

Oznaka poročila: ARRS-RPROJ-ZP-2014/71



ZAKLJUČNO POROČILO RAZISKOVALNEGA PROJEKTA

A. PODATKI O RAZISKOVALNEM PROJEKTU

1. Osnovni podatki o raziskovalnem projektu

Šifra projekta	Z1-4219
Naslov projekta	Reakcije N-heterocikličnih karbenov s silicijevimi spojinami
Vodja projekta	28565 Matjaž Koželj
Tip projekta	Z Podoktorski projekt
Obseg raziskovalnih ur	3400
Cenovni razred	A
Trajanje projekta	07.2011 - 06.2013
Nosilna raziskovalna organizacija	104 Kemijski inštitut
Raziskovalne organizacije - soizvajalke	
Raziskovalno področje po šifrantu ARRS	1 NARAVOSLOVJE 1.04 Kemija 1.04.04 Organska kemija
Družbeno-ekonomski cilj	13.01 Naravoslovne vede - RiR financiran iz drugih virov (ne iz SUF)
Raziskovalno področje po šifrantu FOS	1 Naravoslovne vede 1.04 Kemija

B. REZULTATI IN DOSEŽKI RAZISKOVALNEGA PROJEKTA

2. Povzetek raziskovalnega projekta¹

SLO

V projektu sem poskušal združiti dve najhitreje rastoči raziskovalni veji na področju organske/organokovinske kemije, ki nista vključeni v obstoječe raziskovalno delo slovenskih znanstvenikov. Kemija organskih silicijevih spojin je bila v Sloveniji omejena le na nekaj primerov sol-gel postopkov alkoxisilanov, na drugi strani pa je kemija N-heterocikličnih karbenov (NHC) skoraj popolnoma prezrta. Silicijeva spojine postajajo iz dneva v dan pomembnejše pri pripravi posebnih materialov, ki so zasnovani že na molekularnem nivoju, zato je ta projekt lahko ključen pri zagotavljanju

podpore novim tehnologijam. Znanje, ki bo pridobljeno o NHC spojinah tekom tega projekta, se lahko v prihodnosti uporabit tudi za pripravo kompleksov prehodnih kovin, ki so pomembni katalizatorji v organskih pretvorbah, tako je zagotovljeno nadaljevanje tega projekta.

Osnovna ideja je preučiti uporabo N-heterocikličnih karbenov kot katalizatorjev v pretvorbah, ki vključujejo reakcije na silicijevem centru. Ocenjujem, da lahko karbeni aktivirajo silicijeve spojine, tako da so te bolj reaktivne, pretvorbe pa zato potečejo hitreje. N-heterociklični karbeni lahko delujejo kot močne baze in tudi kot močni nukleofili, ti dve lastnosti sta odločilni pri zagotavljanju dovolj velike katalitske učinkovitosti pri kataliziranju reakcij na siliciju.

Prvi cilj projekta je bil preveriti uporabnost N-heterocikličnih karbenov pri pripravi poliedričnih silseskvioksanov, to je preveriti, kako in ali sploh karbeni pospešujejo kondenzacijo, dekondenzacijo in rekondenzacijo trifunkcionalnih siloksanov (T-siloksanov).

Drugi cilj je bil pojasniti mehanizem delovanja/aktiviranja silicijevih spojin, še posebej pa trifunkcionalnih silanov, z N-heterocikličnimi karbeni. To vključuje pripravo in izolacijo stabilnih kompleksov N-heterocikličnih karbenov s siloksanskimi silicijevimi spojinami. Tu je predvsem zanimivo področje raziskav stabilnosti 1,3-disubstituiranih imidazolijevih silanolatov, ki bi lahko služili kot stabilni prekursorji za *in situ* pripravo prostih karbenov.

Tretji cilj je bil preveriti interakcije med N-heterocikličnimi karbeni in ostalimi silicijevimi spojinami, še posebej tistimi, ki so tehnološko pomembne. To so najprej reakcije utrjevanja/premreževanja polisiloksanov, kar bi lahko dosegli z uporabo N-heterocikličnih karbenov ali njihovih prekursorjev kot katalizatorjev.

Nosilec projekta/vlagatelj ima bogate izkušnje s pripravo organskih silicijevih spojin, še posebej z alkoxisilani (doktorska disertacija). NHC so v veliko primerih tesno povezani z imidazolijevimi ionskimi tekočinami, ki so tudi bile predmet omenjene disertacije. Zato je bil ta projekt zamišljen kot logično nadaljevanje raziskav, ki so bile opravljene v času doktorskega študija. Razlog za nadaljevanje raziskav na področju silicijeve kemije so prav gotovo odlični in zanimivi rezultati, ki so bili doseženi na tem področju v preteklosti, saj sta bili kar dve odkritji implementirani v svetovno pomembne industrijske proizvodne procese.

ANG

In this project I tried to combine the two fastest-growing branches of research in organic/organometallic chemistry, which have not been very much involved in the existing research work of Slovenian scientists. Chemistry of organic silicon compounds in Slovenia was limited to a few examples of sol-gel processing of alkoxysilanes. On the other hand, the chemistry of N-heterocyclic carbenes (NHC) has been almost completely ignored. Silicon compounds became more and more important for the preparation of special materials, which are tailored on molecular scale so this kind of project could be very strategic in order to support novel technologies. The knowledge, which will be gained on the NHC compounds during this project could be further exploited for the preparation of transition metallic complexes, which are important catalysts for organic transformations. This ensures a possible continuation of this project.

The basic idea is to investigate the use of N-heterocyclic carbenes as potential catalysts in transformations involving reactions on silicon center. I estimate that carbenes could activate silicon compounds, so they are more reactive and the reaction proceeds faster, resulting in shorter conversion

periods. N-heterocyclic carbenes can act as a strong base, as well as strong nucleophiles, these two features are critical in ensuring sufficient catalytic efficiency in reactions on silicon.

The first objective of the project was to examine the suitability of N-heterocyclic carbenes in preparation of polyhedral silsesquioxanes, that is to examine how and if carbenes promote condensation, decondensation and recondensation of trifunctional silanes (T-siloxanes).

The second objective was to clarify the mechanism of catalytic action / activation of silicon derivatives, especially trifunctional silanes with N-heterocyclic carbenes. This includes the preparation and isolation of stable complexes of N-heterocyclic carbenes with siloxane silicon compounds. A particularly interesting area of this study research is the stability of 1.3-disubstituted imidazolium silanates, which could serve as stable precursors for *in situ* preparation of free carbenes.

Another aim was to check the interactions between N-heterocyclic carbenes and other silicon compounds, especially those which have significant technological importance. The crosslinking/hardening of siloxanes polymers could be catalyzed by N-heterocyclic carbenes or their cryptoforms.

The project leader/applicant has extensive experience in preparing organic silicon compounds, especially with alkoxysilanes (PhD thesis). NHCs are in many cases closely related to imidazolium ionic liquids, which were also subject to that thesis. Therefore, this project was conceived as a logical follow-up to surveys conducted during the doctoral program. The reason for the continuation of research in the field of silicon chemistry were certainly excellent and interesting results that have been achieved in this area in the past because they were implemented into two inventions in the world's important industrial manufacturing processes.

3. Poročilo o realizaciji predloženega programa dela na raziskovalnem projektu²

Delo v okviru projekta je potekalo v skladu z načrtom, ki je bil predložen prijavi. Poleg načrtovanega dela pri tem projektu, se je vodja raziskovalnega projekta še podoktorsko izpopolnjeval v Kanadi na Institut de Recherche d'Hydro-Quebec, kjer je opravila raziskave na ionskih tekočinah, ki vsebujejo siloksanske substituentne in na pripravi novih prevodnih soli, ki so v nekaterih primerih derivati petčlenskih heterociklov (azolati), tako da je bilo tudi delo v Kanadi tesno povezano s tematiko, ki je bila obravnavana v tem projektu.

Največ dela je bilo posvečeno sintezi prekurzorjev heterocikličnih karbenov in kriptokarbenov (WP1 in WP2) ter interakciji karbenov s poliedričnimi silseskvioksani (WP3). Delo, ki je bilo predlagano v okviru teh delovnih sklopov je bilo skoraj v celoti realizirano, zmanjšal sem le količino časa posvečenega pripravi nekaterih neobstojećih kriptokarbenov, ker kljub intenzivnem eksperimentiranju spojine niso bile stabilne in kot take niso bile primerne za uporabo v katalitskih reakcijah. Rezultati tega dela so bili objavljeni kot en patent in en članek v Dalton Transactions, katerega lahko najdete v priložnosti in se ne bom spuščal v podrobno analizo teh rezultatov.

V zadnjem letu projekta pa sem večino časa posvetil študiju interakcije s silanoli (WP4) in drugimi silicijevimi spojinami (WP5). Interakcije silanolov so zapletene in kljub več poskusom priprave imidazolijev silanolatov, teh spojin nisem mogel izolirati, saj je takoj potekla kondenzacija silanolov v siloksane in posledično so karbeni hidrolizirali v prisotnosti vode. eksperimenti so bili izvedeni tako z alkil kot fenil silanoli. Pri vseh je bila kondenzacija na sobni temperaturi zelo hitra. Delo na WP4 ni bilo mogoče dokončati v skladu s predpostavljenimi cilji, ker je bila reaktivnost silanolov in karbenov nepredvidena. Tako ostajajo te usmeritve za delo v prihodnje.

