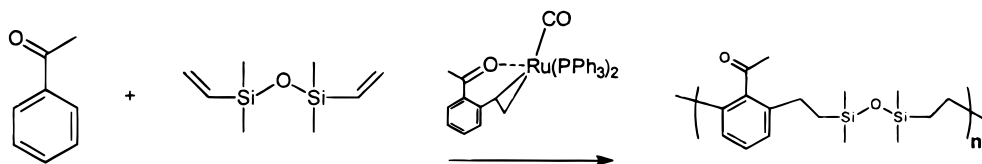


Figure 5.

Table 1. Dimensions for the 1:1 Complex of *o*-Acetylstyrene and Carbonylbis(triphenylphosphine)ruthenium

space group	$P2_1/c$
a	19.421(1) Å
b	10.715(1) Å
c	19.495(6) Å
β	107.62(3)°
vol.	3866.5 Å ³

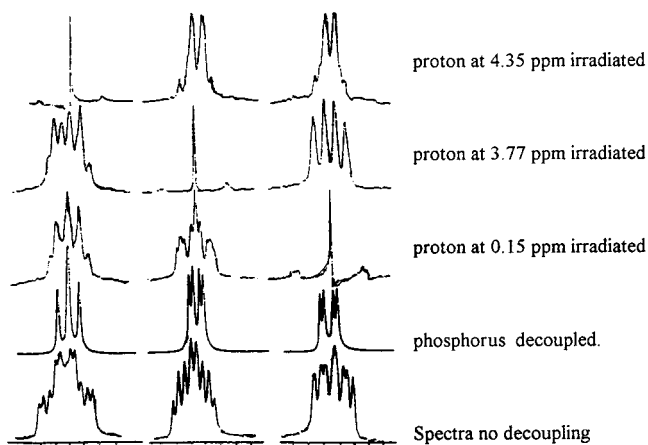
Table 2. Important Bond Distances (Å) and Angles (deg) for the 1:1 Complex of *o*-Acetylstyrene and Carbonylbis(triphenylphosphine)ruthenium

Bond Distances			
Ru-C ₁	1.79(1)	Ru-P ₁	2.333(2)
Ru-C ₂	2.121(8)	Ru-P ₂	2.352(2)
Ru-C ₃	2.167(9)	C ₂ -C ₃	1.43(1)
Ru-O ₁	2.130(6)		
Angles			
C ₁ -Ru-C ₂	92.4(3)	O ₁ -Ru-C ₂	81.1(3)
O ₁ -Ru-C ₁	172.3(3)	C ₃ -Ru-C ₁	92.9(4)
C ₃ -Ru-C ₂	38.9(0.3)	C ₃ -Ru-O ₁	84.6(3)
P ₁ -Ru-C ₁	96.0(3)	P ₁ -Ru-C ₂	106.6(2)
P ₁ -Ru-O ₁	82.1(2)	P ₁ -Ru-C ₃	144.8(2)
P ₂ -Ru-C ₁	88.6(3)	P ₂ -Ru-C ₂	143.5(2)
P ₂ -Ru-O ₁	99.1(2)	P ₂ -Ru-C ₃	104.6(2)
P ₂ -Ru-P ₁	109.63(8)	Ru-C ₂ -C ₃	72.3(5)
Ru-C ₃ -C ₂	68.8(5)		

with benzene as the eluent. Dry toluene (5 mL) was added. Argon was bubbled through the toluene solution for 15 min. Freshly distilled styrene (58 μ L, 0.5 mmol) was added by injection. The solution was heated to 120 °C for 1 h. After the mixture was cooled to room temperature, a solution of *o*-acetylstyrene (73 mg, 0.5 mmol) in 5 mL of dry toluene was added by syringe. The mixture was heated at 120 °C for 2 h. A deep-brown-colored solution was obtained. All volatiles were removed by evaporation under vacuum. The solid was dissolved in a minimum amount of toluene. Addition of ether caused the precipitation of a very finely divided solid. The supernatant solution was removed by syringe. The solid was recrystallized from 10 to 15 mL of a mixture of toluene, ether and pentane 1:10:5. In this way, an 81% yield (323 mg, 0.4 mmol) of the 1:1 complex, mp 184–185 °C, was obtained.

