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Homogeneous and heterogeneous titanium complexes and their use for selective ethylene trimerization to 1-hexene

Homogenní a heterogenní titaničité komplexy pro selektivní trimerizaci ethylenu na 1-hexen

Diploma thesis

Supervisor: Mgr. Jiří Pinkas, Ph.D.

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Prohlášení

Prohlašuji, že jsem závěrečnou práci zpracoval samostatně a že jsem uvedl všechny použité informační zdroje a literaturu. Tato práce ani její podstatná část nebyla předložena k získání jiného nebo stejného akademického titulu.

V Praze dne ....

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SOUHRN

Cílem předložené diplomové práce je návrh a syntéza nových titaničitých komplexů pro selektivní trimerizaci ethylenu na 1-hexen a využití těchto připravených komplexů pro zakotvení na vybrané nosiče (např. SiO_2, SBA-15).

Byla vypracována syntetická strategie pro přípravu titaničitých komplexů s vhodnou odstupující skupinou pro přímé zakotvení na nosič přes Ti−O vazbu (Cl, O*i*-Pr) a dále vhodně substituované komplexy s volným alkenylovým řetězcem pro zakotvení na $SiMe_2H$ modifikovanou siliku s využitím Pt-katalyzované hydrosilylační reakce.

Připravené materiály byly charakterizovány pomocí spektroskopických metod (IČ, NMR, MS). Heterogenní systémy byly dále studovány pomocí MAS NMR a IČ spektroskopie, práškové XRD, ICP-OES, TGA a texturní parametry byly stanoveny pomocí adsorbčních/desorpčních izoterem. U všech připravených komplexů byla studována katalytická aktivita a selektivita při trimerizaci ethylenu na 1-hexen.

SUMMARY

This diploma thesis is focus on the design and synthesis of new half-sandwich titanium complexes for anchoring to a selected supports (SiO_2, SBA-15) and the study of their catalytic activity and selectivity in ethylene trimerization to 1-hexene.

The synthetic strategy of half-sandwich titanium complexes with a suitable leaving group for direct anchoring through Ti−O bond was carried out (Cl, O*i*-Pr). In addition, the titanium complexes with pendant alkenyl group were prepared and utilised for anchoring to a $SiMe_2H$ modified support by Pt-catalysed hydrosilylation reaction.

Prepared compounds were characterised by standard spectroscopic methods (IR, NMR, MS). The heterogeneous systems were characterised by MAS NMR and IR spectroscopy, powder XRD, ICP-OES, TGA and the textural parameters were determined from nitrogen adsorption/desorption isotherms.

For all prepared materials was studied the catalytic activity for ethylene trimerization and the selectivity to 1-hexene.

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Zde na tomto místě bych chtěl předně poděkovat svému trpělivému školiteli, Mgr. Jiřímu Pinkasovi, Ph.D., za jeho cenné rady a trpělivý přístup, bez kterého by tato práce jen sotva mohla vzniknout. Bylo by osudným omylem opomenout v této chvíli i ostatní kolegy z oddělení Syntézy a katalýzy Ústavu fyzikální chemie J. Heyrovského AV ČR, v.v.i. kteří se chtě nechtě postarali o příjemné prostředí, které provázelo tvorbu této práce. Jmenovitě skládám velké díky RNDr. Martinu Lamačovi, Ph.D. (NMR) a Mgr. Michalu Horáčkovi, Ph.D. (GC-MS), Ing. Naděždě Žilkové (GC-FID), Ing. Arnoštu Zukalovi, CSc. (měření texturních vlastností), Ing. Martinu Kubů, Ph.D. (XRD) a RNDr. Vojtechu Vargovi, CSc. (katalytické experimenty) za jejich podporu a měření mých, mnohdy beznadějných, výtvorů. Dále děkuji RNDr. Janu Rohovcovi z Geologického ústavu AV ČR, v.v.i. za stanovení obsahu titanu naneseného na nosiče (ICP OES) a Wallace O. Parkerovi z Eni S.p.A. za měření NMR pevné fáze (CP MAS NMR).

