Notes

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

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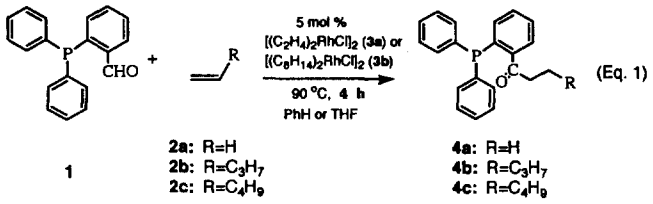
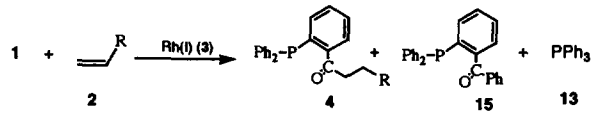
The chelate-assisted oxidative addition is a reaction of potential utility for the selective activation of organic functional groups.[1] Application of this methodology gives an understanding of its scope and limitations. To this end some model compounds, such as 8-quinolinecarboxaldehyde,[2] aldimine[3] and 2-(diphenylphosphino)benzaldehyde,[4] were applied for oxidative addition of aldehyde or aldimine group by transition metals. Oxidative addition of these model compounds afforded quite stable transition metal acyl or iminoacyl hydride. We have tried to expand this C-H bond cleavage of aldehyde or aldimine group to hydroacylation.[5] Among model substrates, 2-(diphenylphosphino)benzaldehyde (**1**) is quite interesting because the reactions with transition metals give various metal complexes depending on catalyst used.[6] In homogeneous catalytic reaction, phosphorus-carbon (P-C) bond cleavage was noted to be an one mode of tertiary arylphosphine catalyst deactivations.[7] This report deals with hydroacylation of various 1-alkene with a model compound using 2-(diphenylphosphino) benzldehyde as substrate and generation of P-C bond cleavage product.



2-(Diphenylphosphino)benzaldehyde (**1**) was reacted with ethylene (**2a**) in benzene at 90 ℃ for 4 h under 5 mol % of $[(C_2H_4)_2RhCl]_2$ (**3a**) as catalyst to give 2-(diphenylphosphino)propiophenone (**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 ω-olefins such as 1-pentene (**2b**) and 1-hexene (**2c**) were applied in this hydroacylation reaction in THF with 5 mol % $[(C_8H_{14})_2RhCl]_2$ (**3b**) as catalyst under the identical reaction conditions, 2-(diphenylphosphino)hexanophenone (**4b**) and 2-(diphenylphosphino)heptanophenone (**4c**) were obtained in 76 and 66% yield, respectively (Table 1, entry 2 and 3).

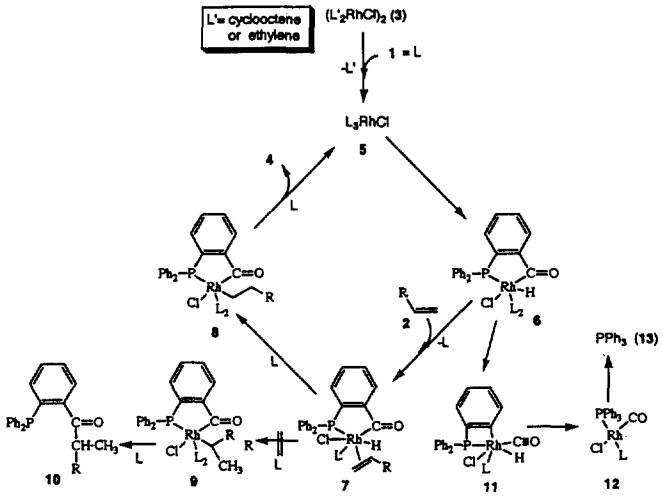
The hydroacylation mechanism of 1-alkene with **1** is shown in Scheme 1. The first step must be ligand exchange reaction of **3** with **1** to give **5**, similar to Wilkinson's complex. The C-H bond of one of the coordinated **1** in **5** is cleaved by Rh(I) to generate **6**, followed by olefin 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 meant 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**).[8] Someti-

Table 1. Hydroacylation of vinyl of derivatives (**2**) with 2-(diphenylphosphino)benzaldehyde (**1**)[a] under 5 mol% Rh(I)[b] catalyst (**3**) at 90 ℃ for 4 h



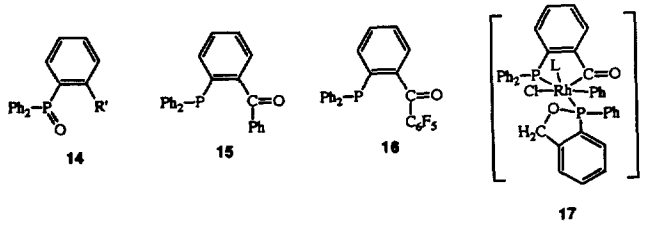
Entry	R	Ratio of **4**/**15**/**13**[c]	Isolated yield of **4**
1[d]	H (**2a**)	100 : 0 : 0	74% (**4a**)
2	n-C_3H_5 (**2b**)	100 : 0 : 0	76% (**4b**)
3	n-C_4H_9 (**2c**)	100 : 0 : 0	66% (**4c**)
4	C_6H_5 (**2d**)	46 : 16 : 38[e]	23% (**4d**)
5	C_6F_5 (**2e**)	77 : 12 : 11[f]	68% (**4e**)

