

Efficient Removal of Ruthenium-Based Catalysts using SiliaBond® Metal Scavengers

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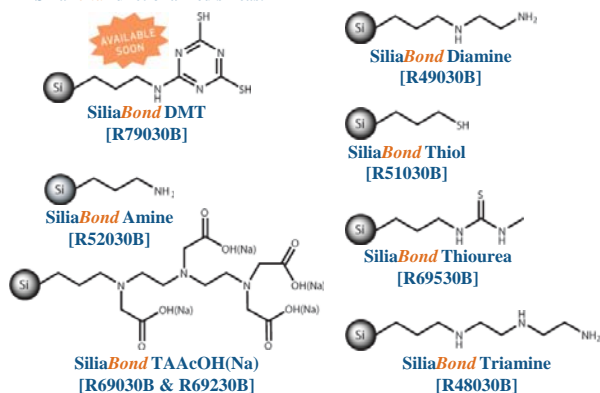
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Introduction

Ruthenium-based catalysts are commonly used in organic synthesis, mainly in olefin metathesis reaction (ROMP) and RCM. Grubbs and Hoveyda-Grubbs catalysts are certainly the most popular ruthenium-based complexes in that field of applications. Complete ruthenium removal can be tedious using conventional methods. SiliCycle has developed innovative functionalized silica-based products that allow to reach the maximal tolerated concentration of the residual ruthenium concentration: the SiliaBond Metal Scavengers.

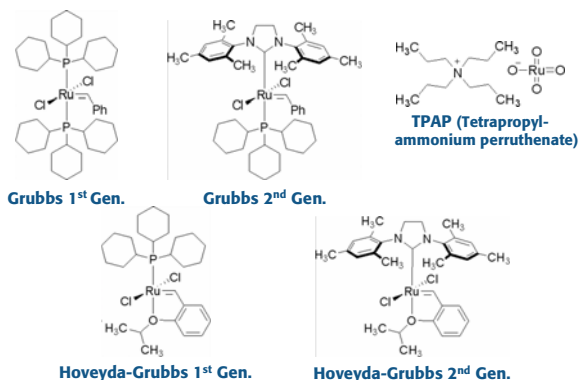
The silica matrix offers many advantages: no swelling, mechanical and thermal stabilities, scalable and ease of use (SPE, flash cartridges and, bulk formats).

Here are the results of ruthenium scavenging efficiency using different SiliaBond functionalized silicas.



Ruthenium-Based Catalysts Scavenged

The following ruthenium-based catalysts were studied using SiliaBond Metal Scavengers under several experimental conditions.



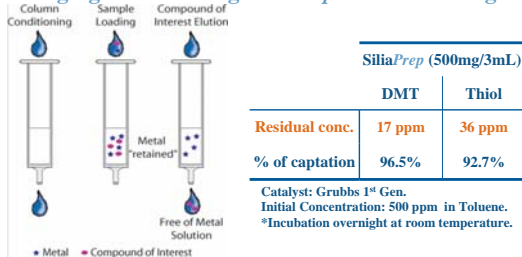
Ruthenium-Based Catalysts Scavenging Results in BULK

A ruthenium scavenging study using SiliaBond Metal Scavengers was conducted with various ruthenium-based catalysts commonly used in organic synthesis to determine the effectiveness and selectivity of silica-bound metal scavengers to remove ruthenium down to very low ppm level. Various parameters were investigated in order to learn more on their influence on the scavengers' robustness as well as to establish the best experimental conditions.

