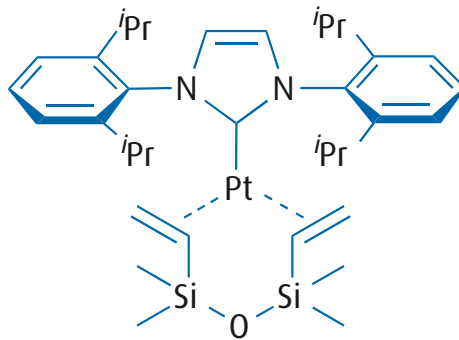
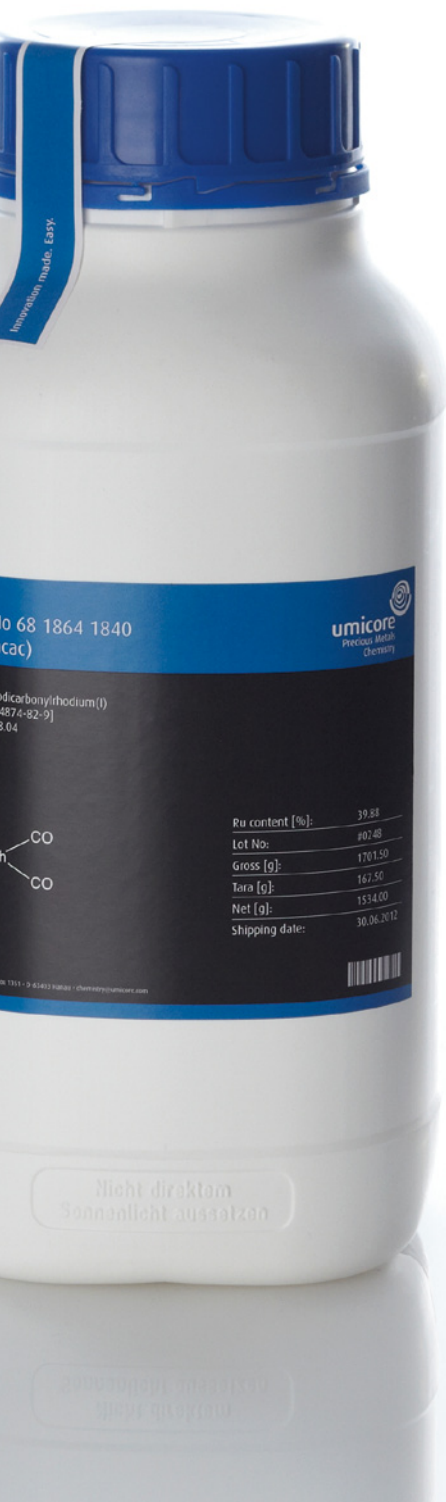
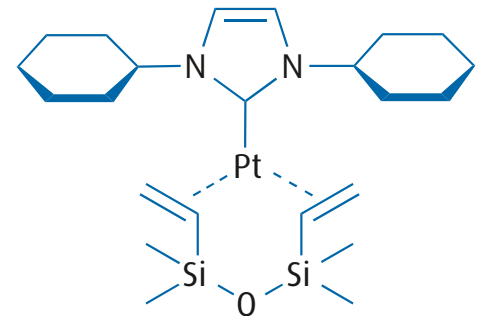


New Catalysts for Hydrosilylation Reactions



Umicore HS425 (IPr)Pt(vs)



Umicore HS432 (ICy)Pt(vs)

Offering Advantages

- » high selectivity, activity and productivity
- » no formation of platinum colloids
- » suppressed side reactions (isomerization or hydrogenation)

Umicore HS Catalysts

Hydrosilylation Catalysts

Advanced proprietary platinum N-heterocyclic carbene catalysts for hydrosilylation applications in both silicone and fine chemical industries