Bylo by neodpustitelným hříchem zapomenout na své nejbližší, kteří v průběhu mého studia na mne nezanevřeli, a jejich díl podpory se neustále nese spolu se mnou, i když o mém konání i dalším studiu neměli nejmenšího zdání a budiž jim tato práce věnována. Děkuji svým rodičům, bratru a přátelům, kteří jsou tímto podpůrným sloupem a nezanevřeli na mě! V průběhu svých studií jsem se setkal s mnohými lidmi, kteří na mě chtě nechtě zapůsobili a zanechali ve mně patřičný dojem, a bylo by sobecké, kdybych je nevzpomenul při této slavnostní příležitosti, ale nemám dostatek prostoru, abych je všechny jmenoval …

V neposlední řadě stále pociťuji potřebu vyjádřit vděk svým prarodičům, kteří mne podporují a neztrácí víru v mé schopnosti. Děkuji!

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1. INTRODUCTION

In 1828, the German chemist, Friedrich Wöhler, razed the philosophical border between the inorganic chemistry and the organic chemistry. One of the youngest sectors of chemistry is the organometallics that applies the metal core as the central atom that is generally coordinated with a suitable organic ligand. The organometallic compounds are known even more than two centuries and the most famous representative is Zeise's salt, $K[PtCl_3(\eta^2-C_2H_4)]$, that is even the first described π-complex of ethylene with transition metal.

The importance of these compounds is given by their reactivity which is different in comparison with non-coordinated compounds. In 1963, the Nobel Prize was awarded to two ingenious men, Karl Ziegler and Giulio Natta. They developed and applied a robust catalytic system for polymerization of olefins based on a combination of $TiCl_4$ and Et_3Al. This catalytic system produced stereoregular polymers that are desirable for a widespread application.[1]

Polymeric materials are widely utilised in daily life and their presence is, up today, irreplaceable, because of their unique properties. The combination of their weight, strength, workability, stability etc. and finally price makes these materials competitive with the others materials such as wood, metal, glass, ceramics etc. One of the most general utilisation of polymers is their application as packing materials.[2] For this application is crucial a good elasticity, chemical and physical stability. The packing materials are often made from a low-density polyethylene (LDPE) that is easily produced via free radical polymerization. Modern trend is focused on the linear low-density polyethylene (LLDPE). It is a copolymer of ethylene and other olefins such as 1-hexene, 1-octene or similar homologues. The big demand for these materials forces scientists and developers on the easier and cheaper synthesis of expensive co-monomers (1-hexene, 1-octene etc.) *e.g.* from ethylene. One of these promising approaches is a selective synthesis of these co-monomers *e.g.* based on a metal-mediated selective oligomerization reaction such as trimerization, tetramerization etc.[3]

1.1 OLEFINS AND POLYETHYLENES

Polyethylene (PE) was firstly synthesised in 1898. The inventor was Hans von Pechmann, a German chemist mostly known as a investigator of diazomethane in synthetic practise. The produced polyethylene was a by-product during of his investigation with diazomethane, because this substance is strongly reactive, unstable and smoothly undergoes to polymerization. Polyethylene consists of the huge amount of repeating ethylene units (**Fig. 1**) and is processed from ethylene under a various conditions.[4]

$$CH_2{=}CH_2 \longrightarrow -\!\!\left[CH_2{-}CH_2\right]\!\!-_n$$

Fig. 1: Schematic synthesis of polyethylene

Up to 1950s, the PE was produced by a free radical polymerization and this type of PE is called low-density polyethylene (LDPE). In 1955, a German chemist Karl Ziegler accidentally discovered that a catalytic system based on titanium(IV) chloride with triethylaluminum causes the polymerization of ethylene which properties are different in comparison with LDPE. It evolved the huge interest on metal-mediated polymerization, predominantly based on titanium with a suitable co-catalyst such as organoaluminium compounds (Ziegler-Natta catalyst).[1]

Polyethylenes is a general label for extensive crowd of thermoplastic polymeric materials that are different in the properties (physical and chemical) and the process of producing as well. According to their chemical structure and density are polyethylenes divided to:[5]

– **VLDPE** (= *very-low-density polyethylene*, ρ = 870-920 kg·m^{-3})[6]
– **LDPE** (= *low-density polyethylene*, ρ = 900-910 kg·m^{-3})
– **LLDPE** (= *linear low-density polyethylene*, ρ = 910-930 kg·m^{-3})
– **UHMWPE** (= *ultra-high-molecular-weight polyethylene*, ρ = 928-941 kg·m^{-3})[7]
– **MDPE** (= *medium-density polyethylene*, ρ = 930-940 kg·m^{-3})
– **HDPE** (= *high-density polyethylene*, ρ = 940-965 kg·m^{-3}) and others …

The characteristic properties of polyethylenes depend on their molecular structure, thus most of them are excellent chemically resistant, tough etc. For example, the properties of LDPE are – low density (ρ = 900-910 kg·m^{-3}), good chemical resistance, lower crystallinity, flexible, tough, but due to a higher amounts of branches, its breakable and less workable than other types of PE.

