Hydrosilylation Catalysed by Activated Nickel

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Activated nickel, prepared by lithium reduction of nickel iodide under sonication, efficiently catalyses the hydrosilylation of hexene, styrene, vinyl butyl ether and acrylonitrile under mild conditions.

Homogeneous platinum and rhodium complexes are the most effective hydrosilylation catalysts, producing high yields of adducts under mild conditions.[1] Unfortunately, the inability to recover these catalysts adds significantly to the cost of the process. Among heterogeneous catalysts, only the precious metals promote hydrosilylation at a useful rate.[2,3] The literature on the less regal metals, in a variety of heterogeneous forms[4,5] or as soluble complexes,[6] reveals generally modest performance and little promise as important catalysts for hydrosilylation.[7] Recently, however, we discovered that activated nickel catalysed the coupling of hydrosilanes and recorded the Ni–H absorption resulting from oxidative addition of the hydrosilane linkage to nickel metal.[8]

We now report that nickel powder,[9] produced by lithium or sodium reduction of nickel iodide in tetrahydrofuran (THF), will efficiently catalyse the hydrosilylation of some simple and complex alkenes. We obtained high yields of adduct under very mild conditions, recovered the catalyst quantitatively by transferring the product mixture from the reaction flask, recharged the vessel with silane and alkene, and reused the catalyst several times without significant loss of activity. Our results are summarized in Table 1. Commercial nickel powder was inert, even after intensity sonication.[10] Sonication during reduction of nickel iodide to nickel powder accelerates that rate[11] and the rate of hydrosilylation.

For the reaction of hex-1-ene with trichlorosilane, we

Table 1 Hydrosilylation of alkenes catalysed by activated nickel[a]

Entry	Alkene	Silane	Product	Yield (%)[b]
1	Hex-1-ene	Cl_3SiH	$Cl_3Si(CH_2)_5Me$	94
2	Hex-1-ene	$MeCl_2SiH$	$MeCl_2Si(CH_2)_5Me$	92
3	Styrene	Cl_3SiH	$Cl_3SiCH_2CH_2C_6H_5$	88
4	Vinyl butyl ether	Cl_3SiH	$Cl_3SiCH_2CH_2OC_4H_9$	78
5	Vinyl butyl ether	$MeCl_2SiH$	$MeCl_2SiCH_2CH_2OBu$	71
6	Acrylonitrile	Cl_3SiH	$MeCH(SiCl_3)CN$	93
7	Acrylonitrile	$MeCl_2SiH$	$MeCH(SiCl_2Me)CN$	93

[a] 0.04 : 0.05 : 8.5 × 10^{-3} mol of alkene : silane : activated Ni (Ni*) in 10 ml of THF at 20–25 °C. [b] Isolated yields of products >95% pure by NMR after distillation.

Table 2 Nickel catalysed hydrosilylation of hex-l-ene

Entry	Hex-l-ene /mmol	$HSiCl_3$ /mmol	Ni* /mmol	Yield (%)[a]	Induction period/min	Time to reach final yield/min[b]
1	40	40	8.51	50	20	70
2	20	40	8.51	90	30	50
3	10	40	8.51	100	20	40
4	40	20	8.51	50	30	90
5	40	10	8.51	Trace[c]		
6	40	40	2.13	Trace[c]		
7	40	40	4.26	80	30	150
8	40	40	17.0	50	20	50

[a] All yields were determined by GC with dodecane as the internal standard. [b] Includes induction period. The reactions were monitored for an additional hour showing no change in yield. [c] Less than 1% of product was observed after 150 min.

examined the effects of varying concentrations (Table 2). We observed that excess trichlorosilane promoted hydrosilylation (entries 2 and 3) and that an excess of hex-1-ene inhibited the reaction (entry 4). Equimolar ratios of alkene and silane result in lower yields of adduct and/or longer reaction times at three different catalyst loads (entries 1, 7 and 8). When the silane : alkene ratio was reduced to 1:4, little product was formed (entry 5). A minimum quantity of nickel is required. We observed little or no hydrosilylation after 150 min with 5 mol% relative to alkene or silane (entry 6). For the reactions in Tables 1 and 2, the alkene and the silane were added simultaneously to the activated nickel in THF. In all cases we observed an induction period of at least 20 min, suggesting that essential intermediates may form prior to the onset of reaction.

When freshly generated nickel powder was allowed to react with hex-1-ene for 40 min prior to the addition of trichlorosilane, the induction period was only about 10 min. Switching the order of addition gave an induction of about 5 min. That an induction period was required in each experiment implies that both reagents must be adsorbed on the surface for the reaction to proceed.[12] If there were no induction period for either experiment, it would suggest that only one reagent need be adsorbed and that the second reagent reacts with the adsorbed species.[12]

These preliminary results raise the intriguing possibility of replacing platinum with the far less expensive nickel. The source of this unexpected reactivity of freshly prepared nickel dispersion in the hydrosilylation reaction may be the high surface area, some unique surface species, or a combination of the two.[13] We are investigating the scope of activated nickel catalysis and the role of surface species in these reactions.

Received, 12th July 1991; Com. 1/03559B

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