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Design and synthesis of supported catalysts on a molecular base

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Abstract

The latest developments in the immobilization of well-defined transition metal-based catalysts relevant for C–C and C–Si coupling reactions are summarized. In this context, both ruthenium- and molybdenum-based metathesis as well as hydrosylation catalysts are covered. Particular attention will be attributed to synthetic aspects of the novel immobilization techniques as well as comparisons between the catalytic activities of the immobilized catalysts and their parent homogeneous systems. Finally, the influence of the chemical nature of both the support and linker on catalysts characteristics will be discussed.

Keywords: Metal-based catalysts; ROMP; Immobilization techniques; Metathesis; Hydrosilylation reactions

1. Introduction

For various reasons, there is an increasing demand for supported versions of modern, highly selective and active catalysts [1]. Modern catalysts significantly add to the total costs of a product, therefore regeneration or reuse are highly desirable. In addition, supported catalysts offer access to high-throughput techniques and continuous flow reactors, respectively. Key issues associated with supported catalysts are: (i) preservation of high activity, (enantio-) selectivity and reaction rates observed with homogeneous catalysts; (ii) ease of catalyst separation; (iii) (multiple) catalyst recycling; and (iv) metal- and contaminant-free products, particularly important in pharmaceutical chemistry. This article is intended to provide a selection of the most significant achievements in this venture related to C–C and C–Si coupling reactions.

2. Results and discussion

2.1. Immobilization strategies

For catalyst immobilization, some important points need to be addressed. In principle, any well-defined organometallic catalyst should be immobilized in a way that its immobilized version resembles the parent catalyst to the maximum extent. In addition, immobilization should be carried out in way that only one single catalytic species is formed. This implies that post polymerization transformations should be reduced to the absolute minimum. In terms of linkers, these should provide enough stability to ensure the permanent fixation of the entire catalyst, i.e. metal and ligand sphere, to the support. In addition, the support and linker should be chosen in a way that the immobilized catalyst remains accessible to the substrate, i.e. diffusion shall be reduced to a minimum. Finally, no additional restriction in terms of accessibility or steric constraints must be added by the support, since this would result in significant changes of the ligand sphere around the metal center. Particularly, in cases where this ligand sphere is chiral, this must be expected to give raise to unwanted changes in enantioselectivity.

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2.2. Immobilization of metathesis catalysts

Metathesis belongs nowadays to the most potent C–C bond forming reactions [2–5], allowing the synthesis of both well-defined, functional polymers and complex architectures including medium-sized [6] and large ring structures [7,8]. The findings that these reactions can be carried out in an enantioselective way [9,10] widened the range of applications from commodity chemicals to the synthesis of chiral compounds relevant to pharmaceutical chemistry. From a synthetic chemist's point of view, the applicability of metathesis to both polymer and organic chemistry must be regarded as a direct consequence of the achievements in organometallic chemistry [11–13]. The development of well-defined, single component metathesis catalysts smoothed the way for metathesis-based reactions such as ring-opening metathesis polymerization (ROMP), 1-alkyne polymerization, acyclic diene metathesis (ADMET), cross-metathesis (CM), tandem metathesis, enyne metathesis, and ring-opening cross metathesis (ROCM), and made them attractive for the scientific community [8,10,14–19]. Comprehensive summaries on supported metathesis catalysts have been given recently [20–23], however, the most relevant contributions by our group are outlined in the following.

2.2.1. Immobilization through the N-heterocyclic carbene ligand

The first Ru-based metathesis catalyst was immobilized on poly(styrene-*co*-divinylbenzene) via the *N*-heterocyclic carbene (NHC-) as reported by Blechert and coworkers [24,25]. In order to overcome diffusion problems related to the swollen, low cross-linked network of the Merrifield support, we aimed on the synthesis of non-porous supports