The modern trend of the last few decades is an utilisation of linear low-density polyethylene (LLDPE), which is commonly used as a packing material with high elasticity (**Fig. 2**). In contrast with the common LDPE, this polymer is tougher with density ρ = 910-940 kg·m^{-3} and melting temperature range 120 °C to 160 °C and elongation almost 500%.

a **b**

Fig. 2: Examples of LLDPE (**a**)[8] and packing foil from LLDPE (**b**)[9]

Ever growing demand for short linear α-olefins motivates their production in a higher amount with an acceptable price and predominantly with great purity that is guaranteed by selective synthesis. These olefins are produced by fraction distillation of oil, but this production is unsatisfactory for the growing demand for them. This problem can be solved by application of selective synthesis based on metal-mediated trimerization, tetramerization or generally the oligomerization reaction. Difference between the oligomerization process and polymerization is set on the reaction mechanism of metal-catalysed reaction, but also kinetic aspects may play the important role in the selectivity of the oligomerization reaction. In general, by the view of kinetics, it can be declared, that the oligomerization process is supported by a faster termination step in comparison to propagation. In opposite, the polymerization reaction is supported by slower termination step that promotes the propagation of olefins. The second aspect, that leads the selectivity, is a reaction mechanism (see below).[10]

The proposed mechanism, so called Cossee-Arlman mechanism, of polymerization is clearly illustrated in **Fig. 3**. The mechanism counts with many times repeated coordination/insertion of ethylene on the catalytic active species up to final termination by *e.g.* β-elimination.

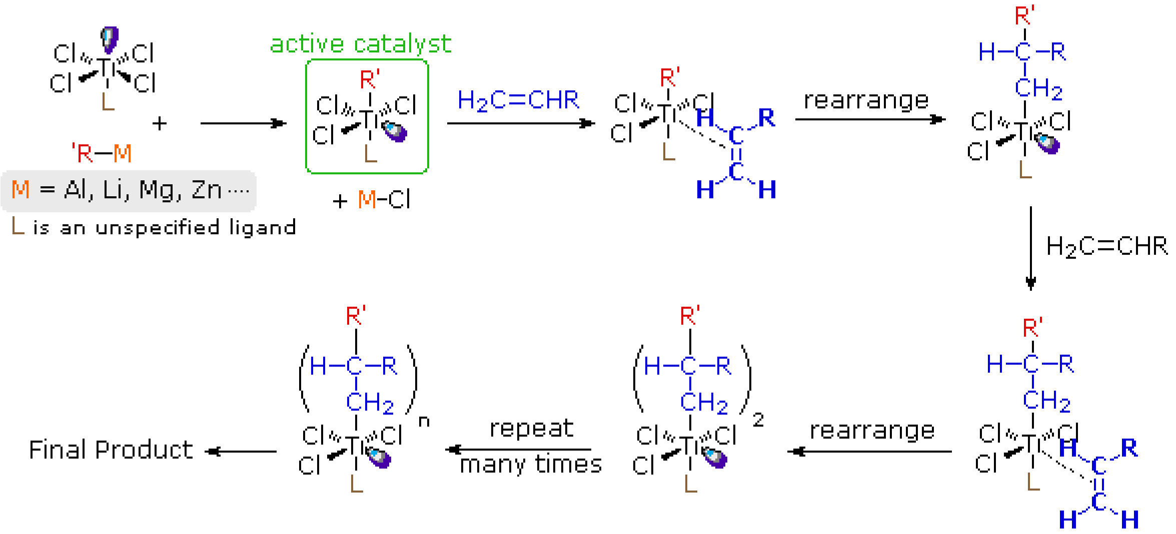


Fig. 3: Proposed reaction mechanism of polymerization via Ziegler-Natta type catalyst

The most widespread utilised oligomerization process is Shell higher olefin process, labelled SHOP process.[11] The SHOP process was developed already in 1968 and represents, maybe, one of the mostly applied examples of oligomerization of ethylene to terminal olefins (**Fig. 4**). The catalyst is nickel complex with cyclooctadiene and 2-(diphenylphosphino)acetic acid used as ligands. The catalytic cycle starts with nickel hydride complex. Further ethylene insertion into Ni−H bond gives nickel ethyl complex, repeating ethylene insertion followed by β-elimination leads to linear α-olefins and the active catalyst is restored. The products of this oligomerization are predominantly C_{12} to C_{18} olefins, which are further processed, and higher homologues are isomerised by metathesis and used for other application – hydroformylation (so called oxo-process) etc.