Od ostalih silicijevih spojin sem podrobno preučeval tudi alkoksisilane, ki so najbolj pogosto zastopane silicijeve spojine. Kljub nekaterim teoretičnim izračunom, da naj bi tvorili stabilne hipervalentne komplekse z N-heterocikličnimi karbeni, takšnih kompleksov kljub trudu in večkratnem preizkušanju nisem uspel izolirati ne zaznati s spektroskopskimi tehnikami (NMR).

Kljub temu pa sem uspel raziskati preestrenje alkoksisilanov in drugih estrov z mediacijo N-heterocikličnih karbenov, kar je gotovo zanimiva ugotovitev, katere rezultati bodo v prihodnosti predstavljeni znanstveni skupnosti kot znanstveni članek.

4. Ocena stopnje realizacije programa dela na raziskovalnem projektu in zastavljenih raziskovalnih ciljev³

Projekt je bil zasnovan na več nivojih, prvi nivo je bila sinteza različnih azolijevih soli, ki lahko služijo kot prekursorji N-heterocikličnih karbenov ali prekursorji ionskih tekočin, če le vsebujejo primerne anione, ki znižajo temperaturo tališča azolijevih soli. V sklopu projekta sem pripravil več različnih prekursorjev heterocikličnih karbenov, predvsem imidazolijeve in imidazolinijeve soli, iz katerih se pridobi karbene z deprotonacijo. Imidazol-2-ilidene sem pripravil tudi z redukcijo imidazol-2-tionov s kovinskim kalijem. Na podoktorski izmenjavi v Kanadi sem izpopolnil svoje znanje na področju ionskih tekočin in elektrokemijskih lastnosti le teh in jih uporabil za pripravo elektrolitov za elektrokemijske sklope. Po klasični kondenzacijski reakciji (Pellizzari) sem pripravil tudi serijo različnih 1,2,4-triazolijevih soli, s pomočjo teh spojin bomo v prihodnosti študirali vpliv substitucije na toplotne lastnosti teh soli, kar je pomembno pri načrtovanju elektrolitov, ki temeljijo na ionskih tekočinah.

Glavne raziskovalne hipoteze pa so bile iz področja silicijeve kemije in sicer: **kataliza priprave poliedričnih silseskvioksanov z N-heterocikličnimi karbeni**, ki je bila zelo dobro raziskana in predstavlja glavnino publiciranih rezultatov; **pojasniti katalizo pretvorb silicijevih spojin z N-heterocikličnimi karbeni**, ta naloga je zelo zahtevna, saj sem pri svojih eksperimentih dobil rezultate, ki govorijo v prid tako Brønstedtovi kot Lewisovi bazni katalizi in ni bilo mogoče narediti jasnih in nedvoumnih zaključkov; **interakcije N-heterocikličnih karbenov z ostalimi silicijevimi spojinami** so bile preverjene na modelnih spojinah, vendar detekcija teh kompleksov s tehnikami, ki so bile na voljo ni bilo mogoče. Poleg pokazane katalize pri kondenzaciji silseskvioksanskih silicijevih zvrsteh sem raziskal tudi katalizo preestrenja različnih estrov silicijevih kislin (alkoksisilanov) in estrov karboksilnih kislin. Karbeni so učinkoviti katalizatorji teh pretvorb, zato v prihodnosti načrtujem publikacijo teh rezultatov. Kljub nekaj dobrim rezultatom še vedno ostaja nekaj nadaljnjih možnosti za raziskovanje na področju karbenov in silicijevih spojin.

5. Utemeljitev morebitnih sprememb programa raziskovalnega projekta oziroma sprememb, povečanja ali zmanjšanja sestave projektne skupine⁴

V zadnjem letu trajanja projekta do spremembe sestave programske skupine ni prišlo (podoktorski projekt). Zaprošil sem edino za podaljšanje trajanja projekta, ker je kljub temu, da se bi moral projekt zaključiti, bilo še vedno potrebno izvesti eksperimente, ki niso bili predlagani ob začetku projekta, vendar se je tekom raziskovalnega dela pokazalo, da je njihova izvedba nujna za izpopolnitev rezultatov in tako omogočiti dobro publikacijo rezultatov projekta. Ker v tistem trenutku nisem mogel oceniti koliko časa natančno bo to trajalo, sem predlagal podaljšanje do skrajnega roka.

6. Najpomembnejši znanstveni rezultati projektne skupine⁵

Znanstveni dosežek		
1.	COBISS ID	5241626
	Vir:	COBISS.SI
Naslov	SLO	N-heterociklični karbeni - katalizatorji za pripravo poliedričnih silseskvioksanov
	ANG	N-Heterocyclic carbenes - catalysts for the preparation of polyhedral silsesquioxanes
Opis	SLO	Ta publikacija je najpomembnejši rezultat slovenskega projekta Z1-4219. V tem delu je predstavljena sinteza določenih N-heterocikličnih karbenov (NHC) in njihovih prekursorjev. NHC lahko uporabimo kot učinkovite katalizatorje za poliedrične silseskvioksane. NHC katalizirajo tudi premestitve skupin med dvema že tvorjenima skeletoma. V tem postopku lahko uporabimo obstojne NHC, ki jih je mogoče izolirati, ali njihove prekursorje, imenovane tudi kriptokarbeni. Poliedrične silseskvioksane lahko pripravimo iz hidrolizatov funkcionalnih trialkoksisilanov, silseskvioksanskih smol ali iz že obstoječih poliedričnih silseskvioksanov, če jih izpostavimo organokatalitičnem delovanju NHC v

		organskem topilu na ustrezni temperaturi. Ker so karbeni odlično topni v reakcijski zmesi, lahko dosežemo dobre izkoristke priprave poliedričnih silsesquioxanov tudi pri koncentracijah NHC nižjih od 1 mol %.
	ANG	This publication is important result of slovenian research project Z1-4219. Syntheses of various N-Heterocyclic carbenes (NHC) and their precursors is presented. NHC could be used as powerful catalysts for the preparation of various polyhedral silsesquioxanes. NHCs also catalyze a rearrangement of existing cages and a scrambling between two different cages. For this purpose either free isolable carbenes or their cryptoforms could be used. Polyhedral silsesquioxanes could be prepared from hydrolyzates of trifunctional silanes, silsesquioxane resins or existing silsesquioxane cages in process where these precursors are exposed to organocatalytic action of carbenes in organic solvent at appropriate temperature. Carbenes are excellently soluble in reaction media so they are active at a concentrations as low as 1 mol%.
Objavljeno v		Royal Society of Chemistry; Dalton transactions; 2013; Vol. 42, iss. 26; str. 9432-9436; Impact Factor: 3.806; Srednja vrednost revije / Medium Category Impact Factor: 2.298; A': 1; WoS: EC; Avtorji / Authors: Koželj Matjaž, Orel Boris
Tipologija		1.01 Izvirni znanstveni članek
2.	COBISS ID	5112858 Vir: COBISS.SI
	Naslov	SLO Uporaba POSS spojin za spreminjanje omakalnih lastnosti TISS premazov ANG Application of POSS compounds for modification of the wetting properties of TISS paint coatings
	Opis	SLO V tem poglavju so opisane možnosti za krojenje površinskih lastnosti od debeline neodvisnih spektralno selektivnih premazov. POSS nanokompoziti so bili uporabljeni kot dodatki za zmanjševanje površinske energije grobih TISS premazov, kjer so pokazali izrazito povečanje omakalnih kotov za vodo in je na ta način možno doseči samočistilne lastnosti teh premazov. Prav tako so bili POSS spojine v različnih koncentracijah dodane gladkim lakom za zaščito polimernih pokrivnih plošč, vendar tu ni bilo možno doseči velikih omakalnih kotov za vodo. ANG In this chapter possibilities for tuning of surface properties of thickness insensitive spectrally selective paint coating is discussed. POSS nano-composites were used as low surface energy additives for rough TISS coatings, where considerable improvements of contact angles for water in same manner anti-wetting properties of coatings with smooth surfaces for use as protective lacquers for polymeric glazing were studied in relation to the concentration of POSS compound in prepared coatings.
	Objavljeno v	Wiley-VCL; Polymeric materials for solar thermal applications; 2012; str. 267-286; Avtorji / Authors: Jerman Ivan, Orel Boris, Koželj Matjaž
	Tipologija	1.16 Samostojni znanstveni sestavek ali poglavje v monografski publikaciji
3.	COBISS ID	5198618 Vir: COBISS.SI
	Naslov	SLO Materiali pri pripravi selektivnih premazov za uporabo v gradbeništvu ANG Materials aspects of solar paint coatings for building applications
	Opis	SLO To poglavje je sestavljeno iz dveh delov. V prvem je predstavljen kratek zgodovinski pregled premazov za izkoriščanje sončeve energije skupaj z osnovnimi zakonitostmi, ki omogočajo pripravo spektralno selektivnih premazov. Poasnjene so tudi razločujoče lastnosti od debeline odvisnih spektralno selektivnih (TSSS) in od debeline neodvisnih spektralno selektivnih (TISS) premazov; prav tako smo predlagali in pokazali možnost uporabe zadnjih kot hladnih premazov. Drugi del vsebuje informacije o kemizmu priprave premazov in pojasni kako z uporabo primernih