[a]product yield lower than 1% is ignored; [b]contains 5% oxide form (**14**) of **1**; [c]$[(C_8H_{14})_2RhCl]_2$ (**3b**) is used as catalyst except entry 1; [d]the ratio is determined by GC-MSD; [e]$[(C_2H_4)_2RhCl]_2$ (**3a**) is used as catalyst; [f]54% is starting material **1** and oxide form of **1**; [g]4% is *o*-tolyldiphenylphosphine.

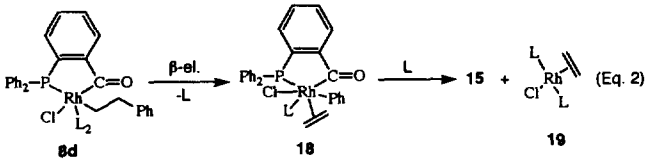


Scheme 1.

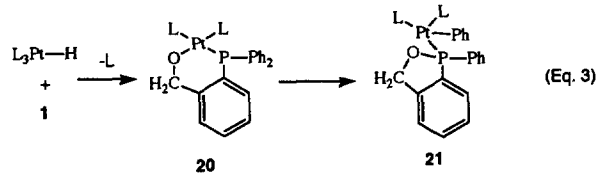
mes during isolation process by column chromatography some of phosphines were oxidized to give corresponding phosphine oxide (**14**) determined by GC-MSD..



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 compartively 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[9], similar to β-hydrogen elimination, to give **18**, followed by reductive elimination to lead **15** and **19** as shown in Eq. 2.



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 labile to undergo P-C bond scission depending on the specific reaction conditions.[6,10] Van Leeuwen studied the P-C bond cleavage mechanism of **1** during the reduction of **1** with platinum metal hydride[11] (Eq. 3).



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**).[12]

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 involing organometallic reagents were done under an atmosphere of argon, using standard drybox techniques. Compound **1**[13] and **3**[14] 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-Dichlorotetraethylene dirhodium(I) (**3a**), $RhCl_3$ · hydrate, ethylene (**2a**), 1-pentene (**2b**), 1-hexene (**2c**), styrene (**2d**) and pntafluorostyrene (**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 ^1H NMR and ^{13}C NMR resonances were expressed in ppm relative to internal Me_4Si. Infrared spectra were recorded with Nicolet Instrument Corp. Impact 400 FT-IR spectrophotomer. Mass spectra were obtained with a Shimadzu GCMS-QP2000A. Column chromatography was performed on Merck Silica Gel 60 (230-400 mesh).

2-(Diphenylphosphino)propiophenone (4a). A Kontes quarz pressure vessel was charged with 98 mg (0.34 mmol) of 2-(diphenylphosphino)bezaldehyde (**1**) and 5 mg (0.026 mmol: 7 mol% based on **1**) of $[(C_2H_4)_2RhCl]_2$ (**3b**). The reaction mixture was dissolved in 2 mL of benzene and the solution was flushed with nitrogen. After the mixture was completely freezed by dryice-acetone bath and evacuated by vacuum, ethylene gas (**2a**) was added for about 3 min. After closing the valve, the reaction vessel was heated at 90 ℃ for 4 h. The reaction mixture was purified by column-chromatography to give 80 mg (74% yield) of 2-(diphenylphosphino)propiophenone (**4a**). **4a**: ^1H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.88 (m, 1H, 6-H in propiophenone), 7.43-7.01 (m, 13H, $2C_6H_5$ & C_6H_3), 2.96 (q, J=7.2 Hz, 2H, α-CH_2 to CO), 1.13 (t, J=7.1 Hz, 3H, CH_3); ^{13}C NMR (75 MHZ, $CDCl_3$) δ (ppm) 202.01 (CO), 141.61-128.12 (Cs of three phenyl group), 33.26 (α-C to CO), 8.18 (C of CH_3); IR spectrum (neat) 3055, 2983, 2935, 1669 (CO), 1442, 1226, 1094, 961, 756, 698 cm^{-1}; mass spectrum (assignment, relative intensity) 318 (M^+, 18.7), 304 ($Ph_2PC_6H_4C(OH)=CH_2^+$, 22.3), 303 ($M^+-C_2H_5$, 100), 225 (12.0), 183 (14.0).