One of the mostly utilised α-olefin for copolymerization with ethylene to LLDPE is 1-hexene. This alkene is colorless liquid, insoluble in water, which boils at 63 °C. 1-Hexene is used as co-monomer approximately in 2-10% with ethylene. Up today, the 1-hexene is manufactured by fraction distillation of oil or by oligomerization process similar to SHOP process, but still growing applicable potential of 1-hexene leads to developing of the selective trimerization of ethylene to 1-hexene.[12]

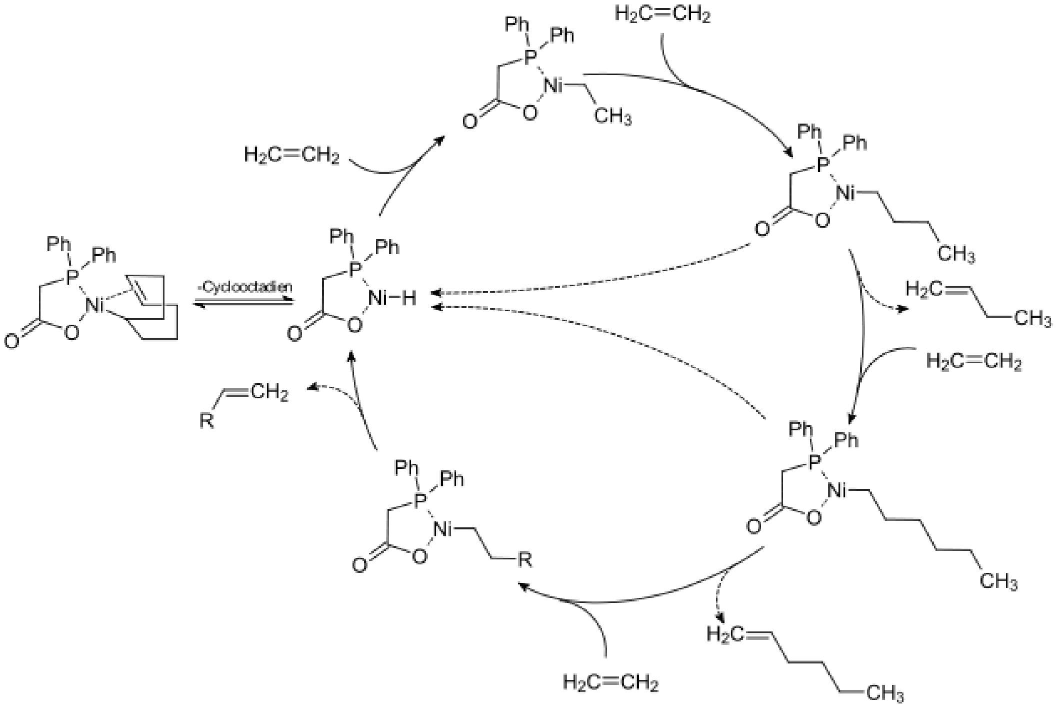


Fig. 4: Shell higher olefin process – reaction mechanism

1.2. TRIMERIZATION OF ETHYLENE

Motivated by a higher cost of 1-hexene isolated from oil, a great interest was focused on the selective synthesis of it by the trimerization of ethylene (as a cheap feedstock).[12, 13] This reaction is catalysed by metal-based catalyst. The first widespread utilised catalyst contains chromium atom as a central core such as Philips trimerization catalyst (**Fig. 5**). This catalyst represents the vast majority system, which is the only ethylene trimerization system that was commercialized. This system was developed by Morgan and co-workers and produces annually almost 47 000 tons of 1-hexene. The catalyst consists of chromium complex, 2,5-dimethylpyrrole and alkylating agent such as Et_3Al, thus role is to generate the catalytic active species. The proposed mechanism of the chromium-mediated trimerization operates with Cr(II) and Cr(IV) catalytic system. But in contrast with this study, Gambarotta and co-workers set up the proved evidence of different catalytic system based on Cr(I) and Cr(III) and this approach was supported by electron paramagnetic resonance (EPR) study.[3]

