

Organic Peroxide Assisted Transition Metal Hydrosilylation Catalysis

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Summary:

The catalytic activity of rhodium complexes for the hydrosilylation of substrates such as alkenes, 1,3-dienes, 1-alkynes, or ketones, is enhanced by the addition of organic oxidizing agents, such as *t*-butyl hydroperoxide, hydrogen peroxide, or *m*-chloroperbenzoic acid. Similar enhancement is found for the Group VIA hexacarbonyls in the hydrosilylation of 1,3-dienes.

Article:

Introduction

The concept of using a co-catalyst in conjunction with an inactive or weakly active transition metal complex is exemplified by the activation of transition metal salts by alkyl aluminum compounds to form the extensively used Ziegler-Natta systems⁽¹⁾. These systems have been used to catalyze the hydrosilylation of a variety of unsaturated organic species, often with novel results⁽²⁾. Another type of co-catalysts which has been used, involves the oxidation of a ligand to form a weakly co-ordinating ligand oxide, thus generating a coordinatively unsaturated catalytically active complex⁽³⁻⁴⁾. Oxidizing agents that have been used include molecular oxygen (in systems such as W(CO)₆-EtAlCl₂-O₂ for the metathesis of olefins⁽³⁾) and peroxides [such as the system (PPh₃)₃RhCl- H₂O₂ for the hydrogenation of olefins]. We have been investigating the use of co-catalysts such as organic peroxides or molecular oxygen and report here on our use of organic peroxides as co-catalysts in hydrosilylation reactions. During the course of our studies reports by others have appeared where an organic peroxide has been used as a co-catalyst for the hydrosilylation reaction^(5,6)

Results and Discussion

Rhodium complexes

We have made use of bis(triphenylphosphine)carbonylchlororhodium(I), (*1*), as this is only moderately active for hydrosilylation reactions at room temperature⁽⁷⁾. As can be seen from Table 1, the activity of this catalyst is greatly increased by the addition of an approximately 50% molar excess of *t*-butyl hydroperoxide as co-catalyst. The activity increases by a factor of four to five for most combinations of organic unsaturate and silane. No attempt to optimize the reaction conditions was undertaken. The yields increase for the hydrosilylation of 1-octene by triethoxysilane, from 4% to 75% as the *t*-BuOOH : Rh ratio increases from zero to fifteen.(Table 2).

The yield is maximized with respect to *t*-BuOOH: Rh ratio at a value of 7.4 :1. An optimum ratio of *t*-BuOOH : M (M = Rh, Ir) of 4 : 1 was observed for [RhCl(PPh₃)₃] or [IrCl-(CO)(PPh₃)₂] in hydrosilylation reactions, but decomposition of the catalysts was observed at higher *t*-BuOOH : M ratios (10 : 1)⁽⁶⁾. Decomposition was not observed in our case, the catalyst system remaining active at ratios of *t*-BuOOH : Rh of 15 :1. As the catalysts contain different ligands it is not surprising that their responses differ.

The increase in activity has been attributed⁽⁶⁾ to the oxidation of either co-ordinated carbon monoxide to weakly coordinating carbon dioxide, as has been shown to occur stoichiometrically⁽⁸⁾, or by oxidation of co-ordinated triphenylphosphine to triphenylphosphine oxide, which has been proposed to account for the increase in the rate

of hydroformylation caused by addition of cyclohexenyl hydroperoxide to (1)⁽⁹⁾. This would lead to the coordinatively unsaturated species [RhCl(PPh₃)₂] or [RhCl(CO)PPh₃] which would be expected to show enhanced activity. The fact that a different catalytic species is involved is indicated by the change in ratio of *cis*:*trans*-olefin formed with the hydrosilylation of 1-pentyne by triethylsilane, a ratio which has been shown to be very sensitive to changes in catalyst⁽¹⁰⁾ (Table 1).

Table 1. Hydrosilylations using [RhCl(CO)(PPh₃)₂] and co-catalysts^{a)}.