		<p>disperzantov doseči enakomerno porazdelitev fino zmletih pigmentnih delcev v polimernem vezivu. Pomembnost POSS molekul (nov večfunkcionalen material) je pokazana z opisom premazov s hidrofobnimi in oleofobnimi lastnostmi in možnostjo priprave samočistilnih hladnih premazov.</p>				
	ANG	<p>This chapter consists of two parts. In the first one a brief historical overview of the development of solar paint coatings is given together with the basic principles that make paint coatings spectrally selective. Distinctive properties of Thickness Sensitive Spectrally Selective (TSSS) and Thickness Insensitive Spectrally Selective (TISS) are outlined and the use of the latter paint coatings as cool paints is proposed and demonstrated. Materials' aspects of the colored cool TISS paint coatings are given by the description of cool pigments, metallic and metallized flake pigments and polymeric resin binders which are used for the production of solar paint coatings. Second part contains information about the chemistries of the paint production showing how to achieve with the help of dispersant molecules uniform distribution of the finely ground pigment particles in the polymeric resin binder. Intentionally, we focused on organo (silicon) i.e. silane dispersants because they enable the stabilization of many different nanoparticle systems and also commercial pigments. Basics of the sol-gel chemistry of silanes are given and the preparation of polyhedral oligomeric silsesquioxane (POSS) molecules is described and the dispersive effect of the latter on pigments demonstrated. The importance of the POSS molecules representing a new multifunctional nanocomposite materials is revealed by describing paints and lacquers with hydrophobic and oleophobic properties and the possibility to attain anti-soiling properties of cool paints is also discussed.</p>				
	Objavljeno v	Bentham Science Publishers; Advances in the development of cool materials for the built environment; 2013; Str. 120-173; Avtorji / Authors: Orel Boris, Jerman Ivan, Koželj Matjaž, Slemenik Perše Lidija, Kunič Roman				
	Tipologija	1.16 Samostojni znanstveni sestavek ali poglavje v monografski publikaciji				
4.	COBISS ID	5112602 Vir: COBISS.SI				
	Naslov	<table border="1"> <tr> <td>SLO</td> <td>Premazi za polimerne sončne sprejemnike in njihovo nanašanje</td> </tr> <tr> <td>ANG</td> <td>Paint coatings for polymeric solar absorbers and their applications</td> </tr> </table>	SLO	Premazi za polimerne sončne sprejemnike in njihovo nanašanje	ANG	Paint coatings for polymeric solar absorbers and their applications
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	Objavljeno v	Wiley-VCL; Polymeric materials for solar thermal applications; 2012; str. 167-186; Avtorji / Authors: Jerman Ivan, Koželj Matjaž, Slemenik Perše Lidija, Orel Boris				
	Tipologija	1.16 Samostojni znanstveni sestavek ali poglavje v monografski publikaciji				

5.	COBISS ID	4764698	Vir: COBISS.SI
Naslov	SLO	Vpliv dodatka amino funkcionalnih POSS na korozijske lastnosti (3-glicidoksiopropil)trimetoksisilanskih prevlek na zlitini AA 2024	
	ANG	Influence of amino functionalised POSS additive on the corrosion properties of(3-glycidoxypropyl)trimethoxysilane coatings on AA 2024 alloy	
Opis	SLO	S preučevanjem protikorozijskih lastnosti prevlek, smo študirali vpliv dodatka mešanice POSS spojin, ki so substituirane v enakih deležih z aminopropilnimi in izobutilnimi skupinami, na sol-gel prevleke pripravljene iz (3-glicidoksiopropil)trimetoksisilana (GPTMS). AP4IB4 POSS je predstavnik skupine poliedričnih silseskvioksanov katerih aminska skupina omogoča premreženje z epoksidnimi skupinami GPMTS. Poleg tega se molekule GPTMS povežejo med seboj s hidrolizo in kondenzacijo trimetoksisilanske skupine. Ta proces je kataliziran z 0,1 M KF. Rezultati Ramanskih in IR meritev so pokazali, da je molsko razmerje med GPTMS:H ₂ O = 1:3 bolj ugodno kot 2:3 za pripravo sol-gel prevlek. Protikorozijske lastnosti mešanih prevlek GPTMS/POSS nanešenih na AA 2024 so bile preverjene s potenciodinamičnimi elektrokemijskimi meritvami in testom slane komore. Mešane prevleke GPTMS/POSS imajo boljše protikorozijske lastnosti kot čiste GPTMS ali POSS prevleke.	
	ANG	The influence of the addition of a mixture of POSS compounds substituted equally by 3-aminopropyl and isobutyl groups (AP4IB4 POSS) on sol-gel coatings prepared from (3-glycidoxypropyl)trimethoxysilane (GPTMS) was evaluated from the point of view of their anticorrosion properties. AP4IB4 POSS belong to a group of polyhedral oligomeric silsesquioxanes and their functionalisation with amino groups enables cross-linking with the epoxy groups of GPTMS. Additionally, GPTMS molecules react among themselves through hydrolysis and condensation processes of trimethoxysilane groups when catalysed by 0.1 M KF. The results of the Raman and IR measurements revealed that a molar ratio of GPTMS:H ₂ O = 1:3 is more beneficial than a molar ratio of 1:1.5 for the preparation of sol-gel coatings. The anticorrosion properties of the mixed GPTMS/POSS coatings deposited on AA 2024 aluminium alloy were tested using potentiodynamic electrochemical measurements and a salt-spray chamber test. It was found that the mixed GPTMS/POSS coatings showed improved corrosion protective properties vs. either pure GPTMS or POSS coatings.	
Objavljeno v	Elsevier Sequoia; Progress in organic coatings; 2011; Vol. 72, issue 3; str. 334-342; Impact Factor: 1.977; Srednja vrednost revije / Medium Category Impact Factor: 1.183; A': 1; WoS: DW, QG; Avtorji / Authors: Jerman Ivan, Šurca Vuk Angela, Koželj Matjaž, Švegl Franc, Orel Boris		
Tipologija	1.01 Izvirni znanstveni članek		

7. Najpomembnejši družbeno-ekonomski rezultati projektne skupine⁶

	Družbeno-ekonomski dosežek		
1.	COBISS ID	4380186	Vir: COBISS.SI
Naslov	SLO	Postopek za pripravo poliedričnih silseskvioksanov	
	ANG	Procedure for preparation of polyhedral silsesquioxanes	
Opis	SLO	Pričujoči izum obsega splošni postopek za pripravo poliedričnih silseskvioksanov. Postopek vključuje uporabo anorganskih hidrogen difluoridov in polietrov, kar ni bilo še uporabljeno za pripravo poliedričnih silseskvioksanov in daje višje izkoristke pri nižji koncentraciji katalizatorjev kot dosedanje metode. Hidrogen difluoridi so kisli katalizatorji, kar je bistveno drugače kot v dosedaj objavljenih metodah, kjer so uporabljali izključno bazične katalizatorje.	

		ANG	The present invention comprises a general procedure for preparation of polyedric silsesquioxanes. The procedure includes the use of inorganic or organic hydrogen difluorides and polyeters for preparation of polyedric silsesquioxanes at reflux conditions and gives higher yields at a lower concentration of catalysts. The applied catalysts - hydrogen difluorides - are acid catalysts, which is essentially otherwise than in the case of known application of basic catalysts.
	Šifra	F.32	Mednarodni patent
	Objavljeno v	Urad Republike Slovenije za intelektualno lastnino; 2011; 30 str.; Avtorji / Authors: Koželj Matjaž, Orel Boris, Jerman Ivan	
	Tipologija	2.24	Patent
2.	COBISS ID		Vir: vpis v poročilo
	Naslov	SLO	Priprava poliedričnih silseskvioksanov z N-heterocikličnimi karbeni
		ANG	N-heterocyclic-carbene-mediated preparation of polyhedral silsesquioxanes
	Opis	SLO	V patentu je opisan organokatalitski postopek za uporabo N-heterocikličnih karbenov, NHC, v procesu priprave poliedričnih silseskvioksanov. V tem postopku lahko uporabimo obstojne NHC, ki jih je mogoče izolirati, ali njihove prekursorje, imenovane tudi kriptokarbeni. Poliedrične silseskvioksane lahko pripravimo iz hidrolizatov funkcionalnih trialkoksisilanov, silseskvioksanskih smol ali iz že obstoječih poliedričnih silseskvioksanov, če jih izpostavimo organokatalitičnem delovanju NHC v organskem topilu na ustrezni temperaturi. Ker so karbeni odlično topni v reakcijski zmesi, lahko dosežemo dobre izkoristke priprave poliedričnih silseskvioksanov tudi pri koncentracijah NHC nižjih od 1 mol %.
		ANG	An organocatalytic method for a preparation of polyhedral silsesquioxanes characterized by use of N-heterocyclic carbenes, NHC, as organocatalysts, is described in present invention. Stable, isolable NHCs or their precursors that are called also cryptocarbenes could be used in disclosed process. Polyhedral silsesquioxanes could be prepared from hydrolyzates of functional trialkoxysilanes, silsesquioxane resins or from other already existing polyhedral silsesquioxanes compounds by mixing them with an organocatalytic NHC in an organic solvent at an appropriate temperature. Because of excellent solubility of carbenes in a reaction media high yields of polyhedral silsesquioxanes are obtained even at a concentration of NHC lower than 1 mol %.
	Šifra	F.32	Mednarodni patent
	Objavljeno v	Urad Republike Slovenije za intelektualno lastnino; 2013; 19 str.; Avtorji / Authors: Koželj Matjaž, Orel Boris,	
	Tipologija	2.24	Patent
3.	COBISS ID	4929050	Vir: COBISS.SI
	Naslov	SLO	Barvni večplastni premazi z nizko sončno absorptivnostjo in visoko toplotno emisivnostjo
		ANG	Multilayer color coatings with low solar absorption and high heat emission
	Opis	SLO	Predloženi izum se nanaša na: i) barvne večplastne premaze z nizko sončno absorptivnostjo in visoko toplotno emisivnostjo, ki se jih da uporabiti za uravnavanje najvišje temperature premazanih površin izpostavljenih direktni sončni svetlobi; ii) postopek za nanašanje premaza; in iii) hladne površine pripravljene z nanosom teh premazov. Sestavki za barvne premaze so narejeni z mešanjem visoko odsevnih kovinskih ali metaliziranih lusk, za IR prozornih ali IR odsevnih barvil v raznih vezjih; njihova visoka toplotna emisivnost pa je zagotovljena z nanosom prozornega vrhnjega sloja z visoko toplotno emisivnostjo. Premaze se da