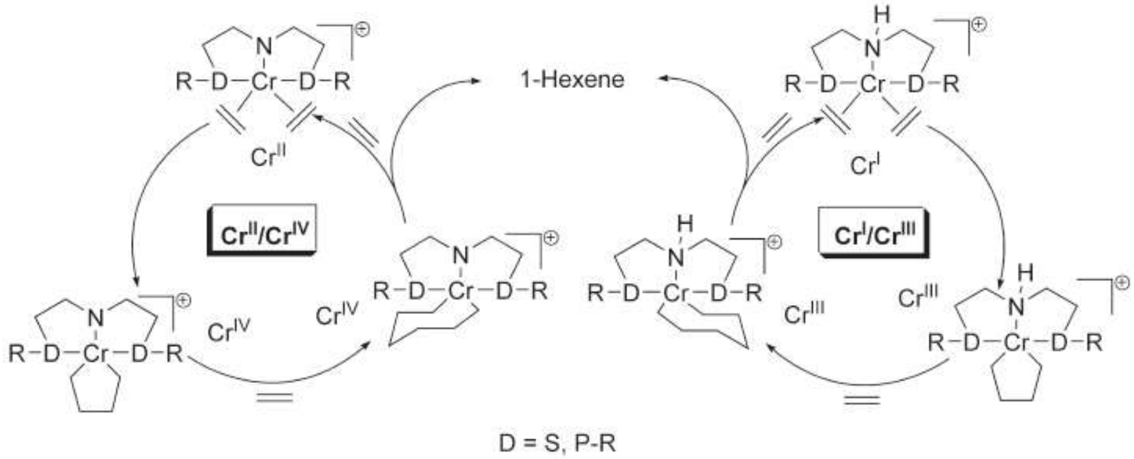


Fig. 5: Proposed trimerization pathways based on chromium catalytic systems[3]

Next to the chromium-based catalysts, the trimerization catalytic system can be derived from the other transition metals. The reasons for their application are potential catalytic improvements and also environmental impacts of chromium residues from catalyst in final product. The catalytic systems were derived from early transition metals as well as late transition metals.

1.2.1. EARLY TRANSITION METALS BASED CATALYSTS

In this case, the catalytic system is mainly based on the metal from the group 4 and 5 of the periodic table, namely zirconium, titanium, vanadium and tantalum.

Although, zirconium is a common transition metal used in synthesis, its application as a suitable trimerization catalyst has not been confirmed. For example, Negishi reagent, *in situ* generated by reaction of zirconocene dichloride with 2 equivalents of *n*-BuLi, smoothly performs the dimerization of olefins or alkynes to 5-membered metallacycles, but 1-hexene was formed maximally in 55% yield after a series of optimization steps. PE was always formed as a major by-product and a catalytic activity was also very low, concretely 153 g/g of Zr per hour.[14]

An interesting catalytic behaviour was observed, when the trimerization catalyst was derived from tantalum. The catalytic active species could be generated *in situ*, where $TaCl_5$ is used as a precursor that is alkylated by $EtAlCl_2$ or Me_2Zn. Nuclear magnetic resonance (NMR) study revealed that the intermediate of the active species has formula Me_2TaCl_3 and during the catalytic cycle no ligand is required. This behaviour is unusual and the selectivity to 1-hexene is driven by stability of metallacycle in the catalytic process.[3]

Probably, the major interest is focused on the catalysts derived from titanium as a central atom. The most active catalysts consist of arene-substituted cyclopentadienyl ligand designed by Hessen and co-workers (**Fig. 6**).[15] These derivatives are characterised by a great selectivity to 1-hexene (up to 90%) with an excellent turnover frequencies (up to 240 000 h^{-1}) and the only by-product is C_{10} fraction (including co-trimerization product of 1-hexene with 2 molecules of ethylene) and almost negligible amount of polyethylene. A big disadvantage is that the catalytic active species are formed using alkylating agents in a huge molar excess (up to 500 to 1000 or even more equivalents). The most popular alkylation agent is methylaluminoxane (MAO). These results motivate many researchers to develop the successfully competing catalyst based on non-chromium complexes.

