Hydroacylation of 1-Alkene with 2-(Diphenylphosphino)benzaldehyde by Rh(I)

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The chelate-assisted oxidative addition is a reaction of potential utility for the selective activation of organic functional groups. Application of this methodology gives an understanding of its scope and limitations. To this end some model compounds, such as 8-quinolincarboxaldehyde, aldime and 2-(diphenylphosphino)benzaldehyde, were applied for oxidative addition of aldehyde or aldime group by transition metals. Oxidative addition of these model compounds afforded quite stable transition metal acyl or iminocarbonyl hydride. We have tried to expand this C-H bond cleavage of aldehyde or aldime group to hydroacylation. Among model substrates, 2-(diphenylphosphino)benzaldehyde (1) is quite interesting because the reactions with transition metals give various metal complexes depending on catalyst used. In homogeneous catalytic reaction, phosphorus-carbon (P-C) bond cleavage was noted to be an one mode of tertiary arylphosphine catalyst deactivations. This report deals with hydroacylation of various 1-alkene with a model compound using 2-(diphenylphosphino) benzaldehyde as substrate and generation of P-C bond cleavage product.

2-(Diphenylphosphino) benzaldehyde (1) was reacted with ethylene (2a) in benzene at 90 °C for 4 h under 5 mol% of [(C6H5)2RhCl2] (3a) as catalyst to give 2-(diphenylphosphino) propophenone (4a), isolated in 74% yield after chromatographic isolation (Eq. 1). The reaction is facile and any other side-product was not isolated. When longer chain a-olefins such as 1-pentene (2b) and 1-hexene (2c) were applied in this hydroacylation reaction in THF with 5 mol% [(C6H5)2RhCl2] (3b) as catalyst under the identical reaction conditions, 2-(diphenylphosphino) hexamethylenophenone (4b) and 2-(diphenylphosphino)heptanophenone (4c) were obtained in 76 and 66% yield, respectively (Table 1, entry 2 and 3).

The hydroacylation mechanism of 1-alkene with 1 is shown in Scheme 1. The first step must be ligand exchange reaction of 3 with 1 to give 5, similar to Wilkinson's complex. The C-H bond of one of the coordinated 1 in 5 is cleaved by Rh(I) to generate 6, followed by olefin exchange reaction with 2 to lead 7. Hydrometallation in 7 and subsequent reductive elimination of the resulting acylrhodium (III) alkyl intermediate 8 produces 4 with regeneration of the initial catalytic species 5. Any branched alkyl ketone 10 was not detected in the product, which means that hydrometallation process in 7 followed anti-Markownikoff's rule due to the steric congestion of the intermediate 9. If the step 6 to 7 is not facile, triphenylphosphine (13) is supposed to be produced through decarbonylation of 6 via 11 and 12. However, hydroacylation of normal 1-alkene did not show any decarbonylation product. When styrene (2d) was used as substrate (Table 1, entry 4), the results were different from those of hydroacylation of normal 1-alkene in much lower yield (23%) than those of normal 1-alkene (Table 1, entry 1-3). This reaction introduces two new side products, triphenylphosphine (13) and 2-(diphenylphosphino) benzophenone (15). Someti-

Table 1. Hydroacylation of vinyl of derivatives (2) with 2-(diphenylphosphino)benzaldehyde (1) at 90 °C for 4 h

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Ratio of 4/15</th>
<th>Isolated yield of 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H (2a)</td>
<td>100:0:0</td>
<td>74% (4a)</td>
</tr>
<tr>
<td>2</td>
<td>n-C6H5 (2b)</td>
<td>100:0:0</td>
<td>76% (4b)</td>
</tr>
<tr>
<td>3</td>
<td>n-C6H5 (2c)</td>
<td>100:0:0</td>
<td>66% (4c)</td>
</tr>
<tr>
<td>4</td>
<td>C6H5 (2d)</td>
<td>46:16:38%</td>
<td>23% (4d)</td>
</tr>
<tr>
<td>5</td>
<td>C6F5 (2e)</td>
<td>77:12:11%</td>
<td>68% (4e)</td>
</tr>
</tbody>
</table>

*product yield lower than 1% is ignored; *contains 5% oxide form (14) of: 1°[(C6H5)2RhCl2] (3b) is used as catalyst except entry 1; *the ratio is determined by GC-MS; *[(C6H5)2RhCl2] (3a) is used as catalyst; *54% is starting material 1 and oxide form of 1; *4% is o-tolylidiphenylphosphine.