		nanašati z razpršilnim nanašanjem ali s postopkom tračnega nanašanja (coil coating).
	ANG	The invention refers to: i) multilayer color coatings with low solar absorption and high heat emission which can be used for leveling the highest temperature of coated surfaces exposed to direct sun light; ii) process for applying the coating; and iii) cold surfaces prepared with applying said coatings. Compositions for color coatings are made with mixing metal or metalized scales with high reflection in different binders for IR porous or IR reflecting coatings; their high heat emission is achieved with applying of porous top coating with high heat emission. Coatings can be applied with spraying or coil coating.
	Šifra	F.32 Mednarodni patent
	Objavljeno v	Urad Republike Slovenije za intelektualno lastnino; 2012; 21 str., 4 str. pril.; Avtorji / Authors: Orel Boris, Koželj Matjaž, Jerman Ivan, Mihelčič Mohor, Spreizer Helena, Slemenik Perše Lidija
	Tipologija	2.24 Patent
4.	COBISS ID	5360922 Vir: COBISS.SI
	Naslov	SLO Ionske spojine s siloksi skupino
		ANG Ionic compounds having a silyloxy group
	Opis	SLO Podane so ionske spojine na katere je vezane siloksi skupina. Opisane so tudi postopki za pripravo takih ionskih spojin kot tudi pripravo elektrolitov, elektrokemijskih celic in električnih kondenzatorjev, ki vsebuje te ionske spojine.
		ANG There is provided an ionic compound having attached thereto a silyloxy group. There is also provided methods of making this ionic compound as well as electrolytes, electrochemical cells and capacitors comprising this ionic compound.
	Šifra	F.32 Mednarodni patent
	Objavljeno v	World Intellectual Property Organization, International Bureau; 2013; 91 str.; Avtorji / Authors: Koželj Matjaž, Guerfi Abdelbast, Trottier Julie, Zaghbi Karim
	Tipologija	2.23 Patentna prijava
5.	COBISS ID	Vir: vpis v poročilo
	Naslov	SLO Član upravnega odbora CMST COST Action CM1206 - EXIL (Exchange on Ionic Liquids)
		ANG Member of Managing Committee of CMST COST Action CM1206 - EXIL (Exchange on Ionic Liquids)
	Opis	SLO V letu 2013 sem bil potrjen kot član UO CMST COST Action CM1206 - EXIL (Exchange on Ionic Liquids), ki združuje večino evropskih strokovnjakov s področja ionskih tekočin, tako da je članstvo v tem združenju zelo pomembno za izmenjavo znanja in ljudi v evropskem prostoru. Združenje organizira vsakoletne sestanke, ki imajo značaj znanstvenih konferenc. Tako sem imel priložnost že na prvem srečanju predstaviti svoje delo na področju ionskih tekočin. Ta tematika je tesno povezana z mojim končanim podoktorskim projektom.
		ANG In 2013 I was confirmed as a member of Management committee of CMST COST Action CM1206 - EXIL (Exchange on Ionic Liquids), which gathers all European experts from this field, so membership in this organisation is very important for exchange of knowledge and people inside EU. Group organises meetings which have character of scientific conferences dedicated to ionic liquids. I had opportunity to participate on such conference with a presentation of my work on ionic liquids. This topic is

	strongly connected with my finished postdoc project.
Šifra	D.03 Članstvo v tujih/mednarodnih odborih/komitejih
Objavljeno v	http://www.cost.eu/domains_actions/cmst/Actions/CM1206?management
Tipologija	3.16 Vabljen predavanje na konferenci brez natisa

8. Drugi pomembni rezultati projektne skupine⁷

Deljena 1. nagrada za najboljši inventivni/inovativni projekt za ekonomijo, podeljena na Konferenci za prenos tehnologij, 26.-27. september 2012 na Inštitut Jožef Stefan.

Avtorji:

doc. dr. Ivan Jerman, prof. dr. Boris Orel, dr. Matjaž Koželj and Mr. Mohor Mihelčič za inovacijo »Go solar, go future« - sol-gel spektralno selektivni premazi za sončne sprejemnike

The 1st prize FOR BEST INVENTIVE/INNOVATIVE PROJECTS FROM PRO's FOR THE ECONOMY has been distributed equally among two participants:

Award was presented at Technology Transfer Conference
September 26. - 27. 2012, at Institut Jozef Stefan.

Autors: doc. dr. Ivan Jerman, prof. dr. Boris Orel, dr. Matjaž Koželj and Mr. Mohor Mihelčič for their innovation called »Go solar, go future« - a sol-gel based spectrally selective solar absorber coatings.

9. Pomen raziskovalnih rezultatov projektne skupine⁸

9.1. Pomen za razvoj znanosti⁹

SLO

Projekt »Reakcije N-heterocikličnih karbenov s silicijevimi spojinami« je imel oznako temeljnega projekta, saj je poskušal odgovoriti na nekaj, po mojem mnenju zelo zanimivih vprašanj reaktivnosti, tako silicijevih spojin kot tudi N-heterocikličnih karbenov. Obe veji kemije doživljata razcvet v zadnjih 10–20 letih in sta po mojem mnenju dve najhitreje rastoči raziskovalni veji na področju organske/organokovinske kemije. To velja še posebej za N-heterociklične karbene, ki so iz obskurnih neulovljivih intermediatov v kemijskih reakcijah postali izjemni ligandi v katalitsko učinkovitih organokovinskih kompleksih in še več, tudi sami zase so karbeni pomembno katalitsko orodje za sintezo organskih (to je ogljikovih spojin). Demonstrirano je, da prosti karbeni sami po sebi katalizirajo nekatere organske reakcije, še posebej reakcije na karbonilnih sistemih (benzoinska kondenzacija je na primer katalizirana s thiazol-2-ilidni, tudi sinteza poliestrov je katalizirana z imidazolskimi karbeni).

Silicijeva kemija je področje s katerim se ne ukvarja toliko znanstvenikov kot na primer s čisto organsko sintezo, zato je možnosti za raziskovanje neprimerno več. Tudi silicij predstavlja z možnostjo tvorbe hipervalentnih kompleksov neprimerno širši substrat kot ogljik, ki je v veliki večini spojin zgolj tetravalenten. In ravno ta sposobnost (koordinacija večja od 4) je osnova za mnoge pretvorbe (tudi sol-gel procese), ki imajo velik pomen v tehnologiji priprave materialov. Poznavanje kemijskih lastnosti silicijevih spojin pa daje slutiti, da bi lahko karbeni postali pomembni katalizatorji tudi za pretvorbe silicijevih spojin. Ocenjujem, da je to področje uporabe karbenov še premalo razvito in nudi zato izjemno široko polje raziskovanja fundamentalnih zakonitosti interakcij karben-silicij, kar pomeni, da ne smemo odlašati z raziskovanjem tega nadvse zanimivega področja; to ej bil tudi glavni vzrok predlaganja teh raziskav Agenciji.

Končani projekt, pa je poskušal v prvi vrsti osvetliti problematiko sinteze poliedričnih silseskvioksanov s pomočjo karbenov. Te pretvorbe sem poskušal razložiti s pomočjo vrste eksperimentov in pokazati, kako v resnici delujejo karbeni v procesih kondenzacije in dekondenzacije siloksanskih zvrsti. To je v strokovni javnosti precej pereče vprašanje, ki še ni

bilo pojasnjeno, saj so poročali le o reakcijah na dvofunkcionalnih siloksanih, a tudi tam niso uspeli pojasniti katalize; področje trifunkcionalnih in monofunkcionalnih silanov je še popolnoma neraziskano. Rezultati tega projekta pa so osvetlili to problematiko. Kombinacija dveh zelo napredujočih področij kemijskih raziskav je bila odločilna pri zagotavljanju odmevnosti pridobljenih rezultatov, zato menim, da je bilo sprejetje tega projekta pravilna odločitev.

ANG

The project "Reactions of N-heterocyclic carbenes with silicon compounds" was marked as a basic project, as it tried to answer to some very interesting questions about the reactivity of both silicon compounds as well as N-heterocyclic carbenes. These two branches of the chemistry experienced a boom-progress in the last 10–20 years and are still, in my opinion, two of the fastest growing in the field of organic/organometallic chemistry. This is especially true for N-heterocyclic carbenes, which changed from obscure elusive intermediates in reactions into excellent ligands for the preparation of catalytic organometallic complexes. Moreover, free carbenes are excellent catalysts for the synthesis of organic (i.e. carbon) compounds. It was shown many times that free carbenes catalyze some organic reactions, particularly reactions of carbonyl systems (benzoin condensation catalyzed by thiazol-2-ylidenes, synthesis of polyesters by imidazole carbenes).