2-(Diphenylphosphino)hexanophenone (4b). A 2.5 mL screw-capped pressure vial was charged with 5 mg (0.014 mmol: 5 mol% based on **1**) of $[(C_8H_{14})_2RhCl]_2$ (**3**) dissolved in 2 mL of THF, and 98 mg (0.34 mmol) of 2-(diphenylphos-

phino)bezaldehyde (**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 ℃ for 4 h. The reaction mixture was purified by column-chromatography to give 93 mg (76% yield) of 2-(diphenylphosphino)hexanophenone (**4b**). **4b**: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.89 (dd, J=3.9 Hz, J=7.5 Hz, 1H, 6-H in hexanophenone), 7.42-7.02 (m , 13H, $2C_6H_5$ & C_6H_3), 2.91 (t, J=7.5 Hz, 2H, α-CH_2 to CO), 1.65 (m, 2H, β-CH_2 to CO), 1.30-1.22 (m, 4H, γ-and δ-CH_2 to CO), 0.86 (t, J=6.8 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) 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 (C of CH_3); 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 (assignmemt, relative intensity) 361 (MH^+, 14.6), 360 (M^+, 13.9), 304 ($Ph_2PC_6H_4C(OH)=CH_2^+$, 66.2), 303 (M^+-C_4H_9, 100), 290 (M^+-C_5H_{10}, 12.0), 225 (42.8), 183(47.5).

2-(Diphenylphosphino)heptanophenone (4c). The same procedure was taken as described in the preparation of **4b**. **4c** (66% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.88 (dd, J=3.8 Hz, J=7.4 Hz, 1H, 6-H in heptanophenone), 7.52-6.98 (m, 13H, $2C_6H_5$ & C_6H_3), 2.91 (t, J=7.3 Hz, 2H, α-CH_2 to CO), 1.64 (m, 2H, β-CH_2 to CO), 1.25-1.17 (m, 6H, γ-, δ and ε-CH_2 to CO), 0.85 (t, J=4.8 Hz, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 201.95 (CO), 134.81-128.12 (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), 22.46 (ε-C to CO), 14.03 (C of CH_3); IR spectrum (neat) 3055, 2928, 2861, 1674 (CO), 1584, 1460, 1437, 1367, 1275, 1123, 1100, 1030, 978, 749, 697 cm^{-1}; mass spectrum (assignment, relative intensity) 375 (MH^+, 11.1), 374 (M^+, 11.6), 304 ($Ph_2PC_6H_4C(OH)=CH_2^+$, 52.5), 303 (M^+-C_5H_{11}, 100), 225 (27.8), 183 (27.9).

2′-(Diphenylphosphino) 3-phenylpropanoylbenzene (4d). The same procedure was taken as described in the preparation of **4b**. **4d** (21% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.75 (m, 1H, 6-H in 3-phenylpropanoylbenzene), 7.52-7.01 (m, 18H, 3 C_6H_5 & C_6H_3), 3.24 (t, J=7.4 Hz, 2H, α-CH_2 to CO), 3.00 (t, J=7.9 Hz, 2H, β-CH_2 to CO); ^{13}C NMR (75 MHz $CDCl_3$) δ (ppm) 200.50 (CO), 141.24-126.02 (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 (MH^+, 11.1), 374 (M^+, 11.6), 304 ($Ph_2PC_6H_4C(OH)=CH_2^+$, 52.5), 303 (M^+-$C_2H_4C_6H_5$, 100), 225 (27.8), 183 (27.9).

2′-(Diphenylphosphino) 3-pentafluorophenylpropanoylbenzene (4e). The same procedure was taken as described in the preparation of **4b**. **4e** (68% yield): ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 7.69 (m, 1H, 6-H in 3-pentafluorophenylpropanoylbenzene), 7.65-6.98 (m, 13H, 2 C_6H_5 & C_6H_3), 3.23 (t, J=7.4 Hz, 2H, α-CH_2 to CO), 3.02 (t, J=7.4 Hz, 2H, β-CH_2 to CO); ^{13}C NMR (75 MHz, $CDCl_3$) 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), 1521, 1504, 1437, 1270, 1125, 985, 951, 751, 700 cm^{-1}: mass spectrum (assignment, relative intensity) 375 (MH^+, 11.1), 304 ($Ph_2PC_6H_4C(OH)=CH_2^+$, 21.8), 303 (M^+-$C_2H_4C_6H_5$, 100), 225 (16.5), 183 (5.3).

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8. Compound **15**: mass spectrum (assignment, relative intensity) 367 (MH^+, 13.9), 366 (M^+, 59.6), 338 (M^+-CO, 26. 6), 337 (M^+-CHO, 100), 289 (M^+-C_6H_5, 14.1), 183 (32.4). Identification of compound **15** is as follows: The oxide form (**14**) of **1** was reacted with phenylmagnesium bromide to give o-$Ph_2P(O)C_6H_4CH(OH)Ph$. Oxidation of o-$Ph_2P(O)C_6H_4CH(OH)Ph$ by PCC (Pyridinium Chlorochromate) in CH_2Cl_2 gave o-$Ph_2P(O)C_6H_4COPh$. Deoxygenation of phosphine oxide in o-$Ph_2P(O)C_6H_4COPh$ by hexachlorodisilane lead authentic sample of compound **15**.
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