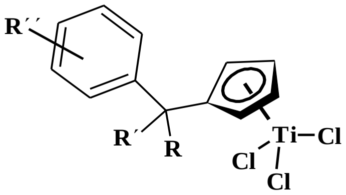


Fig. 6: General formula of Ti-catalysts developed by Hessen and co-workers[3]

1.2.2. LATE TRANSITION METALS BASED CATALYSTS

Such as the early transition metals were deeply studied as promising trimerization catalysts, the late transition metals were also employed. The most representatives are nickel-based complexes, because these derivatives showed the promising potential as oligomerization catalysts (*e.g.* SHOP process described above). After a series of optimisation steps, researchers of Mitsui Chemicals patented the catalytic system using $(Ph_3P)_2NiBr_2$ with MAO or $MeAlCl_2$ as a co-catalyst with a high yield of trimer products (95%), however, the selectivity was rather poor.[16]

Next to these common metal compounds, uranium compounds were studied as trimerization catalysts with a comparable activity and selectivity to chromium-based catalysts. Its widespread utilisation is suppressed due to its cost and an environmental banishment.[17]

1.3. TITANIUM-BASED CATALYSTS

Previous chapters were focused on the general information about oligomerization, clearly trimerization, and polymerization. This part will closely present the modern trend in application of titanium-based catalysts for the selective trimerization of ethylene to 1-hexene.

Titanium is a member of the group 4 of the periodic table. It is a metallic-white in color and its the biggest usage is as a light alloy with aluminium, copper etc. or in medicine as implants, because titanium is biological inert (**Fig. 7a**). The most important compound of titanium is TiO_2 that is widely utilised as a white pigment (**Fig. 7b**). Furthermore, titanium compounds are considerably studied for their catalytic potential.[18]

a **b**

Fig. 7: Elemental titanium (**a**)[19] and titanium dioxide (**b**)[20]

One of the oldest catalytic systems was developed by researchers from Phillips Petroleum. They investigated $TiO(acac)_2$ with pyrrole and Et_3N in ethylene oligomerization and obtained the trimerization product in a modest yield (55%) with 1-hexene as a major representative.[21] In 1999, Pellecchia and co-workers reported an unexpected producing of LLDPE as a product of copolymerization of ethylene with *in situ* prepared 1-hexene. As a catalyst was employed half-sandwich complex of titanium Cp^*TiMe_3 ($Cp^* = \eta^5$-C_5Me_5), which was activated by 1 equivalent of $B(C_6F_5)_3$, and catalysed subsequently ethylene trimerization to 1-hexene, ethylene polymerization, and ethylene/1-hexene copolymerization, respectively. Further, It was approved that the presence of toluene as a reaction medium was a driving force of competitive trimerization process, because toluene cooperated as a ligand during a catalytic cycle.[22] The biggest breakthrough became in 2001, when Hessen group published a highly selective arene-substituted cyclopentadienyl titanium complex (**Fig. 6**), that produced 1-hexene with productivity and selectivity similar to chromium-based catalysts. This discovery has started a big interest of the titanium-mediated trimerization reaction.[15]

Proposed mechanism is similar to the chromium-mediated catalytic cycle and its simplified version is sketched in **Fig. 8**.[23] The active species is generated *in situ* by reaction of catalyst with MAO, which serves mutually as an alkylating agent and Lewis acid forming a cationic titanium complex. Alkylated cationic complex spontaneously undergoes β-elimination and provides the cationic Ti(II) center stabilised by pendant phenyl group that can easily coordinate two molecules of ethylene. This active intermediate is transformed to 5-membered Ti(IV) metallacycle that coordinates other molecule of ethylene. Next step is an insertion of ethylene into Ti−C bond to produce 7-membered metallacycle, which is unstable and undergoes to β-elimination to yield 1-hexene and recovered the active species. Common by-products are 1-butene, C_{10} fraction and PE. This reaction mechanism was deeply studied and its deviations were explained by DFT calculation too.[24, 25]

