Palladium-catalysed Hydrosilation of Olefins and Polyenes

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Summary Palladium compounds and metallic palladium are active catalysts of hydrosilation of olefins and polyenes in the presence of ligands such as triphenylphosphine.

HYDROSILATION of olefins is catalysed by transition-metal compounds, platinum compounds being especially widely used. However palladium compounds are regarded as inactive for hydrosilation because of easy reduction to the metallic state.[1,2] Recently Hagihara *et al.* reported that zero-valent palladium–phosphine complexes catalyse hydrosilation of butadiene.[3] We have found that palladium can be an active catalyst of hydrosilation of olefins when it is combined with phosphine.[4]

Typically, a reaction of oct-1-ene (0·1 mole, 11·2 g), trichlorosilane (0·1 mole, 13·5 g), and tetrakis(triphenylphosphine)palladium (100 mg) at 100° for 5 h gave 1-trichlorosilyloctane in 90·5% yield. The catalyst need not be a zero-valent phosphine complex. Any bivalent palladium compound such as palladium chloride or palladium acetylacetonate is active when 2 or 3 moles of triphenylphosphine or trialkylphosphine are added to the reaction system. Interestingly, even metallic palladium, produced by reduction of palladium chloride with formic acid, can be used in the presence of an excess of triphenylphosphine. Some examples of reactions of hex-1-ene to give 1-trichlorosilylhexane are shown in the Table. Trimethylsilane is less reactive than trichlorosilane, and the reaction with oct-1-ene catalysed by tetrakis(triphenylphosphine)palladium gave 1-trimethylsilyloctane in 15·3% yield.

Butadiene (5·4 g) reacted with trichlorosilane (13·5 g) in the presence of metallic palladium (0·1 g) and triphenylphosphine (1 g) at 100° for 6 h to give 1-trichlorosilylbut-2-ene in 93·5% yield. With trimethylsilane, trimethylsilylocta-2,6-diene was obtained in 90% yield. These are similar to the results reported by Hagihara using a low-valent palladium–phosphine complex.[3]

*Reaction of hex-*1-*ene* (0·1 *mole*) *with trichlorosilane* (0·1 *mole*)

Catalysts(g)	Temp.	Time (h)	Yield (%)
$Pd(PPh_3)_4$ (0·1)	100°	5	90·0
$PdCl_2(PPh_3)_2$ (0·1)	120°	5	91·0
$Pd(OAc)_2$ (0·1) + Bu_3P(1) . .	80°	10	75·6
Pd (0·1) + PPh_3(1) . .	120°	10	92·3

The order of the reactivity of olefins is: conjugated dienes > 1-olefins > inner olefins. Thus octa-1,3,7-triene (0·1 mole) was attacked selectively with trichlorosilane (0·1 mole) at the diene to give 4-trichlorosilyl-octa-2,7-diene (82·3%). Also, only the terminal double bond of *cis*-hexa-1,4-diene was hydrosilated.

In connection with the catalysis by metallic palladium, we have found that it is converted gradually into a yellow crystalline complex, $[Pd(PPh_3)_2]_x$ by heating with excesses of triethylsilane and triphenylphosphine. The same complex was obtained by the reaction of tetrakis(triphenylphosphine)palladium with triethylsilane at room temperature.

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