Advantages vs. "classical" systems "Speier's" and "Karstedt's" catalyst

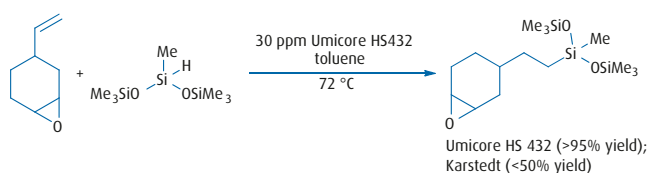
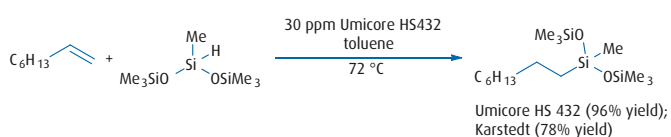
- » Highly active & selective, at typically lower catalyst loading › no undesired by-products by e.g. isomerization & hydrogenation
- » Pt centers stabilized by N-heterocyclic carbene ligand › to avoid formation of Pt colloids
- » Stable towards air & moisture, non-hygroscopic › easy handling, defined complexes

Whether you need to perform a hydrosilylation of functionalized alkenes or alkynes, you will find the right one at Umicore Precious Metals Chemistry. We offer tailor-made Umicore HS catalysts for your most efficient hydrosilylation step.

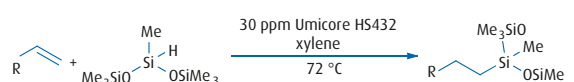


Alkene hydrosilylation

Selective and Efficient Platinum(0)-Carbene Complexes As Hydrosilylation Catalysts.¹



Highly Active and Selective Platinum(0)-Carbene Complexes – Efficient, Catalytic Hydrosilylation of Functionalised Olefins.²

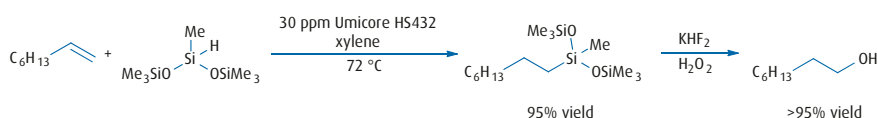


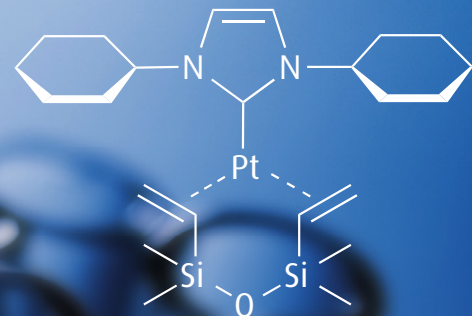
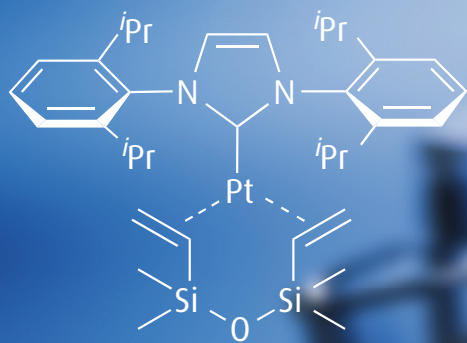
entry	substrate	product	yield [%] ^{a,b}
1	THPO-CH=CH ₂	THPO-CH ₂ CH ₂ -Si(Me) ₂ (OSiMe ₃)	92
2	HO-CH ₂ CH=CH ₂	HO-CH ₂ CH ₂ -Si(Me) ₂ (OSiMe ₃)	96
3	EtO-C(=O)-CH ₂ CH=CH ₂	EtO-C(=O)-CH ₂ CH ₂ -Si(Me) ₂ (OSiMe ₃)	80

^a All yields are isolated, pure compounds. Unless otherwise mentioned, all the conversions are quantitative.

^b In all cases, the use of Karstedt catalyst leads to a mixture of products and to the formation of colloidal platinum species.