Solvent Scavengers	Ruthenium-Based Catalysts – Residual Ruthenium Concentration (% of captation)													
	Grubbs 1 st Gen.			Grubbs 2 nd Gen.			Hoveyda-Grubbs 1 st Gen.			Hoveyda-Grubbs 2 nd Gen.			TPAP	
	DCM ¹	Toluene ²	DMF ²	DCM ¹	Toluene ²	DMF ²	DCM ¹	Toluene ²	DMF ²	DCM ¹	Toluene ²	DMF ²	DCM ¹	MeCN ²
DMT	5.8 ppm ³ (98.8%)	26 ppm (94.8%)	3.9 ppm ³ (99.0%)	63 ppm (87.3%)	2.3 ppm (99.5%)	5.1 ppm ³ (98.7%)	10 ppm ³ (97.9%)	1.7 ppm ³ (99.7%)	7.1 ppm ³ (98.2%)	1.2 ppm (99.8%)	8.8 ppm ³ (98.2%)	6.1 ppm ³ (98.5%)	1.6 ppm ³ (99.6%)	-
Amine	-	24 ppm (95.1%)	15 ppm (96.8%)	-	39 ppm (92.2%)	-	-	-	-	-	-	-	1.2 ppm (99.7%)	-
Diamine	9.0 ppm (98.3%)	7.0 ppm (98.6%)	6.1 ppm (98.8%)	139 ppm (72.3%)	44 ppm (91.3%)	30 ppm (94.0%)	-	1.7 ppm (99.7%)	10 ppm (97.8%)	-	-	52 ppm (89.5%)	13 ppm ³ (96.6%)	-
Thiol	-	50 ppm (90.0%)	22 ppm (95.5%)	-	-	7.5 ppm (98.5%)	-	14 ppm (97.2%)	35 ppm (92.9%)	-	-	-	15 ppm ³ (96.0%)	-
Thiourea	48 ppm (90.3%)	-	11 ppm (97.6%)	-	-	18 ppm (96.3%)	-	15 ppm (97.0%)	11 ppm (97.6%)	-	-	-	< 1 ppm (99.9%)	-
Triamine	49 ppm (90.3%)	-	24 ppm (95.2%)	137 ppm (72.6%)	-	-	-	36 ppm (92.7%)	23 ppm (95.4%)	-	-	23 ppm (95.4%)	< 1 ppm (99.9%)	-
TAAcOH	-	33 ppm (93.4%)	-	-	-	-	-	-	-	-	-	-	< 1 ppm ³ (99.9%)	49 ppm ³ (90.2%)
TAAcONa	-	19 ppm (96.2%)	-	-	18 ppm (96.4%)	-	10 ppm (97.8%)	8.0 ppm (98.4%)	-	-	-	-	26 ppm ³ (93.3%)	-

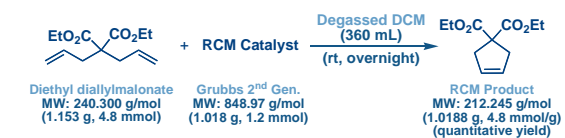
¹Exp. Conditions 8 eq. of SiliaBond Scavenger, 16h, 22°C. ²Exp. Conditions: 8 eq. of SiliaBond Scavenger, 16h, 80°C. ³Only 4 eq. of SiliaBond Scavenger. Initial concentration: 500 ppm for all ruthenium-based catalysts except for TPAP in DCM (385 ppm).

Scavenging Results using SiliaPrep™ SPE Cartridges



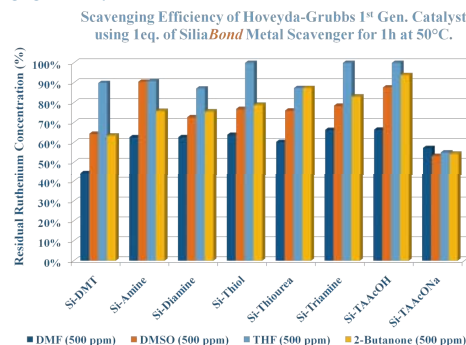
SiliaBond Scavengers-Useful Tool in Organic Synthesis

The use of SiliaBond Metal Scavengers to remove ruthenium catalyst after ring-closing metathesis (RCM) reaction is the most effective purification method (over conventional ones). As demonstrated below, the main advantage is no product lost during the purification step.



Solvent Effect on Scavenging Efficiency

SiliaBond Metal Scavengers can safely be used in any organic and aqueous solvents. However, the nature of the solvent does sometimes influence the scavenging efficiency.



Ruthenium captation	Purification Methods*					
	SiliaBond DMT ¹	Filtration over packed bed of... ² Act. Charcoal	Celite	Silica	Flash Purification Manual	Using SiliaSep TM
	93.3%	72.5%	23.6%	58.3%	69.6%	73.4%

¹Using 4 eq., 16h, 22°C. ²Solution passed directly on a packed bed of various adsorbents, then washed with the same quantity of solvent.

*Quantitative yield obtained for each purification method (adjusted in function of the residual concentration of catalyst). No impurity added with all methods (determined by NMR).

Conclusion

These results illustrate the high efficiency of SiliaBond Metal Scavengers to reach the desired residual ruthenium concentration to single digit ppm of various complexes using different experimental conditions.