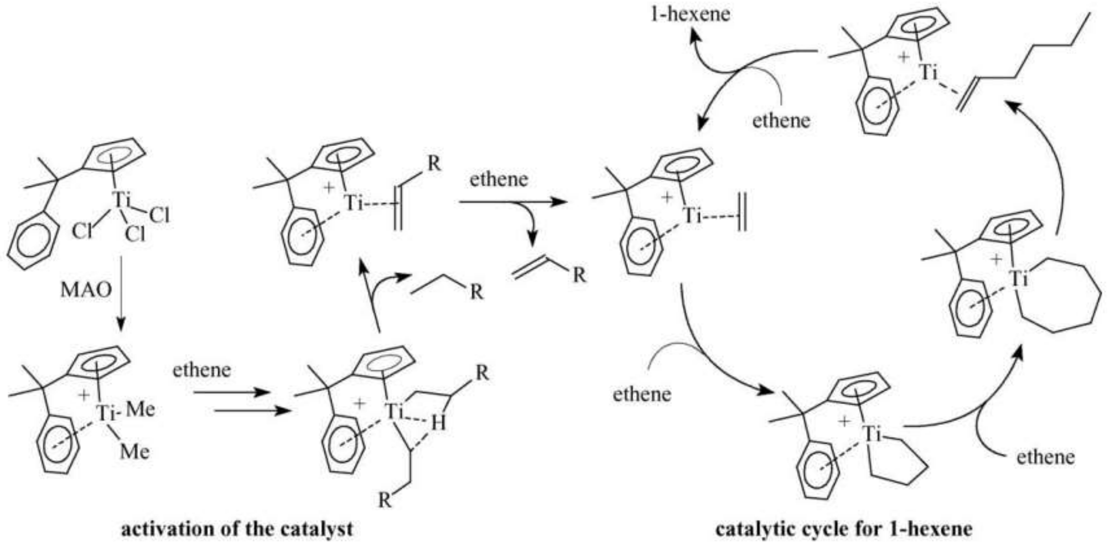
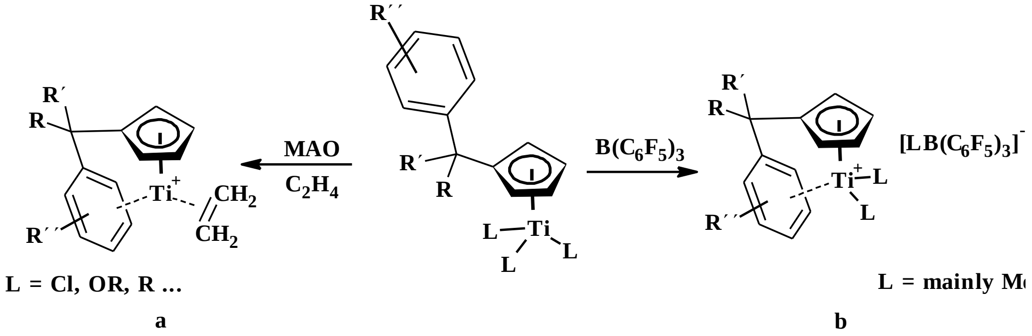


Fig. 8: Proposed mechanism of ethylene trimerization catalysed with cyclopentadienyl-arene Ti complex/MAO system[23]

According to experimental data and DFT calculations, It was approved that catalytic active species is Ti(II) which is stabilised by the coordination of pendant arene unit. The presence of this hemilabile ligand is crucial for the selectivity of trimerization process.[26, 27]

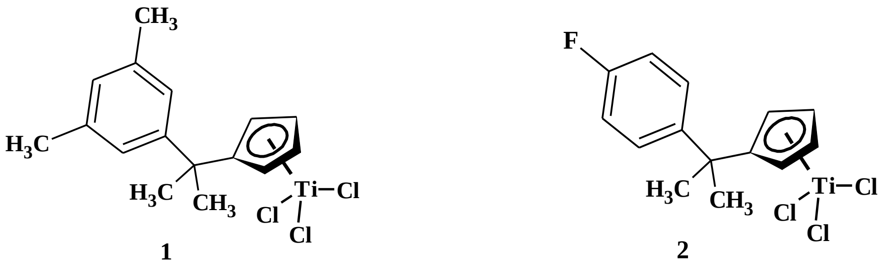
The important approach, which can be modified, is an activation of catalytic active species (**Scheme 1**).[28] Generally is often applied the activation by β-elimination of *in situ* prepared alkyl complex of titanium. The mostly utilised alkylation agent is MAO, which has to be used in a huge molar excess, sometimes even 2000 equivalents to 1 equivalent of Ti. This amount is also crucial, because alkylated complex reacts subsequently with MAO and provides an intermediate, which is inactive in the catalytic cycle. Fortunately, MAO also smoothly reacts with this intermediate and releases the alkylated complex back into space.

