Rhodium Phosphite Clusters as Hydrosilylation Catalysts

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Summary:
The activity of rhodium phosphite complexes as catalyst precursors for hydrosilylation reactions has been investigated. These are found to be active for a wide variety of organic substrates. Both hydride clusters, \([\text{RhH}\{\text{P(OR)}_3\}_2]_n\) and chloride dimers, \([\text{RhCl}\{\text{P(OR)}_3\}_2]_2\) (\(R = \text{methyl or } \alpha\text{-tolyl}\)) were evaluated. The hydrosilylation of 1-hexyne by triethylsilane was investigated as a function of phosphite:rhodium ratio and also with various phosphites as ligand.

Article:

Introduction
There is great current interest in the synthesis of transition metal clusters, especially as such compounds are expected to have novel catalytic activity [1]. Rhodium phosphite clusters, \([\text{RhH}\{\text{P(OR)}_3\}_2]_n\) (\(R = \text{Me}, n = 3; R = \text{i-Pr}, n = 2; \text{etc.}\)), have been investigated extensively by Muetterties and co-workers, who have shown them to be active alkene and alkyne hydrogenation catalysts [2].

We report in this paper on the use of rhodium phosphite complexes as catalyst precursors for the hydrosilylation of a wide variety of unsaturated compounds. Two types of rhodium phosphite complexes were investigated as hydrosilylation catalysts: the bridged hydride clusters, I, and the chloridebridged dimers, II. The chloride bridged dimers

\[
\begin{align*}
\text{Ia} & \quad X = \text{H}, R = \text{Me}, n = 3. \\
\text{Ib} & \quad X = \text{H}, R = 2-\text{C}_6\text{H}_4\text{Me}. \\
\text{IIa} & \quad X = \text{Cl}, R = \text{Me}, n = 2. \\
\text{IIb} & \quad X = \text{Cl}, R = \text{C}_6\text{H}_4\text{Me}.
\end{align*}
\]

were synthesized from dichlorotetrakis(cyclooctene)dirhodium(I), \([\text{RhCl}\{(\text{C}_8\text{H}_{14})_2\}]_2\) and the appropriate amount of phosphite [3, 4]. The corresponding hydride clusters were formed \textit{in situ} from the chloride and lithium triethylborohydride [5]. The catalytic effectiveness of both types of complex was evaluated for the hydrosilylation of a wide variety of unsaturated organic substances.

Experimental

General procedures
All reactions were carried out under pure nitrogen using freshly distilled dry liquids. \(^1\text{H}\) NMR spectra were recorded on a Varian Associates T60 spectrometer. IR spectra were recorded on a Perkin-Elmer 457 grating spectrophotometer. The GC analysis of reaction products was carried out on a Varian A-700 ‘Autoprep’ gas chromatograph using a 6 ft column of 10% SE30 on Chromasorb G. The silanes were purchased or prepared according to literature methods [3, 4]. The phosphites were prepared from phosphorous trichloride and the corresponding phenol [6, 7], except for trimethylphosphite, which was a commercial sample dried over sodium and freshly distilled. \([\text{RhCl}(\text{C}_8\text{H}_{14})_2]_2\) was prepared by a literature method [8].
Hydrosilylations
These were carried out using methods outlined in previous publications [9]. The products of the hydrosilylations in some cases were isolated and identified by comparison of their spectral properties with authentic samples [10], but in most cases were identified by comparison of their GLC characteristics with authentic samples. Results collected in the Tables were obtained by quantitative reactions carried out as outlined in footnotes to the Tables, and yields were calculated using an appropriate internal standard.

Typical experimental procedures are reported in detail below.

Hydrosilylation of 2,3-dimethyl-1,3-butadiene by triethylosilane catalyzed by Ia
IIa (23 mg, 3.0 \times 10^{-2} \text{ mmol}) was placed in a flask and dissolved in 5 ml THF. The solution was cooled to —78 °C and 60 μl of a 1.0 M (6.0 \times 10^{-2} \text{ mmol}) solution of lithium triethylborohydride in THF was added. The solution was allowed to warm to room temperature. The catalyst was then removed under reduced pressure and 2,3-dimethyl-1,3-butadiene (1.0 ml, 0.73 g, 8.8 mmol) and triethylsilane (1.0 ml, 0.73 g, 6.3 mmol) added. The mixture was stirred at room temperature overnight. Quantitative analysis of the reaction mixture by GLC using a 6 ft column of 10% SE30 on Chromosorb G with decane as an internal standard indicated a quantitative yield, based on triethylsilane, of 1:1 adducts, with a 90:10 ratio of 1-triethylsilyl-2,3-dimethylbut-2-ene:4-triethylsilyl-2,3-dimethylbut-1-ene.