Silicon chemistry is not a popular research field like pure organic synthesis, so it offers much more opportunities for interesting research. Silicon possesses the possibility of forming stable (isolable) hypervalent complexes so its chemistry has broader spectrum of reactions than the carbon, which is in the majority of compounds only tetravalent. This ability (coordination higher than 4) is the basis for many conversions of silicon compounds (including sol-gel processes), which are of great importance in technology of the preparation of materials. The knowledge about the chemical properties of silicon compounds suggests that carbenes could act as catalysts for the conversion of silicon compounds. I estimated that this area of carbene chemistry is still underdeveloped and therefore offers an extremely wide fundamental research field of interactions between carbenes and silicon and therefore this theme should be explored as soon as possible, so this was reason for proposing such research project to the Agency. The project was set up primarily to highlight the problem of synthesis of polyhedral silsesquioxanes through carbene catalysis. I tried to explain these conversions by a series of experiments and to show how the carbenes really catalyze the process of condensation and decondensation of siloxane compounds. This issue has not been clarified yet. Scientists reported only catalytic activity in polymerization of difunctional siloxanes, but also there they have not been able to explain catalysis; monofunctional and trifunctional silanes are completely unexplored. The results of this project are significant contribution to understanding of those reactions. The investigation of the carbene hypervalent silicon complexes with alkoxysilanes seems to be very interesting for the professional audience.

A combination of two very progressive areas of chemical research ensures the high impact of the results, so I think that approval of this project was a reasonable and good decision.

9.2. Pomen za razvoj Slovenije¹⁰

SLO

Od temeljnega projekta je nerealno pričakovati, da bi lahko bil kot tak podlaga za intenzivne industrijske procese, a kljub temu sem nekaj izsledkov raziskav patentiral in na ta način zaščitil pravico do uporabe odkritij v industrijske namene, vendar zanimanja za prenos znanja v proizvodnjo ni še nihče izrazil. Projekt sicer ne zagotavlja neposredno hitrega tehnološkega preboja, a kot se je pokazalo pri raziskovalnem delu v času doktorskega študija vodje projekta, so ravno silicijeve spojine omogočile izjemen napredek v tehnologiji priprave spektralno selektivnih premazov in korozijske zaščite sončnih absorberjev. Kljub mojim bogatim izkušnjam pri prenosu tehnologij v proizvodnjo, so rezultati ostali le kot znanstvena publikacija, zato ni nobenega neposrednega vpliva na razvoj katere koli industrijske panoge, ne v Sloveniji, ne v svetu. Torej ima projekt le vpliv na znanost pa še to bolj na znanost v svetu kot pa znanost v Sloveniji, saj je očitno tematika kemije silicijevih spojin, heterocikličnih karbenov in ionskih tekočin ne vredna nadaljevanja financiranja. Kljub temu pa upam na nadaljevanje teh raziskav v sodelovanju s tujimi znanstveniki v okviru COST aktivnosti CM 1206 – Exchange on Ionic Liquids, kar bo dvignilo ugled Kemijskega inštituta.

ANG

It is unrealistic to expect from a basic project a great influence on industrial processes. But still, some findings were patented, the IP protected and so prepared for transfer of the knowledge into production lines; but no interest was shown from potential users of that technology. The project could not provide a direct rapid technological breakthrough, but as was shown in research work during the PhD project of the project leader, silicon compounds are allowed remarkable progress in the technology of preparation of spectrally selective coatings and corrosion protection of solar absorbers. Despite many experiences of the project leader in the field of technology transfer, the results remained only as scientific publication, so the impact of these results on development of industry is negligible in Slovenia as well in whole world. However, the aim of the project were not patents and improvement of industry but rather fundamental knowledge and therefore project has impact on science of silicon and N-heterocyclic carbene chemistry which is more evident internationally than in Slovenia, where continuation of this project dealing with silicon chemistry, ionic liquids and N-heterocyclic carbenes was not recognized as worthy for further financing. I will try to collaborate on this topic with foreign scientists in the frame of COST action CM 1206 - Exchange on Ionic Liquids, what could contribute to higher recognition of National Institute of Chemistry.

**10. Samo za aplikativne projekte in podoktorske projekte iz gospodarstva!
Označite, katerega od navedenih ciljev ste si zastavili pri projektu, katere konkretne rezultate ste dosegli in v kakšni meri so doseženi rezultati uporabljeni**

Cilj		
F.01	Pridobitev novih praktičnih znanj, informacij in veščin	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.02	Pridobitev novih znanstvenih spoznanj	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.03	Večja usposobljenost raziskovalno-razvojnega osebja	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.04	Dvig tehnološke ravni	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.05	Sposobnost za začetek novega tehnološkega razvoja	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.06	Razvoj novega izdelka	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE

	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.07	Izboljšanje obstoječega izdelka	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.08	Razvoj in izdelava prototipa	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.09	Razvoj novega tehnološkega procesa oz. tehnologije	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.10	Izboljšanje obstoječega tehnološkega procesa oz. tehnologije	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.11	Razvoj nove storitve	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.12	Izboljšanje obstoječe storitve	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.13	Razvoj novih proizvodnih metod in instrumentov oz. proizvodnih procesov	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.14	Izboljšanje obstoječih proizvodnih metod in instrumentov oz. proizvodnih procesov	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>

F.15	Razvoj novega informacijskega sistema/podatkovnih baz	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.16	Izboljšanje obstoječega informacijskega sistema/podatkovnih baz	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.17	Prenos obstoječih tehnologij, znanj, metod in postopkov v prakso	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.18	Posredovanje novih znanj neposrednim uporabnikom (seminarji, forumi, konference)	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.19	Znanje, ki vodi k ustanovitvi novega podjetja ("spin off")	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.20	Ustanovitev novega podjetja ("spin off")	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.21	Razvoj novih zdravstvenih/diagnostičnih metod/postopkov	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.22	Izboljšanje obstoječih zdravstvenih/diagnostičnih metod/postopkov	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.23	Razvoj novih sistemskih, normativnih, programskih in metodoloških rešitev	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>

	Uporaba rezultatov	<input type="text"/>
F.24	Izboljšanje obstoječih sistemskih, normativnih, programskih in metodoloških rešitev	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.25	Razvoj novih organizacijskih in upravljavskih rešitev	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.26	Izboljšanje obstoječih organizacijskih in upravljavskih rešitev	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.27	Prispevek k ohranjanju/varovanje naravne in kulturne dediščine	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.28	Priprava/organizacija razstave	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.29	Prispevek k razvoju nacionalne kulturne identitete	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.30	Strokovna ocena stanja	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.31	Razvoj standardov	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.32	Mednarodni patent	
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE

	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.33 Patent v Sloveniji		
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.34 Svetovalna dejavnost		
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>
F.35 Drugo		
	Zastavljen cilj	<input type="radio"/> DA <input type="radio"/> NE
	Rezultat	<input type="text"/>
	Uporaba rezultatov	<input type="text"/>

Komentar

11. Samo za aplikativne projekte in podoktorske projekte iz gospodarstva!
Označite potencialne vplive oziroma učinke vaših rezultatov na navedena področja

	Vpliv	Ni vpliva	Majhen vpliv	Srednji vpliv	Velik vpliv	
G.01	Razvoj visokošolskega izobraževanja					
G.01.01.	Razvoj dodiplomskega izobraževanja	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.01.02.	Razvoj podiplomskega izobraževanja	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.01.03.	Drugo: <input type="text"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.02	Gospodarski razvoj					
G.02.01	Razširitev ponudbe novih izdelkov/storitev na trgu	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.02.02.	Širitev obstoječih trgov	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.02.03.	Znižanje stroškov proizvodnje	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.02.04.	Zmanjšanje porabe materialov in energije	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.02.05.	Razširitev področja dejavnosti	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.02.06.	Večja konkurenčna sposobnost	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.02.07.	Večji delež izvoza	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.02.08.	Povečanje dobička	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.02.09.	Nova delovna mesta	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.02.10.	Dvig izobrazbene strukture zaposlenih	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	

G.02.11.	Nov investicijski zagon	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.02.12.	Drugo:	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.03	Tehnološki razvoj					
G.03.01.	Tehnološka razširitev/posodobitev dejavnosti	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.03.02.	Tehnološko prestrukturiranje dejavnosti	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.03.03.	Uvajanje novih tehnologij	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.03.04.	Drugo:	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.04	Družbeni razvoj					
G.04.01	Dvig kvalitete življenja	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.04.02.	Izboljšanje vodenja in upravljanja	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.04.03.	Izboljšanje delovanja administracije in javne uprave	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.04.04.	Razvoj socialnih dejavnosti	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.04.05.	Razvoj civilne družbe	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.04.06.	Drugo:	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.05.	Ohranjanje in razvoj nacionalne naravne in kulturne dediščine in identitete					
G.06.	Varovanje okolja in trajnostni razvoj					
G.07	Razvoj družbene infrastrukture					
G.07.01.	Informacijsko-komunikacijska infrastruktura	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.07.02.	Prometna infrastruktura	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.07.03.	Energetska infrastruktura	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.07.04.	Drugo:	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	<input type="radio"/>	
G.08.	Varovanje zdravja in razvoj zdravstvenega varstva					
G.09.	Drugo:					

Komentar

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12. Pomen raziskovanja za sofinancerje¹¹

	Sofinancer		
1.	Naziv		
	Naslov		
	Vrednost sofinanciranja za celotno obdobje trajanja projekta je znašala:		EUR
	Odstotek od utemeljenih stroškov projekta:		%
	Najpomembnejši rezultati raziskovanja za sofinancerja	Šifra	
	1.		