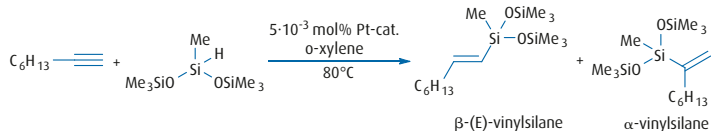
Efficient Tamao-Kumada-Fleming oxidation.²





Alkyne hydrosilylation

Hydrosilylation of Alkynes Mediated by N-Heterocyclic CarbenePlatinum(0) Complexes.³



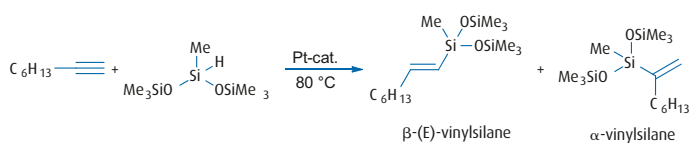
entry ^a	catalyst	ratio β -(E)/ α ^b	time [h] ^c
1	Umicore HS432	2.8	150
2	Umicore HS425	10.6	6

^a Reaction conditions: [1-octyne] = [bis(trimethylsilyloxy)methylsilane] = 0.5 M, [Pt] (0.005 mol%), 80 °C, xylene. The results are the average of at least two runs.

^b Ratio determined by GC analysis.

^c Time to completion of reaction (> 95% conversion).

Highly β -(E)-Selective Hydrosilylation of Terminal and Internal Alkynes Catalyzed by a (IPr)Pt(diene) Complex.⁴



entry ^a	catalyst (mol%)	solvent	T[°C]	time [min]	ratio β -(E)/ α ^b	yield [%] ^c
1	PtCl ₂ (cod) (5 · 10 ⁻³)	THF	60	10	3:1	75
2	Umicore HS425 (5 · 10 ⁻³)	xylene	80	360	11:1	90
3	Umicore HS425 (0.1)	— ^d	60	12 h	10:1	60

^a Reaction conditions: 1-octyne (3.0 mmol, 1 equiv.), bis(trimethylsilyloxy)methylsilane (3.0 mmol, 1 equiv.), dodecane (internal standard, [Pt], solvent, (1.0 M).

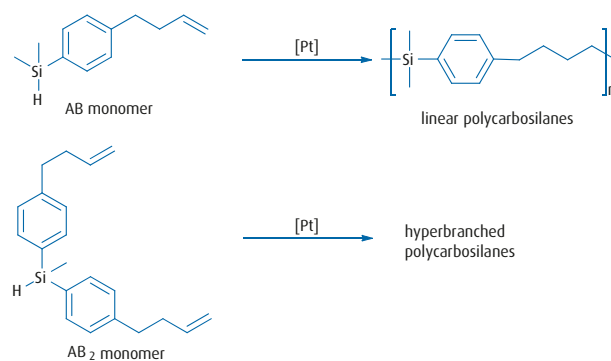
^b Ratio determined by GC analysis of the crude reaction mixture.

^c GC yield of the β -(E) isomer.

^d Solventless conditions.

Polymerization

Hyperbranched Polycarbosilanes of Homogeneous Architecture: Regioselective Hydrosilylation of AB₂ Monomers and Consecutive Functionalization.⁵



entry	monomer	Catalyst ^a	% isomerisation ^b	Mn ^c (g/mol)	PDI ^c
1	AB ₂	H ₂ PtCl ₆ /iPrOH	10	1400	1.30
2	AB ₂	Karstedt catalyst	29	3900	6.38
3	AB ₂		— ^d	18600	2.41
4	AB	Karstedt catalyst	6	4800	2.08
5	AB		— ^d	9500	1.77

^a Reactions with 1 and 3 were stirred at 60 °C for 24 h, reactions with (NHC)Pt(vs) for 48 h

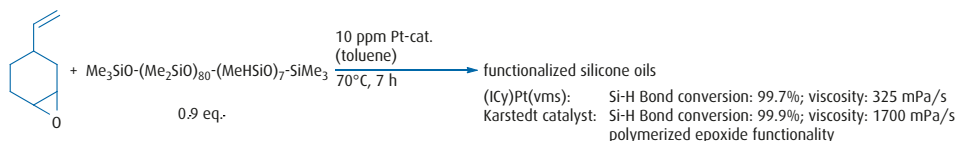
^b Determined by ¹H NMR spectroscopy.