![Scheme 1](image-url)
mes during isolation process by column chromatography some of phosphines were oxidized to give corresponding phosphine oxide (14) determined by GC-MSD.

\[
\begin{array}{c}
\text{Ph-P} \\
\text{Ph-P} \\
\text{Ph-P} \\
\text{Ph-P} \\
\text{Ph-P} \\
\end{array}
\]

Compound 13 must be formed through 11 and 12 by decarbonylation of 6, since olefin exchange in 6 with styrene (2d) is not facile, which results in comparatively low yield of 4d. Another side product, 15, was presumed to be formed from the intermediate 8 in Scheme 1. The phenylethyl rhodium (III) intermediate 8d might undergo β-alkyl elimination, similar to β-hydrogen elimination, to give 18, followed by reductive elimination to lead 15 and 19 as shown in Eq. 2.

\[
\begin{align*}
\text{Ph-P} & \quad \text{Ph-P} \\
\text{Ph-P} & \quad \text{Ph-P} \\
\text{Ph-P} & \quad \text{Ph-P} \\
\text{Ph-P} & \quad \text{Ph-P} \\
\text{Ph-P} & \quad \text{Ph-P} \\
\end{align*}
\]

To identify this postulate, pentafluorostyrene (2e) was applied in this hydroacylation under the identical reaction conditions (Table 1, entry 5). According to the mechanism in Eq. 2, compound 16 should have been obtained instead of 15 as side product. However, still compound 15, not 16, was determined in reaction mixture, which explained that the mechanism was not consistent with that in Eq. 2. Recently it has become clearer that tertiary arylphosphine-metal complexes are chemically reactive and liable to undergo P-C bond scission depending on the specific reaction conditions. Van Leeuwen studied the P-C bond cleavage mechanism of 1 during the reduction of 1 with platinum metal hydride (Eq. 3).

\[
\begin{align*}
\text{Ph-P} & \quad \text{Ph-P} \\
\text{Ph-P} & \quad \text{Ph-P} \\
\text{Ph-P} & \quad \text{Ph-P} \\
\text{Ph-P} & \quad \text{Ph-P} \\
\text{Ph-P} & \quad \text{Ph-P} \\
\end{align*}
\]

According to his study, rearrangement of 20 to 21 is described as a nucleophilic attack of the alkoxy group at the coordinated phosphorus center followed by a shift of a phenyl group from phosphorus to platinum. The formation of 15 can be also explained by the similar mechanism in which 17 is formed from the intermediate 6, followed by reductive elimination of the acylrhodium phenyl intermediate 17. However, 1-phenyl-3H-2,1-benzoxaphosphole liberated from 17 was not observed. The mechanism is not clear, but compound 15 must be formed by reductive elimination of acylrhodium(III) phenyl intermediate generated from P-C bond cleavage. When the yield of 4d (23%) formed from styrene (2d) is compared with that (68%) of 4e formed from 2e, the results are dramatic contrast. The reason seems to be that coordination of electron-deficient olefin, pentafluorostyrene (4e), to the metal catalyst, which is step 6-7 in Scheme 1, might be much more facile than that of styrene (4d). In conclusion, the chelate-assisted hydroacylation of 1-alkene (2) with aldehyde (1) is very facile under Rh(I) catalyst to give ketone (4). The reactivity of styrene is quite different from that of pentafluorostyrene, in which electron-deficient pentafluorostyrene is much more reactive than styrene, maybe due to the differences between coordination abilities of these two substrates to metal catalyst. Some of decomposition product, 15, generated from the P-C bond cleavage in phosphine, was determined.

Experimental

All reactions involving organometallic reagents were done under an atmosphere of argon, using standard drybox techniques. Compound 11 and 3 were prepared by published procedures. Compound 1 used is contaminated with about 5% of oxide form (14) of 1. Inevitably formed during synthesis work-up. Oxide form (14) of 1 did not participate in hydroacylation. μ-Dichloro(ethylenediiridium(1) (3a), RhCl\(_2\) · hydrate, ethylene (2a), 1-pentene (2b), 1-hexene (2c), styrene (2d) and pentafluorostyrene (2e) were purchased from Aldrich Chemical Co. Organic reagents were dried over 4 Å molecular sieves prior to use. All solvents were distilled from sodium-benzophenone ketyl prior to use. The solvent system for column chromatography was a mixture of hexane and ethylacetate in a 5:2 ratio in volume. NMR spectra were recorded with a Bruker AC-300 (300 MHz) spectrometer. The chemical shift values (δ) of the 'H NMR and 13C NMR resonances were expressed in ppm relative to internal Me\(_4\)Si. Infrared spectra were recorded with Nicolet Instrum Corp. Impact 400 FT-IR spectrophotometer. Mass spectra were obtained with a Shimadzu GCMS-QP2000A. Column chromatography was performed on Merck Silica Gel 60 (230-400 mesh).
phino)hexaldehyde (1) was added. To the mixture was added 154 mg (2.20 mmol) of 1-pentene (2b) in argon atmosphere and it was heated at 90 °C for 4 h. The reaction mixture was purified by column-chromatography to give 93 mg (76% yield) of 2-( diphenylphosphino)hexanopenone (4b). 1H NMR (300 MHz, CDCl₃) δ (ppm) 7.89 (dd, J = 3.9 Hz, J = 7.5 Hz, 1H, 6-H in hexanopenone), 7.42-7.02 (m, 15H, 2CH₃ and 2CH₃), 2.91 (t, J = 7.5 Hz, 2H, α-CH₂ to CO), 1.65 (m, 2H, β-CH₂ to CO), 1.30-1.22 (m, 4H, γ and δ-CH₂ to CO), 0.86 (t, J = 6.8 Hz, 3H, CH₃). 13C NMR (75 MHz, CDCl₃) δ ppm 201.86 (CO), 138.39-128.10 (Cs of three phenyl group), 40.15 (α-C to CO), 31.37 (γ-C to CO), 23.95 (β-C to CO), 22.41 (β-C to CO), 22.41 (δ-C to CO), 13.90 (CC₂H₃); IR spectrum (neat) 3010, 2985, 2844, 1670 (CO), 1615, 1581, 1475, 1459, 1431, 1270, 1250, 1200, 1086, 1064, 1023, 993, 965, 925, 740, 692 cm⁻¹; mass spectrum (assignment, relative intensity) 361 (M⁺, 14.6), 360 (M⁺, 13.9), 304 (PhPC₆H₄(OH) = CH₄⁺, 66.2), 303 (M⁺-CH₃, 100), 290 (M⁺-CH₃, 12.0), 225 (42.8), 183 (47.5).