Organic substrate	Silane	Product(s)	Yield without <i>t</i> -BuOOH	Yield with <i>t</i> -BuOOH ^{b)}
<i>n</i> -C ₆ H ₁₃ CH=CH ₂	HSiEt ₃	<i>n</i> -C ₆ H ₁₃ CH ₂ CH ₂ SiEt ₃	15	52
<i>n</i> -C ₆ H ₁₃ CH=CH ₂	HSi(OEt) ₃	<i>n</i> -C ₆ H ₁₃ CH ₂ CH ₂ Si(OEt) ₃	4	50
<i>n</i> -C ₃ H ₇ C≡CH	HSiEt ₃	<i>cis</i> - and <i>trans</i> -C ₃ H ₇ CH=CHSiEt ₃	22	75 ^{d)}
CH ₂ =CMeCMe=CH ₂	HSiEt ₃	Me ₂ C=C(Me)CH ₂ SiEt ₃ + CH ₂ =CMeCH(Me)CH ₂ SiEt ₃	18	77 ^{e)}
(CH ₂) ₅ -C=O	HSiEt ₃	(CH ₂) ₂ -CH(OSiEt ₃)	4	21

^{a)} [RhCl(CO)(PPh₃)₂], 1.27 × 10⁻² mmol; HSiEt₃, 6.3 mmol · HSi(OEt)₃, 5.4 mmol; C₆H₁₃CH=CH₂, 6.4 mmol; C₃H₇C≡CH, 10 mmol; CH₂=C(Me)C(Me)=CH₂, 8.8 mmol; cyclohexanone, 9.7 mmol; at room temperature for 6 h; ^{b)} Based on silane; calculated by quantitative g.l.c.; ^{c)} *t*-BuOOH, 1.87 × 10⁻² mmol; added as benzene solution; ^{d)} *cis*:*trans* adduct ratio: with *t*-BuOOH, 30:70, without *t*-BuOOH, 55:45 (Estimated by g.l.c.); ^{e)} 1,4:1,2-adduct ratio: with *t*-BuOOH, 85:15; without *t*-BuOOH, 85:15 (Estimated by g.l.c.).

Table 2. Effect of *t*-butylhydroperoxide on the hydrosilylation of 1-octene by triethoxysilane.

Catalyst system ^{a)}	Ratio <i>t</i> -BuOOH : Rh	Yield of 1 : 1 ^{b)} adduct (%)
[RhCl(CO)(PPh ₃) ₂]	-	4
[RhCl(CO)(PPh ₃) ₂] + <i>t</i> -BuOOH	1.5 : 1	50
[RhCl(CO)(PPh ₃) ₂] + <i>t</i> -BuOOH	7.4 : 1	73
[RhCl(CO)(PPh ₃) ₂] + <i>t</i> -BuOOH	15 : 1	75

^{a)} [RhCl(CO)(PPh₃)₂], 1.3 × 10⁻² mmol; HSi(OEt)₃, 5.4 mmol; *n*-C₆H₁₃CH=CH₂, 6.4 mmol; *t*-BuOOH added as a benzene solution;

^{b)} Calculated by g.l.c.; based on silane.

Our results for rhodium complexes with other organic oxidizing agents are summarized in Table 3. As can be seen, tris(triphenylphosphine)chlororhodium(I) (Wilkinson's compound) is converted from an inactive room temperature catalyst for the 1-octene-triethylsilane system, into a moderately active system by addition of *m*-chloroperbenzoic acid (mCPBA), *t*-butyl perbenzoate (*t*-BuOOOCPh), cumyl hydro-peroxide (CumOOH) or hydrogen peroxide at a molar ratio of ROOH : Rh of 8 : 1. *m*-Chloroperbenzoic acid activates [RhCl(CO)(PPh₃)₂] for the systems 1-octene : triethylsilane and 1-pentyne : triethylsilane and causes the yields to increase from 15% to 44% and from 22% to 77% respectively. These results parallel those with *t*-butyl hydroperoxide (Table 1) and those obtained by other workers⁽⁶⁾.

Group VIA hexacarbonyls

The Group VIA hexacarbonyls have been reported to be active photocatalysts for the hydrosilylation of 1,3-dienes⁽¹¹⁾, and their activity upon irradiation attributed to the photochemical formation of the species [Mo(CO)₅](M = Cr, Mo, W). As *t*-BuOOH had been shown to oxidize co-ordinated carbon monoxide to weakly co-ordinating carbon dioxide⁽⁸⁾, these compounds appeared to be promising candidates for peroxy co-catalysis. Our results for the hydrosilylation of 2,3-dimethyl-1,3-butadiene are summarized in Table 4. As can be seen, molybdenum hexacarbonyl is an active catalyst *alone* at 100 °C. It had previously been reported to be inactive at 40°⁽¹¹⁾. Chromium hexacarbonyl is a moderate catalyst at this temperature, but can be activated by the addition of a 50% molar excess of *t*-butyl hydroperoxide, the yield of 1 : 1 adduct with 2,3-dimethyl-1,3-butadiene and triethylsilane becoming essentially quantitative. The activity of [Mo(CO)₆] appears to be undiminished upon the addition of *t*-butyl hydroperoxide. Tungsten hexacarbonyl becomes a moderate catalyst