Hydrosilylation of 1-octene by triethoxysilane catalyzed by IIb
IIb (49 mg, 3.0 \times 10^{-2} \text{ mmol}) was added to a degassed solution of 1-octene (1.0 ml, 0.72 g, 6.4 mmol) and triethoxysilane (1.0 ml, 0.96 g, 5.4 mmol). The mixture was placed in an oil bath at 100 °C for 2 h. GLC analysis of the reaction mixture using decane as an internal standard indicated a 67% yield of 1-triethoxysilyloctane, based on silane.

Hydrosilylation of 1-hexyne by triethoxysilane catalyzed by IIId
[RhCl(C_6H_4)_{2}]_2 (21 mg, 3.0 \times 10^{-2} \text{ mmol}) was dissolved in 10 ml dichloromethane. Tris(2,6-xylyl)phosphite (47 mg, 12 \times 10^{-2} \text{ mmol}) was added and the solution was stirred at room temperature for 1 h. The volatiles were then removed under reduced pressure. 1-Hexyne (1.0 ml, 0.72 g, 8.7 mmol) and triethylsilane (1.0 ml, 0.73 g, 6.3 mmol) were added and the mixture was stirred at room temperature overnight. GLC of the reaction mixture using decane as a standard indicated a 38% yield (based on silane) of trans-1-triethylsilyl-1-hexene.

Results and discussion
The rhodium phosphite complexes are moderate hydrosilylation catalysts for a variety of unsaturated organic molecules, as can be seen from the results in Table 1. The activities of the hydride complexes Ia-b and the chloride complexes IIa-b are comparable. This is not surprising, as silanes are effective transition metal reducing agents [11], and could easily reduce the chloride complexes to the corresponding hydrides. The trimethylphosphite clusters Ia and Ha are excellent catalysts for the hydrosilylation of 2,3-dimethyl-1,3-butadiene by triethoxysilane at 25 °C, however the ratio of the two isomeric 2,3-dimethylbutenes formed varies. 1-Triethylsilyl-2,3-dimethyl-2-butene, the 1,4-adduct, is almost exclusively formed with Ia, whereas considerably more 4-triethylsilyl-2,3-dimethyl-1-butene is formed with IIa. This perhaps suggests that there are subtle differences in the catalytic intermediates formed from the two catalysts.

Ia and IIa catalyze the hydrosilylation of carbon-oxygen double bonds by triethoxysilane, both in saturated ketones, i.e. cyclohexanone, and in unsaturated ketones, i.e. mesityl oxide. With both catalysts, the activity increases with temperature. The opposite temperature dependence occurs on hydrosilylation of 1-octene by triethoxysilane, where activity is moderate at 25 °C and poor at 100 °C with both Ia and IIa.

With hydrosilylations involving triethoxysilane, the yields are lower than those obtained with triethylsilane, except those involving 1-octene. Complex IIa is uniformly more active than Ia with triethoxysilane.
We also synthesized the tris-o-tolylphosphite analogues of Ia and IIa, and investigated the catalytic activity of these two complexes, Ib and IIb. Tris-o-tolylphosphite is a sterically more demanding ligand than trimethylphosphite, and its complexes are often coordinatively unsaturated, for example [Ni{P(O-o-C₆H₄Me)_₃}]₃ is readily formed in solution [12]. Such complexes display interesting catalytic activity [13].