¹H NMR (C₆D₆, 250 MHz) δ : 0.126 (ddd, 1H, $J_{H-H} = 10.1$ and 3.1 Hz, $J_{P-H} = 4.7$ Hz), 1.53 (dd, 3H, $J_{P-H} = 1.8$ Hz), 3.75 (ddd, 1H, $J_{H-H} = 8.5$ and 3.1 Hz, $J_{P-H} = 5.8$ Hz), 4.40 (dddd, 1H, $J_{H-H} = 10.1$ and 8.5 Hz, $J_{P-H} = 5.0$ and 2.2 Hz), 6.49 (t, 1H, $J = 6.8$ Hz), 6.88 (d, 2H, $J = 7.2$ Hz), 6.91 (td, 6H, $J = 6.8$ and 1.4 Hz), 6.98 (td, 3H, $J = 7.6$ and 1.4 Hz), 7.09 (dd, 9H, $J = 3.6$ Hz, $J_{P-H} = 1.8$ Hz), 7.22 (d, 1H, $J = 6.8$ Hz), 7.24 (dt, 6H, $J_{P-H} = 8.5$, $J = 1.8$ Hz), 7.71 (ddd, 6H, $J_{P-H} = 9$, $J_{H-H} = 5.5$ and 3.0 Hz). Both ¹H and ³¹P decoupling experiments establish the magnitude of the coupling constants between the vinyl hydrogens and between the vinyl hydrogens and phosphorus (Figure 6).

¹³C NMR (CDCl₃, 90.57 MHz) δ : 25.90, 40.90 (dd, 1C, $J_{C-P} = 24.6$ and 3.1 Hz), 50.44 (dd, 1C, $J_{C-P} = 15.5$ and 4.7 Hz), 119.06, 127.33, 127.44, 127.54, 127.88, 128.27, 128.30, 128.65, 128.68, 130.66, 132.17, 132.88, 133.04, 133.58, 133.71, 137.46 (d, C_{ipso}, $J_{C-P} = 28.18$ Hz), 138.83 (dd, 3C_{ipso}, $J_{C-P} = 30.7$ and 2.4 Hz), 153.57 (t, 1C_{ipso}, $J_{C-P} = 2.8$ Hz), 195.85 (t, C_{C=O}, $J_{C-P} = 3.4$ Hz), 211.03 (t, C_{C=O}, $J_{C-P} = 11.9$ Hz). ³¹P NMR (C₆D₆, 109.35 MHz) δ : 46.64 (d, 1P, $J_{P-P} = 9.7$ Hz), 46.96 (d, 1P, J_{P-P}


Figure 6. ¹H NMR of the ruthenium π -coordinated C=C double bond.

= 9.7 Hz). ³¹P NMR (CDCl₃, 145.78 MHz) δ : 46.21 (d, 1P, $J_{P-P} = 7.5$ Hz), 46.78 (d, 1P, $J_{P-P} = 7.5$ Hz). IR (ν): 3076, 3057, 2858, 1896, 1684, 1653, 1559, 1436, 1163, 745, 697 cm⁻¹. UV λ_{max} nm (ϵ): 500 (2.2 $\times 10^3$), 336 (9.3 $\times 10^3$). Anal. Calcd for C₄₇H₄₀O₂P₂Ru: C, 70.58; H, 5.04; P, 7.74; Ru, 12.64. Found: C, 71.13; H, 5.14; P, 6.17; Ru, 12.65.