for the hydrosilylation of 2,3-dimethyl-1,3-butadiene by triethylsilane in the presence of *t*-BuOOH. In all cases, a preponderance of the 1,4-adduct, 1-silyl-2,3-dimethyl-2-butene, is formed. For molybdenum hexacarbonyl, it is essentially the only adduct formed. Such behavior was also reported for the photocatalytic reaction⁽¹¹⁾. When benzoyl peroxide was used as the peroxide, the catalytic activity of chromium hexacarbonyl was diminished, and a colored precipitate was observed, presumably a metal oxide or alkoxide. Di-*t*-butyl peroxide has been reported to inactive [RhCl(PPh₃)₃] or [IrCl(CO)(PPh₃)₂]⁽⁶⁾.

Again, with a correct choice of peroxy-compound, the activity of the Group VIA hexacarbonyls may be greatly enhanced.

Table 3. Hydrosilylation using triethylsilane catalyzed by other rhodium complexes assisted by organic peroxides^{a)}.

Catalyst	Peroxy Compound ^{b)}	Ratio of Peroxy Rh	Unsaturate	Yield of 1 : 1 adducts ^{c)}
[RhCl(PPh ₃) ₃]	None	–	1-octene	0
[RhCl(PPh ₃) ₃]	<i>m</i> -CPBA	8 : 1	1-octene	32
[RhCl(PPh ₃) ₃]	<i>t</i> -BuOOOCPH	8 : 1	1-octene	30
[RhCl(PPh ₃) ₃]	CumOOH	8 : 1	1-octene	44
[RhCl(PPh ₃) ₃]	H ₂ O ₂	8 : 1	1-octene	52
[RhCl(PPh ₃) ₃]	None	–	DMBD ^{d)}	0
[RhCl(PPh ₃) ₃]	<i>m</i> -CPBA	8 : 1	DMBD ^{d)}	63
[RhCl(CO)(PPh ₃) ₂]	None	–	1-octene	15
[RhCl(CO)(PPh ₃) ₂]	<i>m</i> -CPBA	8 : 1	1-octene	44
[RhCl(CO)(PPh ₃) ₂]	None	–	1-pentyne	22
[RhCl(CO)(PPh ₃) ₂]	<i>m</i> -CPBA	8 : 1	1-pentyne	77

^{a)} 0.010 g of rhodium complexes; appropriate amount of peroxy compound; unsaturate 6–10 mmol; triethylsilane 6.3 mmol. and 1 cm³ of benzene stirred at room temperature for 8 h; ^{b)} *m*-CPBA = *m*-chloroperbenzoic acid; added as a solid: *t*-BuOOOCPH = *t*-butyl perbenzoate; added as a benzene solution: CumOOH = cumyl hydroperoxide; added as a benzene solution; ^{c)} Calculated by quantitative g.l.c.; based on Et₃SiH; ^{d)} DMBD = 2,3-dimethyl-1,3-butadiene.

Table 4. Hydrosilylations of 2,3-Dimethyl-1,3-butadiene by Group VIA Carbonyls and Co-catalysts^{a)}.

Catalyst	Silane	Yield ^{b)}		Ratio of 1,4 : 1,2-adducts ^{a)}	
		without <i>t</i> -BuOOH	with <i>t</i> -BuOOH ^{c)}	without <i>t</i> -BuOOH	with <i>t</i> -BuOOH
[Cr(CO) ₆]	HSiEt ₃	41	100	85 : 15	87 : 13
[Cr(CO) ₆]	HSiEt ₃	41	7 ^{e)}	85 : 15	60 : 40 ^{e)}
[Cr(CO) ₆]	HSi(OEt) ₃	1	3	100 : 0	100 : 0
[Cr(CO) ₆]	HSi(OEt) ₂ Me	28	27	95 : 5	95 : 8
[Mo(CO) ₆]	HSiEt ₃	96	98	91 : 9	92 : 8
[Mo(CO) ₆]	HSi(OEt) ₃	71	72	100 : 0	100 : 0
[Mo(CO) ₆]	HSi(OEt) ₂ Me	85	89	100 : 0	100 : 0
[W(CO) ₆]	HSiEt ₃	9	51	73 : 27	85 : 15
[W(CO) ₆]	HSi(OEt) ₃	1	2	100 : 0	100 : 0

^{a)} [M(CO)₆], 1.27 × 10⁻² mmol; CH₂=CMeCMe=CH₂, 8.8 mmol; HSiEt₃, 6.3 mmol; HSi(OEt)₃, 5.4 mmol; HSi(OEt)₂Me, 6.2 mmol; at 100 °C (bath temperature) for 24 h; ^{b)} Based on silane; calculated by quantitative g.l.c.; ^{c)} *t*-BuOOH, 1.87 × 10⁻² mmol; added as benzene solution; ^{d)} Estimated by g.l.c.; ^{e)} Using benzoyl peroxide (1.87 × 10⁻² mmol) as co-catalyst; added as benzene solution.