	2.		
	3.		
	4.		
	5.		
Komentar			
Ocena			

13. Izjemni dosežek v letu 2013¹²

13.1. Izjemni znanstveni dosežek

13.2. Izjemni družbeno-ekonomski dosežek

C. IZJAVE

Podpisani izjavljam/o, da:

- so vsi podatki, ki jih navajamo v poročilu, resnični in točni
- se strinjamo z obdelavo podatkov v skladu z zakonodajo o varstvu osebnih podatkov za potrebe ocenjevanja ter obdelavo teh podatkov za evidence ARRS
- so vsi podatki v obrazcu v elektronski obliki identični podatkom v obrazcu v pisni obliki
- so z vsebino zaključnega poročila seznanjeni in se strinjajo vsi soizvajalci projekta

Podpisi:

*zastopnik oz. pooblaščen oseba
raziskovalne organizacije:*

in

vodja raziskovalnega projekta:

Kemijski inštitut

Matjaž Koželj

ŽIG

Kraj in datum:

Oznaka prijave: ARRS-RPROJ-ZP-2014/71

¹ Napišite povzetek raziskovalnega projekta (največ 3.000 znakov v slovenskem in angleškem jeziku) [Nazaj](#)

² Napišite kratko vsebinsko poročilo, kjer boste predstavili raziskovalno hipotezo in opis raziskovanja. Navedite ključne ugotovitve, znanstvena spoznanja, rezultate in učinke raziskovalnega projekta in njihovo uporabo ter sodelovanje s tujimi partnerji. Največ 12.000 znakov vključno s presledki (približno dve strani, velikost pisave 11). [Nazaj](#)

³ Realizacija raziskovalne hipoteze. Največ 3.000 znakov vključno s presledki (približno pol strani, velikost pisave 11) [Nazaj](#)

⁴ V primeru bistvenih odstopanj in sprememb od predvidenega programa raziskovalnega projekta, kot je bil zapisan v predlogu raziskovalnega projekta oziroma v primeru sprememb, povečanja ali zmanjšanja sestave projektne skupine v zadnjem letu izvajanja projekta, napišite obrazložitev. V primeru, da sprememb ni bilo, to navedite. Največ 6.000 znakov vključno s presledki (približno ena stran, velikost pisave 11). [Nazaj](#)

⁵ Navedite znanstvene dosežke, ki so nastali v okviru tega projekta. Raziskovalni dosežek iz obdobja izvajanja projekta (do oddaje zaključnega poročila) vpišete tako, da izpolnite COBISS kodo dosežka – sistem nato sam izpolni naslov objave, naziv, IF in srednjo vrednost revije, naziv FOS področja ter podatek, ali je dosežek uvrščen v A'' ali A'. [Nazaj](#)

⁶ Navedite družbeno-ekonomske dosežke, ki so nastali v okviru tega projekta. Družbeno-ekonomski rezultat iz obdobja izvajanja projekta (do oddaje zaključnega poročila) vpišete tako, da izpolnite COBISS kodo dosežka – sistem nato sam izpolni naslov objave, naziv, IF in srednjo vrednost revije, naziv FOS področja ter podatek, ali je dosežek uvrščen v A" ali A'.

Družbeno-ekonomski dosežek je po svoji strukturi drugačen kot znanstveni dosežek. Povzetek znanstvenega dosežka je praviloma povzetek bibliografske enote (članka, knjige), v kateri je dosežek objavljen.

Povzetek družbeno-ekonomskega dosežka praviloma ni povzetek bibliografske enote, ki ta dosežek dokumentira, ker je dosežek sklop več rezultatov raziskovanja, ki je lahko dokumentiran v različnih bibliografskih enotah. COBISS ID zato ni enoznačen, izjemoma pa ga lahko tudi ni (npr. prehod mlajših sodelavcev v gospodarstvo na pomembnih raziskovalnih nalogah, ali ustanovitev podjetja kot rezultat projekta ... - v obeh primerih ni COBISS ID). [Nazaj](#)

⁷ Navedite rezultate raziskovalnega projekta iz obdobja izvajanja projekta (do oddaje zaključnega poročila) v primeru, da katerega od rezultatov ni mogoče navesti v točkah 6 in 7 (npr. ni voden v sistemu COBISS). Največ 2.000 znakov, vključno s presledki. [Nazaj](#)

⁸ Pomen raziskovalnih rezultatov za razvoj znanosti in za razvoj Slovenije bo objavljen na spletni strani: <http://sicris.izum.si/> za posamezen projekt, ki je predmet poročanja [Nazaj](#)

⁹ Največ 4.000 znakov, vključno s presledki [Nazaj](#)

¹⁰ Največ 4.000 znakov, vključno s presledki [Nazaj](#)

¹¹ Rubrike izpolnite / prepisite skladno z obrazcem "izjava sofinancerja" <http://www.arrs.gov.si/sl/progproj/rproj/gradivo/>, ki ga mora izpolniti sofinancer. Podpisan obrazec "Izjava sofinancerja" pridobi in hrani nosilna raziskovalna organizacija – izvajalka projekta. [Nazaj](#)

¹² Navedite en izjemni znanstveni dosežek in/ali en izjemni družbeno-ekonomski dosežek raziskovalnega projekta v letu 2013 (največ 1000 znakov, vključno s presledki). Za dosežek pripravite diapozitiv, ki vsebuje sliko ali drugo slikovno gradivo v zvezi z izjemnim dosežkom (velikost pisave najmanj 16, približno pol strani) in opis izjemnega dosežka (velikost pisave 12, približno pol strani). Diapozitiv/-a priložite kot priložitev/-i k temu poročilu. Vzorec diapozitiva je objavljen na spletni strani ARRS <http://www.arrs.gov.si/sl/gradivo/>, predstavitev dosežkov za pretekla leta pa so objavljena na spletni strani <http://www.arrs.gov.si/sl/analize/dosez/>. [Nazaj](#)

Obrazec: ARRS-RPROJ-ZP/2014 v1.01

BC-80-CE-4C-8C-5B-AE-8B-AB-9B-8F-1D-BA-2E-46-31-31-FA-46-F3

Priloga 1

COMMUNICATION

***N*-Heterocyclic carbenes – catalysts for the preparation of polyhedral silsesquioxane†**Cite this: *Dalton Trans.*, 2013, **42**, 9432Received 12th April 2013,
Accepted 30th April 2013

DOI: 10.1039/c3dt50968k

www.rsc.org/dalton

Matjaž Koželj* and Boris Orel

***N*-Heterocyclic carbenes could be used as powerful catalysts for the preparation of various polyhedral silsesquioxanes. NHCs also catalyze a rearrangement of existing cages and a scrambling between two different cages at a concentration as low as 1 mol%.**

N-Heterocyclic carbenes (NHCs) attracted attention as early as the 1960s, when cryptoforms of imidazol-2-ylidenes were first reported by Wanzlick¹ and Öfele,² but interest in them increased significantly after their isolation as single free compounds in 1991 by Arduengo.³ NHCs are potent ligands for the preparation of organometallic catalysts.⁴ The chemistry of NHCs has been reviewed many times,⁵ recently with particular attention to their catalytic activity in organic transformations.⁶ A number of interesting reports can be found about their interaction with silicon compounds. Kuhn showed that NHCs can form hypervalent compounds with Lewis-acidic halosilanes.⁷ Two groups used NHCs for the preparation of polysiloxanes by ring-opening polymerisation (ROP) of cyclic siloxanes or condensation of linear oligomers.⁸ It was shown that long-chain polydimethylsiloxanes or bulky oligosiloxanes are efficient protection media for NHCs due to the weak carbene–Lewis acid interaction.^{8c} The possible activation of tetravalent silicon compounds has been recently discussed, but there is still too little experimental evidence for the carbene–silicon interaction in the first steps of reactions.⁹

Polyhedral (oligomeric) silsesquioxanes (P(O)SS) have been compounds of increasing interest since the mid-1990s, as a consequence of their being used in the technology of polymers, as catalyst supports, as cores for dendrimers, *etc.*¹⁰ The chemistry of PSS compounds has been reviewed several times.¹¹ Core PSS are always prepared by acid or base catalysed hydrolytic polycondensation of trihalo- and trialkoxy-silanes¹² or by

hydroxide/fluoride catalysed rearrangement of silsesquioxane resins.¹³ However, the majority of functional PSS compounds are prepared *via* organic transformations of already existing cages. In contrast, there have been only a few attempts to prepare PSS *via* non-hydroxide organic base catalysis.¹⁴

Imidazol-2-ylidenes are strong bases, comparable with cyclic amidine bases (DBU, DBN),¹⁵ but their reactivity in protic environments differs noticeably from the common proton-abstracting nitrogen bases. The free NHCs react with water, first forming a carbene–water complex.¹⁶ The further reaction is dependent on the amount of water present in reaction media. If a significant amount of water is present, the carbene–water complex decomposes into hydrated imidazolium hydroxide.^{16b} The stabilisation of an imidazolium–hydroxide ion pair is not possible in systems containing only low concentrations of water, so the initial carbene–water complex hydrolyzes to *N*-substituted 4-formyl-1,4-diaza-but-1-ene.^{16b} Reaction with water is instantaneous for imidazol-2-ylidenes, while imidazol-2-ylidenes are more resistant to hydrolysis.^{8c,16a,17} NHCs are very soluble in the organic solvents used for the preparation of PSS (THF, toluene), which is essential for good homogeneous catalyst activity. In conclusion, the imidazol-2-ylidenes possess the suitable properties of catalysts for the preparation of PSS.