**TABLE 1**

Hydrosilylations using rhodium phosphate cluster complexes

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Silane</th>
<th>Conditions</th>
<th>Yields a</th>
<th>[HRh{P(OMe)₃}]₂</th>
<th>[ClRh{P(OMe)₃}]₂</th>
<th>[HRh{P(OAr)₃}]₂</th>
<th>[ClRh{P(OAr)₃}]₂</th>
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</thead>
<tbody>
<tr>
<td>DMBD d</td>
<td>HSiEt₃</td>
<td>25 °C/18 h</td>
<td>100 (10/90)</td>
<td>96 (30/70)</td>
<td>50 (10/90)</td>
<td>7 (10/90)</td>
<td></td>
</tr>
<tr>
<td>DMBD d</td>
<td>HSiEt₃</td>
<td>100 °C/2 h</td>
<td>50 (10/90)</td>
<td>85 (40/60)</td>
<td>92 (17/83)</td>
<td>89 (17/83)</td>
<td></td>
</tr>
<tr>
<td>1-hexyne</td>
<td>HSiEt₃</td>
<td>25 °C/18 h</td>
<td>96 (55/45)</td>
<td>100 (55/45)</td>
<td>27 (100/0)</td>
<td>41 (100/0)</td>
<td></td>
</tr>
<tr>
<td>1-hexyne</td>
<td>HSiEt₃</td>
<td>100 °C/2 h</td>
<td>65 (55/45)</td>
<td>65 (55/45)</td>
<td>57 (100/0)</td>
<td>68 (100/0)</td>
<td></td>
</tr>
<tr>
<td>cyclohexanone</td>
<td>HSiEt₃</td>
<td>25 °C/6 h</td>
<td>10</td>
<td>41</td>
<td>78</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>cyclohexanone</td>
<td>HSiEt₃</td>
<td>100 °C/2 h</td>
<td>84</td>
<td>51</td>
<td>100</td>
<td>86</td>
<td></td>
</tr>
<tr>
<td>mesityl oxide</td>
<td>HSiEt₃</td>
<td>25 °C/6 h</td>
<td>67</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>mesityl oxide</td>
<td>HSiEt₃</td>
<td>100 °C/2 h</td>
<td>95</td>
<td>100</td>
<td>61</td>
<td>95</td>
<td></td>
</tr>
<tr>
<td>1-octene</td>
<td>HSiEt₃</td>
<td>25 °C/18 h</td>
<td>53</td>
<td>48</td>
<td>48</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>1-octene</td>
<td>HSiEt₃</td>
<td>100 °C/2 h</td>
<td>27</td>
<td>38</td>
<td>38</td>
<td>53</td>
<td></td>
</tr>
<tr>
<td>DMBD d</td>
<td>HSi(OEt)₃</td>
<td>100 °C/2 h</td>
<td>64 (30/70)</td>
<td>70 (20/80)</td>
<td>8</td>
<td>66 (15/85)</td>
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<tr>
<td>1-octene</td>
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<td>25 °C/6 h</td>
<td>0</td>
<td>36</td>
<td>—</td>
<td>67</td>
<td></td>
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<tr>
<td>1-octene</td>
<td>HSi(OEt)₃</td>
<td>100 °C/2 h</td>
<td>6</td>
<td>37</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

a Unsaturate (6 - 10 mmol) and silane (5 - 8 mmol) added to catalyst (3 x 10⁻² mmol).

b Calculated by quantitative GLC; isomer ratios in parentheses where appropriate.

c Ar = 2-C₆H₄Me.

d DMBD = 2,3-dimethyl-1,3-butadiene.

Both Ib and IIb exhibit catalytic activity, although it is slightly more modest than that of the corresponding trimethylphosphite complexes (Table 1). An interesting feature is that higher yields (although not excellent) are obtained with alkoxy silanes and 1-octene with the bulkier phosphite, P(o-OC₆H₄Me)₃, than with P(OMe)₃ as ligand.

**Hydrosilylation of alkynes**

As it has been shown that the product distribution obtained from the hydrosilylation of alkynes is very dependent on subtle changes in the catalyst system used [9], we have investigated the hydrosilylation of 1-hexyne by triethylsilane using the rhodium phosphite complexes IIA-d. The products of this hydrosilylation consisted of trans- and cis-1-triethylsilyl-1-hexenes (eqn. (1)).

\[
[RhCl{P(OR)₃}]₂
\]

Ila R = Me  
Ilb R = 2-C₆H₄Me  
IIC R = 2-C₆H₄Bu  
IID R = 2,6-C₆H₄Me₂

\[
\mathrm{[RhCl(OR)₃]}_2 \rightarrow \text{trans-} \mathrm{[RhCl(OR)₃]} \rightarrow \text{cis-}
\]

\[
\text{n-C₆H₄C=CH + HSiEt₃ \rightarrow cis-/trans-n-C₆H₄C=CHSiEt₃}
\] (1)

Table 2 shows the variation in yield and isomer ratio for the hydrosilylation of 1-hexyne by triethylsilane catalyzed by [RhCl(PO₃)]₂, as different phosphites were used as ligands. The yield at 25 °C after 18 h drops as o-substituted aryl phosphites are used in place of P(OMe)₃. This is due to their increasing steric hindrance; however, the selectivity is much greater for the bulky phosphites, as they give only trans-1-triethylsilyl-1-hexene, by cis-addition of the silane.
Table 3 presents the results obtained when the ratio of trimethylphosphite:rhodium is varied. The yield of 1-triethylsilyl-1-hexene is essentially quantitative at trimethylphosphite:rhodium ratios of 1:1 and 2:1. These results are similar to those obtained with triphenylphosphine rhodium complexes in the hydrosilylation of 1-pentyne by triethylsilane, where the yield of 1-triethylsilyl-1-pentene reaches a maximum at triphenylphosphine:rhodium ratios of 0.5:1 and 1:1 [9]. The yield for the trimethylphosphite:rhodium system shows a dramatic decrease as the trimethylphosphite:rhodium ratio is increased past the optimum.

**Catalytically active intermediates**

The nuclearity of the catalytically active intermediates is unknown at this time, and cluster fragmentation cannot be ruled out based on the product distributions obtained.

**References**