Conclusions

The catalytic activity of rhodium complexes and the Group VIA hexacarbonyls can be enhanced for the hydrosilylation of a wide variety of organic substrates by silanes, using organic oxidizing agents as co-catalysts. The enhancement depends on the particular combination of reagents used, although the use of *t*-butyl hydroperoxide as the oxidizing agent is to be recommended in the light of its higher activity for all combinations of reactants and catalysts, and its ease of use.

Experimental

General procedures

All reactions were carried out under pure nitrogen, using freshly distilled, dry liquids. ¹H n.m.r. were recorded on a Varian Associates T 60 Spectrometer. I.r. spectra were taken with a Perkin-Elmer 457 grating spectrophotometer as thin films. The g.l.c. analysis of the reaction products was carried out on a Varian

Aerograph A-700 "Autoprep" Gas Chromatograph, using a 6 ft. column of 10% SE-30 on Chromosorb G, using indan, decane, or dodecane as internal standards. The silanes were purchased or prepared according to literature methods⁽²⁾. All the unsaturated organic compounds were commercial products, dried and distilled prior to use, with the exception of 2,3-dimethyl-1,3-butadiene which was prepared by the dehydration of pinacol⁽¹²⁾.

Preparative reactions

These were all carried out using the same general method. This will be detailed for the hydrosilylation of 2,3-dimethyl-1,3-butadiene catalyzed by the $[\text{Mo}(\text{CO})_6] : t\text{-BuOOH}$ system.

$\text{Mo}(\text{CO})_6$, (0.050 g, 0.20 mmol) was added to 2,3-dimethyl-1,3-butadiene (3.6 g, 44 mmol) under nitrogen. *t*-Butyl hydroperoxide (30 mmol, 3.0 cm³ of 10 molar benzene solution) was added. This mixture was allowed to stir for 30 minutes at room temperature, before 5.0 cm³ (3.7 g, 32 mmol) triethylsilane was added. The mixture was then heated to 100 °C (oil bath temperature) for 24 hours. The reaction was allowed to cool to room temperature and the volatiles removed under reduced pressure at room temperature. Distillation yielded the 1-triethylsilyl-2,3-dimethylbutenes (5.7 g, 91%) b.p. 56-58 °C/ 0.5 mm Hg. G.l.c. analysis of the product showed an isomer ratio of approximately 90 :10. The major isomer was identified as 1-triethylsilyl-2,3-dimethyl-2-butene by the ¹H n.m.r. spectra of the mixture by comparison with an authentic sample, and its g.l.c. retention time. The minor isomer was assigned as 4-(triethylsilyl)-2,3-dimethyl-1-butene by comparison of its g.l.c. retention time with that of an authentic sample, on several different columns.

The other reaction products were prepared in a similar manner, where two isomers were formed in comparable amounts separation was achieved by preparative g.l.c. using the Varian Aerograph 700 "Autoprep" Gas Chromatograph using a 20' by 3/8" column of SE 30 or Chromosorb G, as described before. Identification was by comparison of the ¹H n.m.r. and g.l.c. characteristics with authentic samples^(2, 10).

Quantitative g.l.c. reactions

These were carried out as above. The reaction of 1-pentyne with triethylsilane catalyzed by $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2] : t\text{-BuOOH}$ will be described in detail as an example.

$[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ (8 mg, 1.27 x 10⁻² mmol) was added to 1-pentyne (0.69 g, 10 mmol). This was followed by *t*-BuOOH (1.9 x 10⁻² mmol, 1.0 cm³ of 0.019 molar benzene solution). The mixture was allowed to stir at room temperature for 30 minutes, before triethylsilane (0.73 g, 6.3 mmol) was added. The solution was stirred at room temperature for 8 h. The yield and ratio of isomers were determined by quantitative g.l.c. on the Varian Aerograph 700 "Autoprep" Gas chromatograph using a 6 ft. column of 10% FFAP on Chromosorb G using indan as an internal standard.

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