1:1 Complex of *o*-Propionylstyrene and Carbonylbis(triphenylphosphine)ruthenium. Prepared in an analogous manner to the method described above, mp 200–202 °C. ¹H NMR (C₆D₆, 250 MHz) δ : -0.13 (ddd, 1H, $J_{H-H} = 9$ and 3.4 Hz, $J_{H-P} = 4.3$ Hz), 0.345 (t, 3H, $J_{H-H} = 7.5$ Hz), 2.01 (sept of t, 2H, $J_{H-H} = 7.5$ Hz, $J_{H-P} = 1.8$ Hz), 3.67 (ddd, 1H, $J_{H-H} = 7$ and 3.4 Hz, $J_{H-P} = 6$ Hz), 4.25 (dddd, 1H, $J_{H-H} = 9$ and 7 Hz, $J_{H-P} = 3.4$ and 1.8 Hz), 6.49 (t, 1H, $J = 7.4$ Hz), 6.83–6.98 (m, 11H), 7.02–7.05 (m, 9H), 7.14–7.22 (m, 7H), 7.34–7.61 (m, 6H). ¹³C NMR (C₆D₆, 125.77 MHz) δ : 10.30, 32.16, 43.00 (dd, 1C, $J_{C-P} = 28.8$ and 7.3 Hz), 52.11 (dd, 1C, $J_{C-P} = 25.1$ and 14.7 Hz), 119.25, 127.75, 127.87, 127.93, 128.23, 128.73, 128.75, 129.05, 129.08, 130.35, 132.31, 133.43, 133.52, 134.19, 134.29, 138.47 (dd, 3C_{ipso}, $J_{C-P} = 32.44$ and 1.1 Hz), 139.58 (dd, 3C_{ipso}, $J_{C-P} = 34.2$ and 2.8 Hz), 154.18 (t, 1C_{ipso}, $J_{C-P} = 1.2$ Hz), 200.89 (t, 1C, $J_{C-P} = 3.4$ Hz), 210.98 (t, 1C, $J_{C-P} = 11.4$ Hz). ³¹P NMR (C₆D₆, 202.47 MHz) δ : 45.29 (d, 1P, $J_{P-P} = 9$ Hz), 45.36 (d, 1P, $J_{P-P} = 9$ Hz). IR, ν : 3053, 1894, 1575, 1478, 1433, 1204, 1160, 743, 696 cm⁻¹. UV λ_{max} nm (ϵ): 500 (2.1 $\times 10^3$), 337 (8.4 $\times 10^3$). Anal. Calcd for C₄₈H₄₂O₂P₂Ru: C, 70.84; H, 5.20; P, 7.61; Ru, 12.42. Found: C, 70.81; H, 5.13; P, 8.46; Ru, 11.53.

Copolymerization of Acetophenone and 1,3-Divinyltetramethylsiloxane by the 1:1 Complex of *o*-Acetylstyrene and Carbonylbis(triphenylphosphine)ruthenium. Copoly(2-acetyl-1,3-phenylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene) has been previously prepared by the reaction of acetophenone and 1,3-divinyltetramethylsiloxane catalyzed by dihydridocarbonyltris(triphenylphosphine)ruthenium, which has been activated by treatment with a stoichiometric amount of styrene. For complete details of the synthesis and characterization of this polymer, see ref 6.

Freshly distilled 1,3-divinyltetramethylsiloxane (1.00 g, 5.4 mmol), acetophenone (0.645 g, 5.4 mmol), and the 1:1 complex of *o*-acetylstyrene and carbonylbis(triphenylphosphine)ruthenium (70 mg, 0.088 mmol) were placed in an Ace

pressure tube with 1.5 mL of dry toluene. Argon gas was bubbled through the mixture for 2 min. The pressure tube was sealed and was heated to 120–140 °C for 50 h. The reaction mixture was precipitated 3 times from THF by addition of methanol. In this way, 0.85 g (~50% yield) of copoly(2-acetyl-1,3-phenylene/3,3,5,5-tetramethyl-4-oxa-3,5-disila-1,7-heptanylene) $M_w/M_n = 9230/6560$ was obtained. The ^1H and ^{13}C NMR spectra of the copolymer were in complete agreement with that previously obtained.^{4,6}

Copolymerization of Acetophenone and 1,3-divinyltetramethyldisiloxane by the 1:1 Complex of *o*-Propionylstyrene and Carbonylbis(triphenylphosphine)ruthenium. This was carried out in an analogous manner to that described above. In this way, 1.00 g (~61% yield) of copolymer $M_w/M_n = 8730/6760$ was obtained, whose spectral properties were in agreement with those previously reported.⁶

Conclusion

While these experiments have provided additional insight into the dihydridocarbonyltris(triphenylphosphine)ruthenium-catalyzed reactions of acetophenone with vinyl silane systems, many questions remain unanswered. When a stoichiometric amount of *o*-

acetylstyrene is added to a solution of activated ruthenium catalyst, why does a 1:1 complex form rather than a high molecular weight polymer? Murai has proposed that the first step in the reaction involves coordination of the catalytically active unsaturated ruthenium complex to the oxygen of the carbonyl group. Our X-ray structure confirms the presence of a strong Ru–O bond. Apparently, however, in the case of *o*-acetylstyrene, the carbonyl-complexed unsaturated ruthenium center prefers to coordinate to the adjacent C–C double bond rather than to insert into the *ortho* C–H bond.

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Supporting Information Available: Tables giving crystal data and refinement details, positional and thermal parameters, and bond distances and angles (9 pages). Ordering information is given on any current masthead page.

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