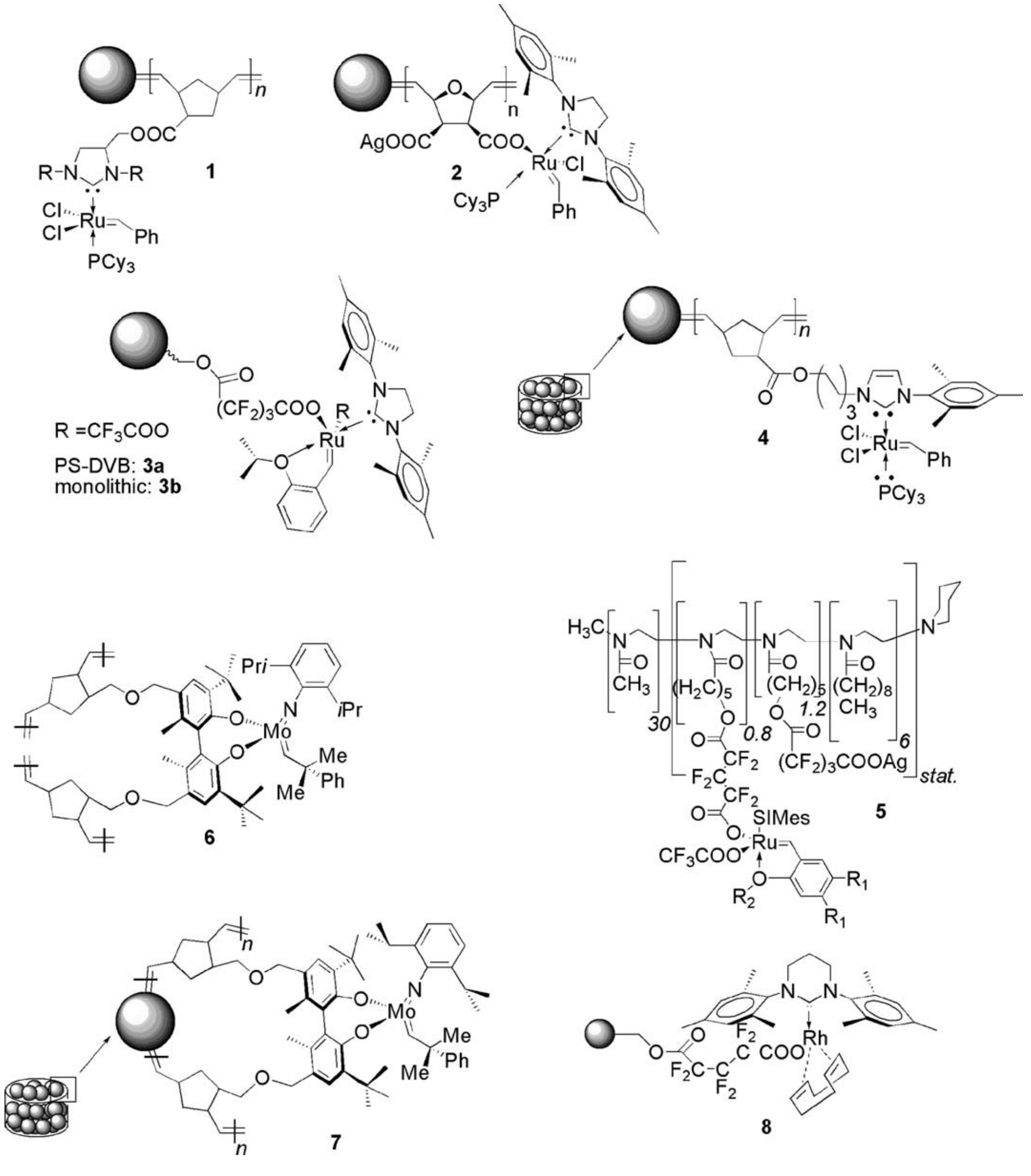


Fig. 1. Structure of supported catalysts **1**–**8**.

