

Silica supported allylmetals as hydrosilylation catalysts

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J.M. Chance, D.L. Linebarrier and T.A. Nile, "Silica supported allylmetals as Hydrosilylation Catalysts," *Trans. Metal Chem.*, 12, 276-277 (1987).

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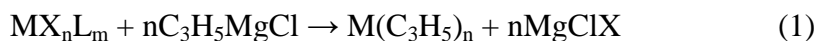
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Article:

The use of metal complexes on supports such as silica and alumina provides a method for heterogenizing homogeneous catalysts, allows easy recovery of catalysts from the product mixture, and also facilitates recovery of such systems in fixed bed reactors. Furthermore, novel enhanced catalytic activity is exhibited by these supported catalysts. Allyl-metals and benzyl-metals supported on silica and alumina are known to be active catalysts for carbonylation, hydrogenation and polymerization of a wide variety of substrates⁽¹⁾. We report our preliminary results using such systems as hydrosilylation catalysts.

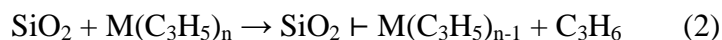
We evaluated platinum, nickel, and rhodium allyls because homogeneous complexes of these metals show extensive catalytic activity for hydrosilylation catalysis(2). We have also investigated the catalytic activity of [Mo₂(C₃H₅)₄] in order to see if the binuclear nature of this complex might lead to novel activity.

The allyl-metals were synthesized by the same general route (Equation 1):



M = Ni, X = acac, n = 2; M = Pt, X = Cl, L = PhCN, n = 2; M = Rh, X = Cl, n = 3; M = Mo₂, X = (AcO)₄, n = 4

The allyl-metals were attached to silica (preactivated at 200° C under vacuum) by reaction at room temperature for 2h (Equation 2).



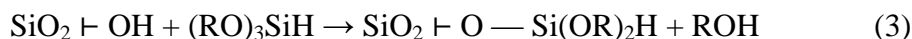
The silica supported allyl-metals were then evaluated for hydrosilylation potential using a range of organic unsaturated substrates. The results are collected in Table 1.

The following features are worthy of note:

a) *SiO₂ \vdash Pt(C₃H₅)*

This system possesses substantial activity. With the system 2, 3-dimethyl-1, 3-butadiene-HSiEt₃ an essentially quantitative yield of 1:1 adducts was obtained at 60° C after 2h with essentially regioselective 1, 4-addition to give 1-triethylsilyl-2, 4-dimethyl-but-2-ene. The same catalyst sample was recycled for seven separate reactions, yields being 100, 81, 91, 96, 100, 43, and 8%. Each cycle represents 2 × 10⁴ turnovers, so a total of 105 turnovers occurs before activity decreases. It seems probable that the diminishing activity is due to the repeated filtration of the small amount SiO₂ \vdash Pt(C₃H₅) used.

SiO₂ † Pt(C₃H₅) also proved extremely active for the 1-hexyne-HSiEt₃ system, but less active for alkoxysilanes although good yields were obtained for the 1-octene-triethoxysilane system (65% after 60° C/6h) and, surprisingly, the yield of 1-octene-trimethoxysilane *increased* if the reaction was carried out in air [25% (N₂) versus 46% (air)]. The low yields for alkoxysilanes are probably due to reactions with surface Si-OH or Si-O-Si species (Equation 3).



We are now undertaking experiments designed to remove reactive surface species by pretreatment of the surface with silylating agents such as Me₃SiCl or (MeO)₄Si. This should create more active species.

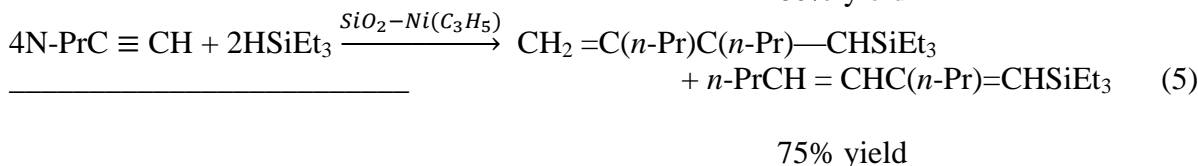
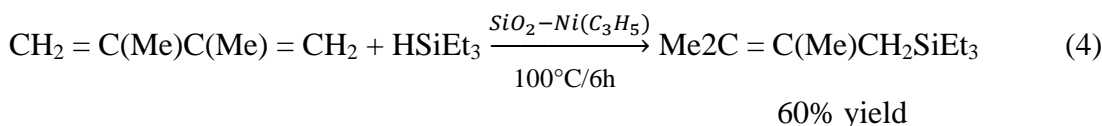
Table 1. Hydrosilylations using supported allyl-metals as catalysts^a