^c Determined by GPC in THF versus polystyrene standards.

^d Only trace amounts of isomerized double bonds were detectable.

Patents

- » Silicone compositions which can preferably be cross linked into elastomers, by catalytic hydrosilylation of at least one polyorganosiloxane bearing an unsaturated bond using at least one polyorganohydrosiloxane can be prepared.^{6,7}
- » Functionalized silicone oils with controlled viscosity by catalytic hydrosilylation can be produced.⁸



- » The preparation of silicone compositions which can preferably be cross linked into elastomers, by catalytic hydrosilylation of at least one polyorganosiloxane bearing an unsaturated bond using at least one polyorganohydrosiloxane is feasible.^{9,10}

References:

- 1 Markó, I. E. et al., Science 2002, 298, 204.
- 2 Markó, I. E. et al., Adv. Synth. Catal. 2004, 346, 1429.
- 3 Markó, I. E. et al., Organometallics 2006, 25, 1881.
- 4 Markó, I. E. et al., J. Org. Chem. 2008, 73, 4190.
- 5 Rieger, B. et al., Macromolecules 2010, 43, 934.
- 6 WO2003 099909
- 7 WO2002 098971.
- 8 WO2002 0014407.
- 9 WO2003 099909.
- 10 WO2002 098971.

Umicore HS425		Chemical Properties		
	Trade Name	Umicore HS425	Chemical Formula	C ₃₅ H ₅₄ N ₂ O ₂ Si ₂ Pt
	Chemical Name	[1,3-Bis(2,6-diisopropylphenyl)imidazol-2-ylidene][1,3,3-tetramethyl-1,3-divinylsiloxane]platinum(0)	Molecular weight [g/mol]	770.07
	Empirical Formula	(IPr)Pt(vs)	Metal	Pt
	CAS No.	849830-54-2	approx. Metal Content [%]	25
	Product No.	68 1834 0625	Physical State	crystalline
			Color	white
			Stability & Reactivity	air and moisture stable

Umicore HS432		Chemical Properties		
	Trade Name	Umicore HS432	Chemical Formula	C ₂₃ H ₄₂ N ₂ O ₂ Si ₂ Pt
	Chemical Name	[1,3-Bis(cyclohexyl)imidazol-2-ylidene][1,3,3-tetramethyl-1,3-divinylsiloxane]platinum(0)	Molecular weight [g/mol]	613.85
	Empirical Formula	(ICy)Pt(vs)	Metal	Pt
	CAS No.	400758-55-6	approx. Metal Content [%]	32
	Product No.	68 1834 0732	Physical State	crystalline
			Color	white
			Stability & Reactivity	air and moisture stable

Handling & Storage Information

Ensure good ventilation and exhaustion at the workplace. Store in original container protected from direct sunlight in a dry, cool and well-ventilated area. Do not store above 25 °C.

For inquiries and additional info please contact

Umicore AG & Co. KG

Rodenbacher Chaussee 4
63457 Hanau-Wolfgang
Germany

Tel.: +49 (6181) 59 6005

Fax: +49 (6181) 59 2970

Email: chemistry@umicore.com

Website: www.chemistry.umicore.com

The information and statements contained herein are provided free of charge. They are believed to be accurate at the time of publication, but Umicore makes no warranty with respect thereto, including but not limited to any results to be obtained or the infringement of any proprietary rights. Use or application of such information or statements is at the user's sole discretion, without any liability on the part of Umicore. Nothing herein shall be construed as a license or recommendation for use which infringes upon any proprietary rights. All sales are subject to Umicore's General Conditions of Sale and Delivery.

© 2012 Umicore AG & Co. KG. Printed in the Federal Republic of Germany.