suitable for continuous flow experiments, e.g. monolithic supports. Using a ROMP-based protocol, we were able to synthesize functionalized monoliths [26–28]. Generally speaking, the term ‘‘monolith’’ applies to any single-body structure containing interconnected repeating cells or channels. Such materials are commonly prepared from inorganic mixtures, e.g. by a sintering process to form ceramics, or from organic compounds, e.g. by a crosslinking polymerization. Here, the term ‘‘monolith’’ comprises crosslinked, organic materials which are characterized by a defined porosity and which support interactions/reactions between this solid and the surrounding liquid phase. Besides advantages such as lower backpressure and enhanced mass transfer between the liquid phase and the surface-bound catalysts, the ease of fabrication as well as the many possibilities in structural alteration are advantageous. For catalyst immobilization, monoliths were designed in a way that only interparticle porosity was generated, whereas the structure-forming microglobules were virtually non-porous. The synthesis itself was simply accomplished by mixing norborn-2-ene with the appropriate crosslinker and the catalysts in a (usually 1:1) mixture of toluene and 2-propanol. After 30 min, the synthesis of the monolithic support was accomplished and small amounts of unreacted monomers and catalyst were removed by flushing of the support. Taking advantage of the ‘‘living’’ character of ruthenium-catalyzed ROMP used for their synthesis and the high tolerance of the catalytic system towards different functional monomers we were able to graft cationic *N*-heterocyclic carbene precursors onto the surface of the monoliths. Tentacle-like polymer chains attached to the surface were formed. The catalyst was quantitatively removed by flushing with ethyl vinyl ether. This procedure was typical for all immobilizations involving monolithic supports. The free NHCs necessary for catalyst formation were then simply generated by passing a strong base over the support. In a last step the catalyst was formed and simultaneously immobilized by passing a solution of $RuCl_2(PCy_3)_2(=CHPh)$ over the rigid rod. Loadings of up to 1.4% of Grubbs-catalyst on NHC base were achieved (Fig. 1, structure **1**) [28]. Both the tentacle-type structure and the designed microstructure of the support reduced diffusion to a minimum. In a benchmark reaction with diethyldiallyl malonate (DEDAM), these properties directly translated into high average turn-over frequencies (TOFs) of up to 0.5 s^{-1}.

2.2.2. Immobilization through halogen exchange

The group of Mol and coworkers were the first to report on the synthesis of a poly(styrene-co-divinylbenzene-) (PS-DVB-) supported version of $RuCl_2(PCy_3)_2(=CHPh)$ [29]. As for other ruthenium catalysts containing phosphine ligands, a rapid decrease in reactivity was observed during consecutive cycles in the RCM of DEDAM. A comparably low total turn-over number (TON) of ca. 60 was reported for this reaction. In addition, the ruthenium content in the products was as high as 3800 ppm. In an alternative approach, we again aimed on a monolith-supported second-generation Grubbs catalysts containing the 1,3-dimesityldihydroimidazolin-2-ylidene (SIMes) ligand [30,31]. Surface-derivatization of the monolith was carried out with 7-oxanorborn-2-ene-5,6-dicarboxylic anhydride followed by conversion of the grafted poly(anhydride) into the corresponding poly-silver salt. This poly-silver salt was used for the halogen exchange with the second-generation Grubbs catalyst $RuCl_2(PCy_3)(SIMes)(=CHPh)$ (Fig. 1, structure **2**). In the benchmark reaction with DEDAM, TONs close to 1000 were achieved. This is comparable to the TON of 1300, which was observed for the parent system $RuCl_2(PCy_3)$(SIMes)(=CHPh) under identical conditions (i.e. solvent, substrate, temperature, concentration, educt: catalyst ratio). It is worth mentioning that these systems benefit from the presence of free silver carboxylate groups, which act as a reversible scavenger for phosphine. Thus, the use of monocarboxylic acids such as 7-oxanorborn-2-ene-5-carboxylic acid instead of the anhydride resulted in a supported catalyst that showed significantly reduced TONs in RCM, accompanied by a rapid loss of phosphine. In view of these results we tried to further enhance the reactivity of Ru-based metathesis catalysts and to avoid the use of phosphine ligands. In due consequence, numerous variations in Hoveyda-type catalysts of the general formula $RuCl_2$(SIMes)(=CH-2-(2-PrO-C_6H_4)) were carried out. Among the most important findings was that the exchange of chlorine by a strongly electron-withdrawing group, in fact, enhanced the reactivity of these systems without sacrificing their high stability [32]. Thus, $Ru(CF_3CO_2)_2$(SIMes)(=CH-2-(2-PrO)-C_6H_4) was a highly active catalyst in RCM both at 45 and 20 °C, respectively, exceeding known ruthenium-based catalysts in catalytic activity. TONs up to 1800 and 1400, respectively, were achieved in the RCM of DEDAM. High activity was also observed in enyne metathesis and ring-opening-cross metathesis using norborn-5-ene and 7-oxanorborn-5-ene-derivatives. Supported versions were synthesized by immobilizing $RuCl_2$(SIMes)(=CH-2-(2-PrO)-C_6H_4) on a perfluoroglutaric acid-derivatized hydroxymethylated Merrifield resin. Ru(polymer-CH_2-O-CO-CF_2-CF_2-CF_2-COO)(CF_3CO_2)(=CH-2-(2-PrO)-C_6H_4)(SIMes) (**3a**) was finally obtained by substitution of the remaining Cl-ligand of the parent catalyst via addition of CF_3COOAg (Fig. 1, structure **3**). Excellent activity in RCM was observed, TONs up to 1100 were achieved in stirred batch RCM experiments. A comparison with the parent system is given in Table 1. Leaching of ruthenium into the reaction mixture was low, resulting in a ruthenium-content <70 ng/g in the final RCM-derived products. Finally, a monolith-supported version (**3b**) of this catalyst was prepared and used in continuous flow experiments [33]. TOFs of 0.11 s^{-1} were observed, TONs were >500. In a similar approach, $RuCl_2(PCy_3)$(1-(2,4,5-trimethylphenyl)-3-(6-hydroxyhexyl)-imidazol-2-ylidene)(CHPh) [34] was immobilized on a norborn-5-ene-2-ylcarboxylic chloride derivatized monolithic support [35]. A catalyst loading of 0.55 wt.%