Catalyst	Unsaturate	Silane	Conditions (° C/h)	Product ^b	Yield ^c (%)
SiO ₂ † Pt(C ₃ H ₅)	DMBD ^d	HSiEt ₃	60/2	Me ₂ C=C(Me)CH ₂ SiEt ₃	100
SiO ₂ † Pt(C ₃ H ₅)	1-Hexyne	HSiEt ₃	60/6	C ₆ H ₁₁ SiEt ₃	81
SiO ₂ † Pt(C ₃ H ₅)	1-Octene	HSi(OEt) ₃	60/6	C ₈ H ₁₇ Si(OEt) ₃	65
SiO ₂ † Pt(C ₃ H ₅)	1-Octene	HSi(OMe) ₃	60/6	C ₈ H ₁₇ Si(OMe) ₃	25 ^e
SiO ₂ † Pt(C ₃ H ₅)	1-Octene	HSi(OMe) ₃	60/6	C ₈ H ₁₇ Si(OMe) ₃	46 ^f
SiO ₂ † Ni(C ₃ H ₅)	DMBD	HSiEt ₃	100/6	Me ₂ C=C(Me)CH ₂ SiEt ₃	60
SiO ₂ † Ni(C ₃ H ₅)	1-Pentyne	HSiEt ₃	100/6	H ₂ C=C(R)C(R)=CH(SiEt ₃) + RCH=CHC(R)=CHSiEt ₃ ^g	75
SiO ₂ † Rh(C ₃ H ₅) ₂	1-Octene	HSiEt ₃	100/2	C ₈ H ₁₇ SiEt ₃	50
SiO ₂ † Rh(C ₃ H ₅) ₂	1-Hexyne	HSiEt ₃	100/2	<i>n</i> -BuCH=CHSiEt ₃	5

^a0.100 g silica (ca. 5 × 10⁻³ mmol metal), 5–10 mmol silane and 8–12 mmol organic substrate mixed and heated (oil bath temperature) for the times listed; ^bidentified by comparison(s) of g.l.c. retention time; ^c%, calcd. by quantitative g.l.c. using appropriate internal standards; ^dDMBD = 2,3-dimethyl-1,3-butadiene; ^eunder N₂; ^fin air; ^gR = *n*-Pr, H₂C=C(R)C(R)=CH(SiEt₃); RCH=CHC(R)=CHSiEt₃ isomer ratio = 70:30.

b) SiO₂ † Ni(C₃H₅)

The supported allyl-nickel, in preliminary investigations, proved to be a moderate catalyst for the hydrosilylation of dienes and 1-alkynes (Equation 4 and 5):



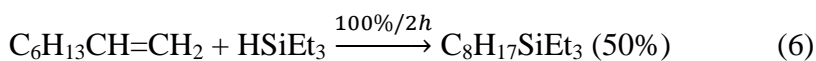
The products and the proportion of isomers formed are essentially the same as those formed using the Ziegler-Natta system, Ni(acac)₂. Et₃Al⁽³⁾, although the activity of the SiO₂ † Ni(C₃H₅) seems lower.

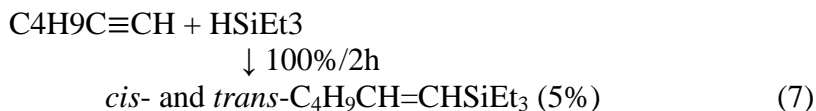
c) SiO₂ † MoO₂(C₃H₅)₃

The supported molybdenum compound was inactive for the hydrosilylation of dienes.

d) SiO₂ † Rh(C₃H₅)₂

Only preliminary studies have been carried out with this system so far, and only modest activity has been exhibited (Equations 6 and 7):





Experimental

Synthesis of allyl-metals

These compounds were prepared by reacting a solution of allyl magnesium chloride in Et₂O with [Ni(C₅H₇O₂)₂], [PtCl₂(PhCN)₂], [Mo₂(OAc)₄] and anhydrous [RhCl₃] according to the literature methods⁽⁴⁻⁶⁾.

Attachment of allyl-metals to silica

Silica (Baker 60-200 mesh) activated by heating at 200° C for 3h *in vacuo* was suspended in PhMe under N₂ and a solution of the allyl-metal in PhMe was added at room temperature. The mixture was stirred for 2h, filtered, washed with PhMe and dried *in vacuo*. The presence of allyl-metal on the silica was confirmed by microanalysis.

Hydrosilylations

The organic substrate (8-15 mmol) was added to the treated silica (0.100 g, 5 x 10⁻³ mmol of metal), the silane (5-10 mmol) was added and the mixture heated under N₂ to the temperature and for the times listed in Table 1. Yields, calculated by quantitative g.l.e., are based on silane. A *ca.* 20-30% molar excess of organic substrate was always used.

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