Polyhedral phenylsilsesquioxanes are very suitable for studying the efficiency of catalysts, because it is possible to control the shape of the final PSS cage simply by selection of the solvent.^{13c} After refluxing phenylsilsesquioxane prepolymer (PhP) and catalysts in toluene, only Ph₈T₈ ((PhSiO_{3/2})₈) was isolated (only crystals which formed during reflux and cooling of the reaction mixture were isolated, crystals were not precipitated with addition of a second solvent). In contrast the dodecamer Ph₁₂T₁₂ was obtained by reflux in THF. These compounds are insoluble in reaction media, so they can be isolated *via* simple filtration.^{13c}

In addition, other silsesquioxane resins/silane hydrolyzates and a 1:1 (mol) mixture of two different PSS cages were exposed to NHC action to confirm the generality of their catalytic activity. The structures of silsesquioxane resins are presented

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†Electronic supplementary information (ESI) available: The detailed experimental section and NMR spectra of some compounds. See DOI: 10.1039/c3dt50968k

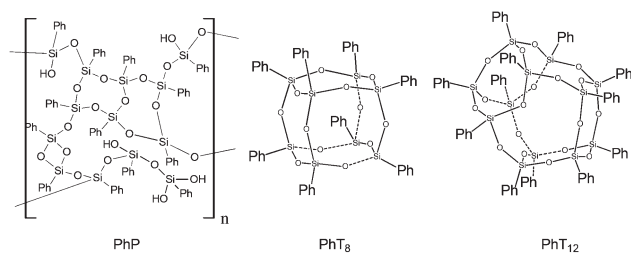


Fig. 1 Structures of phenylsilsesquioxane prepolymer (phenylsilsesquioxane resin, PhP), octa(phenylsilsesquioxane) (PhT₈) and dodeca(phenylsilsesquioxane) (PhT₁₂).

in Fig. 1. Carbon substituted silicon atoms (Ph-Si) are randomly connected with three silsesquioxane bonds produced by the condensation of trisilanol species that are initially formed in hydrolysis of trifunctional silanes. The functionality of silicon atoms in the literature is usually represented by capital letters: M (for monofunctional, *e.g.* trimethylmethoxysilane), D (for difunctional, *e.g.* dimethyldichlorosilane), T (for trifunctional, *e.g.* phenyltrimethoxysilane) and Q (for tetrafunctional, *e.g.* tetramethoxysilanes). The number of siloxane bonds per silicon is represented by the power sign of the corresponding capital letter. Silicon atoms with different degrees of condensation (for example T⁰, T¹, T², T³) have definite intervals of chemical shifts in ²⁹Si NMR. 'Pure' polysilsesquioxane does not contain the silanol group; in other words, only T³ silicon atoms are present. The fact is that silsesquioxane resins and silane hydrolyzates contain a considerable amount of non-condensed silanol groups, which could be seen on ²⁹Si NMR spectra (ESI[†]). PhP contains only T³ (no silanol per silicon) and T² (one silanol) silicon atoms, but the hydrolyzates of isobutyltrimethoxysilane and isooctyltrimethoxysilane also contain the T¹ (two silanols) silicon units, which is a clear sign of a lower degree of condensation.

We chose eight different carbenes (almost all are imidazol-2-ylidenes), either in their free form (**1a–d**, **2**) or in the form of their silver complexes (**3a–e**), which are shown in Fig. 2. All carbenes are unsaturated NHCs, which exhibit better stability, which is a particular advantage in complex reaction media in which water is produced. The condensation of two silanol species produces the siloxane bond (Si–O–Si) and water. Silanol groups are present in silsesquioxane resins (PhP, Fig. 1). The NHCs were prepared following established procedures^{3,18}

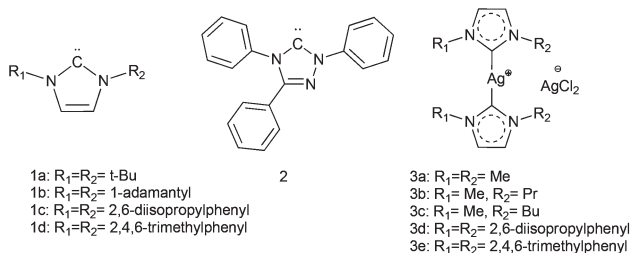


Fig. 2 *N*-Heterocyclic carbenes (**1** and **2**) and NHC–silver complexes (**3**) used for preparation of polyhedral silsesquioxanes.

and NHC–silver complexes were used as reagents for *in situ* formation of free carbenes.¹⁹ The silver complexes of 1,3-dialkylimidazol-2-ylidenes are easily accessible from 1,3-dialkylimidazolium salts by reaction with silver(I) oxide. Imidazolium salts are most conveniently prepared by alkylation of 1-methylimidazole (synthesis of ionic liquids). Preparation of these complexes is straightforward and does not include work with complete exclusion of water and oxygen. These complexes seem to be the first choice, but their catalytic activity must be proved first. We used catalysts in the amount of 1.2 mol% per silicon. Their efficiency for PSS production was compared to potassium *tert*-butoxide, a strong base that is used for the preparation of NHCs. It has previously been shown that samples containing only resins and solvents do not give any product upon reflux.^{13c}

The results of the experiments are presented in Table 1. Almost all employed catalysts facilitated the preparation of PSS compounds. Only Enders' carbene (Table 1, entry 5) and two silver complexes at 110 °C in toluene (entries 10 and 12) yielded no solid polyhedral product but caused the complete condensation of the resin (all silicon atoms in the T³ region of the ²⁹Si NMR spectrum, ESI[†]). The efficiency of the catalysts can be discussed in various ways. The first is preparation of Ph₈T₈. This preparation is characterised by a fairly high reaction temperature (b.p. of toluene is 110 °C), so the thermal

Table 1 Synthesis of polyhedral silsesquioxanes using 1.2 mol% per Si of NHCs

Entry	NHC/catalyst	Starting material	Yield ^f in PhMe/48 h reflux	Yield ^f in THF/7 days reflux
1	1a	PhP ^a	38% Ph ₈ T ₈ (29% Ph ₁₂ T ₁₂)	67% Ph ₁₂ T ₁₂ (10% Ph ₁₂ T ₁₂)
2	1b	PhP	84% Ph ₈ T ₈ (5% Ph ₈ T ₈)	88% Ph ₁₂ T ₁₂
3	1c	PhP	71% Ph ₈ T ₈	86% Ph ₁₂ T ₁₂
4	1d	PhP	31% Ph ₈ T ₈ (24% Ph ₁₂ T ₁₂) ^g	63% Ph ₁₂ T ₁₂ (8% Ph ₁₂ T ₁₂) ^g
5	2	PhP	Very viscous solution	0
6	1b	iBuH ^b	—	67% iBu ₈ T ₈ + 33% iBu ₁₀ T ₁₀ ^h
7	1b	iOCH ^c	—	80% iOC ₈ T ₈ + 20% iOC ₁₀ T ₁₀ ^h
8	1b	iBu ₈ T ₈ ^d ; ClP ₈ T ₈ ^e	—	Mixture of cages only
9	3a	PhP	23% Ph ₈ T ₈	93% Ph ₁₂ T ₁₂
10	3b	PhP	Traces of Ph ₈ T ₈	98% Ph ₁₂ T ₁₂
10a	3b	PhP	71% Ph ₈ T ₈ ⁱ	—
10b	3b	PhP	69% Ph ₈ T ₈ ^j	—
11	3c	PhP	65% Ph ₈ T ₈	90% Ph ₁₂ T ₁₂
12	3d	PhP	Very viscous solution	15% Ph ₁₂ T ₁₂
13	3e	PhP	10% Ph ₈ T ₈	14% Ph ₁₂ T ₁₂
14	<i>t</i> BuOK	PhP	70% Ph ₈ T ₈ (5% Ph ₁₂ T ₁₂)	85% Ph ₁₂ T ₁₂

^a Phenylsilsesquioxane resin. ^b Hydrolyzate of isobutyltrimethoxysilane. ^c Hydrolyzate of isooctyltrimethoxysilane. ^d Octa(isobutylsilsesquioxane). ^e Octa(3-chloropropylsilsesquioxane). ^f Isolated solid product. ^g Yields given in parentheses are isolated after the second precipitation from the filtrate after two days at rt. ^h The molar percentage was estimated from ²⁹Si NMR spectra. ⁱ Obtained after 48 h reflux in benzene. ^j Obtained after 48 h in toluene at 80 °C.