Table 1
Summary of catalytic activities

Compound	Catalyst	Compound (mol%)	TON
DEDAM	Grubbs-Herrmann	0.05	1300
1,7-Octadiene	Grubbs-Herrmann	0.08	1000
Diallyldiphenylsilane	Grubbs-Herrmann	0.10	400
Methyl *trans*-3-pentenoate	Grubbs-Herrmann	0.01	600
t-Butyl *N*,*N*-diallylcarbamide	Grubbs-Herrmann	0.10	770
DEDAM	Grubbs-Hoveyda	0.05	1500
1,7-Octadiene	Grubbs-Hoveyda	0.05	1700
Diallyldiphenylsilane	Grubbs-Hoveyda	0.10	180
Methyl *trans*-3-pentenoate	Grubbs-Hoveyda	0.10	60
t-Butyl *N*,*N*-diallylcarbamide	Grubbs-Hoveyda	0.10	100
DEDAM	**3b**	0.05	200
1,7-Octadiene	**3b**	0.05	1100
Diallyldiphenylsilane	**3b**	0.10	100
t-Butyl *N*,*N*-diallylcarbamide	**3b**	0.10	350
N,*N*-Diallyltrifluoroacetamide	**3b**	0.10	70

Conditions: 2 h, 2 mL CH_2Cl_2, 45 °C; Grubbs-Hoveyda catalyst: $RuCl_2$(=CH-2-(2-Pr-O-C_6H_4)(SIMes).

on the monolithic support was achieved. The monolith was dried, removed from the cartridge, cut in pieces of 0.5 cm thickness and encased. Such encased monolithic discs simultaneously served as support, reaction vessel and filtration unit and were used in commercially available machines for combinatorial chemistry and high-throughput screening, respectively (Fig. 1, structure **4**). The observed reactivity in RCM was again comparable to that obtained with the parent system. In all cases, Ru-leaching was ≤3%, the average contamination of products with ruthenium was around 70 ppm.

In view of the high reactivity of trifluoroacetate-substituted ruthenium-based systems and ongoing projects in the stereo- and regioselective cyclopolymerization of heptadiynes [36–38], we investigated whether these catalysts would be suitable for this purpose. As a matter of fact, $Ru(CF_3COO)_2$(SIMes) (=CH-(2,4,5-$(MeO)_3$-C_6H_4) turned out to be an excellent catalyst for the cyclopolymerization of diethyl dipropargylmalonate (DEDPM), allowing class VI living polymerisations [39]. A supported version of this catalyst was prepared by attaching it to a poly(2-oxazoline)-derived block-copolymer (Fig. 1, structure **5**). This supported catalyst allowed the cyclopolymerization of DEDPM in water under micellar conditions. At this point it should be emphasized that these have been the first Ru-catalyzed (cyclo-) polymerization of alkynes ever reported.