2-(Diphenylphosphino)heptanopenone (4c). The same procedure was taken as described in the preparation of 4b. 4c (66% yield): 1H NMR (300 MHz, CDCl₃) δ (ppm) 7.88 (dd, J = 3.8 Hz, J = 7.4 Hz, 1H, 6-H in heptanopenone), 7.52-6.98 (m, 13H, 2CH₃ and 2CH₃), 2.91 (t, J = 7.3 Hz, 2H, α-CH₂ to CO), 1.64 (m, 2H, β-CH₂ to CO), 1.25-1.17 (m, 6H, γ, δ and ε-CH₂ to CO), 0.85 (t, J = 4.8 Hz, 3H, CH₃). 13C NMR (75 MHz, CDCl₃) δ (ppm) 201.96 (CO), 134.81-128.15 (Cs of three phenyl group), 40.27 (α-C to CO), 31.57 (γ-C to CO), 28.92 (β-C to CO), 24.27 (δ-C to CO), 24.46 (ε-C to CO), 14.03 (CC₂H₃); IR spectrum (neat) 3055, 2928, 2861, 1674 (CO), 1584, 1460, 1437, 1367, 1275, 1123, 1100, 1030, 798, 749, 697 cm⁻¹; mass spectrum (assignment, relative intensity) 375 (M⁺⁺, 11.1), 374 (M⁺⁺, 11.6), 304 (PhPC₆H₄(OH) = CH₄⁺, 32.5), 303 (M⁺⁺-CH₃, 100), 225 (27.8), 183 (27.9).

2-(Diphenylphosphino) 3-phenylpropyrobenzene (4d). The same procedure was taken as described in the preparation of 4b. 4d (21% yield): 1H NMR (300 MHz, CDCl₃) δ (ppm) 7.75 (m, 1H, 6-H in 3-phenylpropyrobenzene), 7.52-7.01 (m, 18H, 3 CH₃ and 2CH₃), 3.24 (t, J = 7.4 Hz, 2H, α-CH₂ to CO), 3.00 (t, J = 7.9 Hz, 2H, β-CH₂ to CO), 1.35 (m, 15H, 2CH₃ and 2CH₃), 1.17-1.15 (m, 6H, γ, δ and ε-CH₂ to CO), 0.85 (t, J = 4.8 Hz, 3H, CH₃); 13C NMR (75 MHz, CDCl₃) δ (ppm) 200.50 (CO), 141.24-128.02 (Cs of four phenyl group), 42.12 (α-C to CO), 30.27 (β-C to CO); IR spectrum (neat) 3045, 2984, 1665 (CO), 1580, 1480, 1447, 1312, 1280,1200, 1024, 975, 925, 740, 690 cm⁻¹; mass spectrum (assignment, relative intensity) 375 (M⁺⁺, 11.1), 374 (M⁺⁺, 11.6), 304 (PhPC₆H₄(OH) = CH₄⁺, 52.5), 303 (M⁺⁺-CH₃, 100), 225 (27.8), 183 (27.9).

2-(Diphenylphosphino) 3-pentafluorophenylpropyrobenzene (4e). The same procedure was taken as described in the preparation of 4b. 4e (68% yield): 1H NMR (300 MHz, CDCl₃) δ (ppm) 7.69 (m, 1H, 6-H in 3-pentafluorophenylpropyrobenzene), 7.65-6.98 (m, 13H, 2CH₃ and 2CH₃), 3.23 (t, J = 7.4 Hz, 2H, α-CH₂ to CO), 3.02 (t, J = 7.4 Hz, 2H, β-CH₂ to CO); 13C NMR (75 MHz, CDCl₃) δ (ppm) 198.64 (CO), 140.27-128.26 (Cs of three phenyl and pentafluorophenyl group), 53.37 (α-C to CO), 38.63 (β-C to CO); IR spectrum (neat) 3056, 2928, 1683 (CO), 1531, 1504, 1437, 1270, 1125, 985, 951, 751, 700 cm⁻¹; mass spectrum (assignment, relative intensity) 375 (M⁺⁺, 11.1), 304 (PhPC₆H₄(OH) = CH₄⁺, 21.8), 303 (M⁺⁺-CH₃, 100), 225 (16.5), 183 (51.3).