stability of carbenes could be a limiting factor. In all cases, the total yield of solid silsesquioxanes (first and second crop) approaches the amount obtained by *t*BuOK, but in many cases the selectivity (ratio $\text{Ph}_8\text{T}_8/\text{Ph}_{12}\text{T}_{12}$) is not very good. However, only the Ph_8T_8 compound was always isolated in the first crop. The best catalyst for the preparation of Ph_8T_8 is the ‘biggest’ 1,3-bis(1-adamantyl)imidazol-2-ylidene (Table 1, entry 2) for which extreme thermal stability is reported (stable at its melting point $240\text{ }^\circ\text{C}^3$). The latter exhibited the best crops and the best selectivity, which also surpassed *t*BuOK. The free 1,3-diaryl substituted carbenes are quite good catalysts (entries 3, 4), but their NHC–silver complexes (entries 12, 13) produced only very low product yields so the use of the latter for PSS preparation is not practical. In contrast, the NHC–silver complexes of 1,3-dialkyl substituted carbenes (entries 9–11) exhibited very diverse behaviour in boiling toluene, only the 1-butyl-3-methylimidazol-2-ylidene (entry 11) gave fair yields. The influence of reaction temperature is reflected in entries 10, 10a, 10b. Reaction in toluene at $110\text{ }^\circ\text{C}$ gave practically no solid product (entry 10), the trial in refluxing benzene ($80\text{ }^\circ\text{C}$) gave the same yield as *t*BuOK (entry 14), to exclude the influence of the solvent the reaction was repeated in toluene at $80\text{ }^\circ\text{C}$, confirming that lower reaction temperatures are preferable for non-hindered carbenes. That behaviour might arise from the low thermal stability of the very simple non-hindered carbenes. The possible mechanism of their inactivation could be the dimerisation,²⁰ so they could be inactivated at such a high temperature, but the lowest of 1,3-dialkyl series, 1,3-dimethylimidazol-2-ylidene, gave a notable yield.

In contrast, the preparation of $\text{Ph}_{12}\text{T}_{12}$ is accomplished by reaction at a much lower temperature ($66\text{ }^\circ\text{C}$), in a more polar solvent and much longer reaction times. THF is known to form complexes with silicon compounds²¹ and this solvent feature could be the reason for formation of the bigger $\text{Ph}_{12}\text{T}_{12}$. In all cases, the yields are considerably higher than in the preparation of Ph_8T_8 . Entries 9–11 show that the most basic and least hindered carbenes stemming from their NHC–silver complexes are the best catalysts in THF, even surpassing *t*BuOK. Results for PhT_{12} preparation suggest that 1,3-diaryl substituted imidazol-2-ylidenes should be used in their isolated form; their silver complexes gave yields below 20%.

Entries 6–8 (Table 1) show that carbenes also catalyze the (de)condensation of alkyl substituted silsesquioxanes. The starting material for entries 6 and 7 was obtained by acidic hydrolysis of the corresponding trimethoxysilanes in THF. The hydrolysate contained many silanol groups (consisting for the most part of T^1 and T^2 silicon species and to a lesser extent fully condensed T^3 species), so a lot of water was formed during the condensation reaction. Despite this, the condensation was quantitative. These examples confirm the excellent catalytic activity of NHCs for condensation of silanol species (similar to the results obtained for condensation of oligo-disiloxanes^{8d}). All starting material is transformed into fully condensed octa- and deca-silsesquioxanes.

However, in entry 8 (Table 1) it is shown that reactions between fully condensed species are also catalysed by carbenes

without the addition of a ‘mediating agent’ or a co-catalyst like alcohol, which was the case in the synthesis of long-chain polymers by the ring-opening polymerisation (ROP) process of oligomeric cyclic D^2 siloxanes.^{8a,b} In our reaction system, there was no alcohol, silanol or water present from which an alkoxide, siloxide or hydroxide could be formed upon action of a carbene base. In the beginning of the reaction there were only completely condensed species in the form of pure homoleptical octa(isobutylsilsesquioxane) and octa(3-chloropropylsilsesquioxane); the carbene caused rearrangement of the cages so a mixture consisting of the remaining octa(isobutylsilsesquioxane) and several heteroleptic octasilsesquioxanes and decasilsesquioxanes with a small amount of dodecasilsesquioxanes was obtained at the end. The octa(3-chloropropylsilsesquioxane) was completely transformed into other cages. This experiment suggested that there could be more in carbene catalysis than just simple Brønsted base catalysis. In general, we showed that transformation from polymeric materials into oligomeric polyhedral species was accomplished in most entries, but previous reports showed exactly the opposite.^{8a,b}

No conclusion could be made about the mechanism of catalytic activity of NHC and their interaction with T type silicon compounds. The first obstacle is the possible dual role of NHCs, which is presented in Fig. 3. They can act as a Brønsted base, *i.e.*, a proton abstracting agent (pathway A), or as nucleophilic activators that are ‘Lewis base catalysts’ (pathway B). PSS can be formed by either catalytic mechanism. It is a common procedure for PSS to be prepared by inorganic hydroxide action on polymeric silsesquioxanes^{13b} (in this work catalysis by *t*BuOK was shown, entry 14, Table 1). The fluoride ion is a very weak base in the aqueous environment ($\text{pK}_a = 3.2$), so its

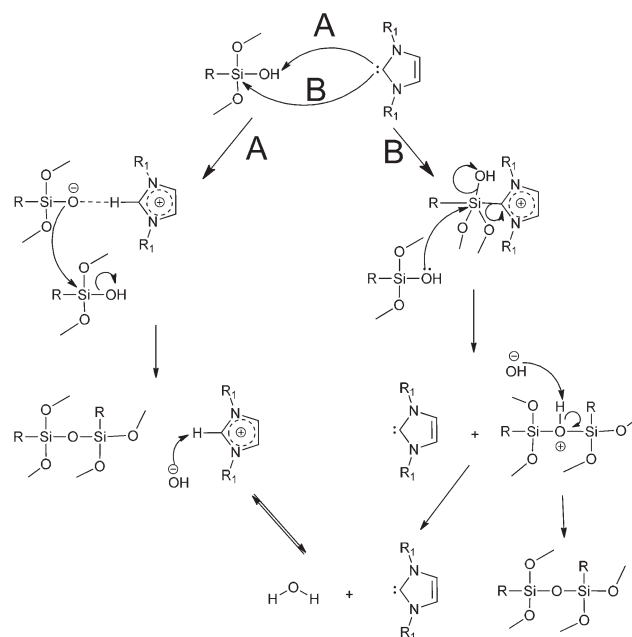


Fig. 3 Two possible pathways for NHC catalysis of a silanol condensation reaction: (A) – NHC acts as a Brønsted base (proton abstractor) and (B) – NHC acts as a Lewis base catalyst = activates silicon by changing its coordination.

action in accelerating the condensation of silanol species in sol-gel processes (preparation of PSS is one type of sol-gel process) can be most reasonably explained by the Lewis base catalysis concept.²² NHCs exhibit a considerable basicity and strong nucleophilic character, so both pathways are highly probable. The Lewis base catalysis includes the formation of a hypervalent penta-coordinated silicon complex between the free NHC and the siloxane species; in the case of NHC **1a** and **1b** (Fig. 1) this is not very probable for steric reasons. However, complexation with carbenes formed from **3a-c** (Fig. 2) (similar to those used by Kuhn) should not be problematic. When entries 1 and 2 are compared with entries 9–11, a clear dependence of PSS yield on steric factors could not be recognised. The dependence on steric factors should be more expressed in the case of Lewis base catalysis. Moreover, in Brønsted base catalysis the most basic reagent should provide the highest yields, but when entries 1, 2, 8, 9 are compared to the most basic catalyst, *i.e.* *t*BuOK, under entry 10 (Table 1), this was not the case. The unclear correlation between yields and the type of the catalyst could be a consequence of complex reaction pathways leading to final products. The reaction proceeds at silicon atoms, which are tri-functional and the final PSS combines at least eight such centres, so there are many possibilities of obtaining the resulting cage. In addition, it should be noted that the shape of the final product is not exclusively dependent on the solvent. In several runs, both cages were obtained, which might be a sign of a different action of the NHC than fluoride or hydroxide base;¹³ the shape of the product seems to be more catalyst dependent.

In summary, NHC catalysis was shown to be an efficient method for the condensation of silanol species and rearrangement of silsesquioxanes, resulting in the rapid preparation of various PSS. Several NHCs or their precursors can be used for the preparation of PSS. 1,3-Diarylimidazol-2-ylidenes should be used in their free form, although the 1,3-dialkylimidazol-2-ylidenes could be used in the form of their silver complexes in order to obtain good to excellent yields of polyhedral silsesquioxanes from polymeric precursors. The mechanism of the NHC's interaction with the silsesquioxane (T) silicon species will be investigated in due course.

Experimental

General procedure for preparation of polyhedral phenylsilsesquioxanes with NHC

To a 25 ml round-bottomed flask, 15 ml of a freshly distilled and degassed solvent, a stirring bar and 21 mmol of silsesquioxane resin are placed and stirred until the siloxane is completely dissolved. Then 0.25 mmol of NHC (or the corresponding amount of its silver complex) is added under nitrogen and refluxed for a given time period (48 hours/7 days). The white solid product was filtered off and thoroughly washed with fresh toluene, acetone and finally with methanol and dried in a vacuum oven. The product thus obtained was re-crystallised from CH₂Cl₂, which is necessary for obtaining

clear NMR data. The spectral properties correspond to those previously reported (see ESI† for detailed description and spectra).^{13c}

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