2.3. Molybdenum-based catalysts

Chiral, molybdenum-based Schrock catalysts are still the standard in asymmetric metathesis reactions. In principle, Schrock catalysts can be immobilized either via the alkylidene, the imido, the alkoxide [40,41] or phenoxide ligand, respectively. In contrast to systems immobilized via the alkylidene, neither the imido nor the alkoxide ligand of a Schrock catalyst disassociates from the metal center in course of the catalytic cycle of a metathesis reaction. The first immobilized version of this catalyst was described by Schrock and coworkers utilizing free radical polymerisation [42,43]. Alternatively, a permanently polymer-immobilized version of Schrock's molybdenum catalyst was realized by our group via polymerization of chiral 5,5′-bis(norborn-5-ene-2-ylmethylenoxymethyl)-3,3′-di-*t*-butyl-6,6′-dimethyl-biphen-2,2′-diol followed by reaction with the catalyst precursor Mo(*N*-2,6-*i*-$Pr_2C_6H_3$)($CHCMe_2Ph$)$(OSO_2CF_3)_2$(-$CH_3OCH_2CH_2OCH_3$) (Fig. 1, structure **6**) [44]. With this supported catalyst, chiral 5-, 6- and 7-membered heterocycles were synthesized via RCM from (pro-) chiral substrates. High yields and enantiomeric excess (ee) similar to that obtained with the parent system were achieved within short reaction times (Table 2). The catalyst showed low molybdenum leaching during RCM, and was easily separated and recycled. A monolith-supported version was prepared by a similar protocol as was used for the immobilization of $RuCl_2(PCy_3)$(1-(2,4,5-trimethylphenyl)-3-(6-hydroxyhexyl)-imidazol-2-ylidene)(CHPh) (vide supra). After rod formation was complete and unreacted monomer had been removed from the support, the polymerizable analogue of BIPHEN, i.e. (R)-5,5′-bis-(norborn-5-ene-2-ylmethyleneoxymethyl)-3,3'-di-*t*butyl-6,6′-dimethyl-biphen-2,2′-diol [42], was grafted to the surface. The grafted phenolic moieties were deprotonated by adding $KN(Si(CH_3)_3)_2$ and subsequently reacted with the catalyst precursor Mo(*N*-2,6-*i*Pr_2-C_6H_3)($CHCMe_2Ph$)$(OTf)_2$ DME (Fig. 1, structure **7**).

Table 2
Comparison of reactivity in asymmetric RCM and desymmetrization reactions

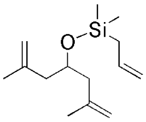
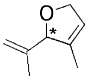
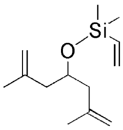
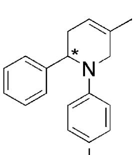
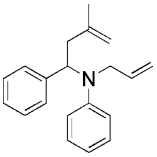
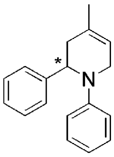
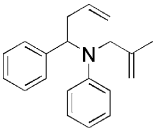
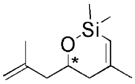
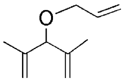
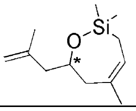
Educt	Product	**6** (mol%)	**6**		Parent system	
			Yield	ee	Yield	ee
		3.4	97	90 ± 1	86	89
		3.3	61	95 ± 1	–	–
		5.2	22	50 ± 5	21	45
		2.8	16	53 ± 5	35	47
		4.0	96	90 ± 2	97	89

Table 3
Summary of results for the hydrosilylation of alkynes and alkenes using parent RhCl(1,3-bis(2,4,6-trimethylphenyl)-3, 4, 5, 6-tetrahydropyrimidin-2-ylidene(COD) (**8a**) and the supported version (**8**)

Main product	Catalyst (mol%) yield (%)	TON$_{max}$	Catalyst (mol%) yield (%)	TON$_{max}$
1-Phenyl-2-(triethylsilyl)ethene	**8a** (0.08) 54	680	**8** (0.07) 38	540
1-Phenyl-2-(dichloromethylsilyl)ethene	**8a** (0.08) 65	810	**8** (0.07) 85	1210
1-Phenyl-2-(trimethoxysilyl)ethene	**8a** (0.08) 34	430	**8** (0.07) 46	660
1-(Triphenylsilyl)hex-1-ene	**8a** (0.07) 24	340	**8** (0.05) 45	900
1-(Dichloromethylsilyl)hex-1-ene	**8a** (0.08) 72	900	**8** (0.07) 89	1270
1-(Trimethylsilyl)-2-(dichloromethylsilyl)ethene	**8a** (0.08) 41	510	**8** (007) 34	490
1-(Trimethoxysilyl)hex-1-ene	**8a** (0.08) 61	760	**8** (0.05) 66	1320
1-(Triethylsilyl)stilbene	**8a** (0.08) 62	780	**8** (0.07) 52	740
1-(Triethylsilyl)hex-1-ene	**8a** (0.08) 71	890	**8** (0.06) 34	570
1-Phenyl-2-(triethylsilyl)ethane	**8a** (0.08) 37	460	**8** (0.05) 44	880
1-(Triethylsilyl)hexane	**8a** (0.1) 18	180	**8** (0.07) 11	160
1-(Triethylsilyloxy)cyclohexene	**8a** (0.08) 80	1000	**8** (0.07) 51	730
1-(Triphenylsilyloxy)cyclohexene	**8a** (0.08) 25	310	**8** (0.05) 11	220
Triethylsilyloxymethylbenzene	**8a** (0.1) 53	530	**8** (0.09) 44	490
1-(Triethylsilyloxy)-1-(4-chlorophenyl)ethane	**8a** (0.09) 27	300	**8** (0.1) 22	220
Triethylsilyloxymethyl-4-fluorobenzene	**8a** (0.09) 75	830	**8** (0.07) 22	310

Reactions were run in dimethoxyethane for 12 h, $T = 80$ °C.

Following this protocol, a catalyst loading of 0.7 wt.% was achieved [35]. The catalyst-loaded monolith was again cut in pieces 1 cm in height and encased and used in high-throughput screening (HTS) enantioselective RCM experiments. Yields and ee's were again comparable to those reported for the parent system.

2.4. Immobilization of Rh-catalysts for hydrosylation

So far, immobilization of Rh-based hydrosylation catalysts on both organic and inorganic supports has been accomplished by various routes [45]. Alternatively, recycling issues have successfully been addressed by a fluorous approach [46]. For the immobilization of RhCl(1,3-bis(2,4,6-trimethylphenyl)-3, 4, 5, 6-tetrahydropyrimidin-2-ylidene(COD) (**8a**), (COD = cycloocta-1,5-diene) the approach described for the immobilization of ruthenium-based metathesis catalysts was chosen (vide supra) [30–33]. Thus, hydroxymethylated poly(styrene-*co*-divinylbenzene) (hydroxymethyl PS-DVB) was reacted with hexafluoroglutaric anhydride to yield the corresponding polymer-immobilized perfluorocarboxylic acid. Conversion into the silver salt was accomplished via reaction with NaOH and $AgNO_3$. Finally, this polymer-bound silver salt was reacted with the precursor to yield the polymer-supported version (**8**) of the catalyst (Fig. 1, structure **8**) [45]. A catalyst loading of 0.6 wt.% was accomplished. Both the parent system and the supported catalyst were used in the hydrosylation of alkynes and 1-alkenes. Interestingly, the supported version displayed similar, in most cases enhanced reactivity in the hydrosylation of alkynes, 1-alkenes, aldehydes and ketones. Thus, TONs in the range of 160–1320 were obtained using 0.05–0.07 mol% of catalyst (Table 3). This can be explained by the heterogeneous nature of the catalysts, effectively reducing bimetallic decomposition reactions. Leaching of the metal from the supported catalyst into reaction mixture was comparably low, resulting in an average Rh-content of 130 ppm.

3. Summary

Various immobilization techniques have been presented. As a basic idea, preformed catalysts are used for immobilization, reducing the immobilization step itself to one or two synthetic steps. This results in well-defined supported catalysts, whose reactivity can be compared to the parent systems, a fact, which is best illustrated by the use of chiral catalysts. In addition, influences of the support and/or linker can be identified. In general, metal leaching is low, allowing the synthesis of products with metal contaminations in the low ppb range.

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