The second approach to generating the active species is a mutual reaction of alkyl complex of Ti-catalyst with perfluoroaryl borane $B(C_6F_5)_3$.[29, 30] The product of this reaction is a cationic complex with weakly coordinating borate anion. Big disadvantage of this activation is a strong effect of impurities of solvents, because once generated active species is sensitive to them.



Scheme 1: Activation of the catalyst – MAO activation (**a**) and activation with perfluoroaryl boranes (**b**)

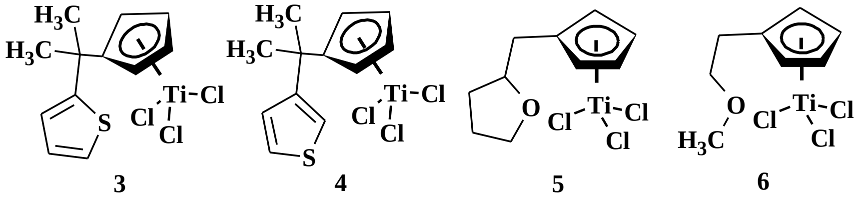
The activity and selectivity of catalyst can be influenced by several pathways.[15] The first is the substitution of pendant arene unit (**Fig. 9**). This approach was marginally studied and it was shown that the substitution of phenyl with methyl group (giving the complex **1**) significantly decreases the catalytic activity.[3] In contrast with this observation, Huang et al. studied the effect of electron-withdrawing group (EWG) in phenyl *para*-position, namely fluoride atom (giving rise to the complex **2**), and based on their results can be declared that the favourable coordination in the catalytic cycle is provided by the phenyl group itself with no substituent.[31]



1 **2**

Fig.9: Examples of arene-substituted catalysts

Other pathway to influence the activity is an exchange of the pendant hemilabile arene unit to other weekly coordinating group. One option is using the thienyl group instead of phenyl one (**Fig. 10**). Huang prepared derivatives **3** and **4** and found that position of sulphur atom is important for the activity. Thien-2-yl derivative **3** was more efficient almost 10 times in comparison to thien-3-yl derivative **4**, probably due to the more efficient coordination of sulphur atom to titanium centre during the catalytic process.[32] In addition to thienyl derivatives, Wu and co-workers prepared derivatives with pendant etheric function such as tetrahydrofuranyl **5** or methoxy **6** group. A stabilisation of the cationic Ti(II) centre by pendant oxygen donor was proposed similarly as for thienyl derivatives. These compounds exhibited a modest catalytic activity with TOFs up to 2000 h^{-1}.[33]



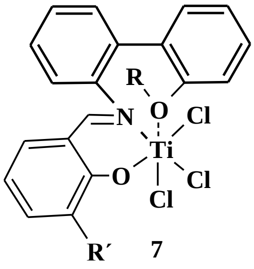
3 **4** **5** **6**

Fig. 10: Examples of catalysts with different pendant moiety

Finally, the modification of cyclopentadienyl (Cp) ligand was studied as well, because the electron density of ligand affects the stability of complex. The other approach is to exchange Cp ligand to *e.g.* indenyl ring.[34, 35]

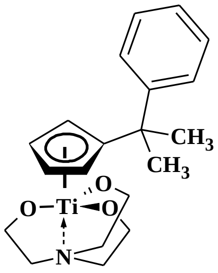
Next to Hessen's complexes, the phenoxyimines derivatives (**Fig. 11**), such as **7**, were used as a hopeful trimerization catalysts and was observed that these derivatives are even more active (TOF almost 12 000 000 h^{-1}) in comparison to half-sandwich complexes with a high selectivity to 1-hexene (up to 92%).[36]

Surprisingly, the only one study was done to explore the effect of substitution of σ-bonding ligand on titanium. Authors employed an electron-rich tetradentate trianionic ligand $[N(CH_2CH_2O)_3]^{-3}$ directly bonded to titanium **8** and found a beneficial influence on the activity to 1-hexene. They proposed an increased rate of alkylation of **8** with MAO in comparison to Hessen's complex. The attention was targeted on the activation of catalyst by MAO, because the active species is proposed without these σ-ligands.[37]



7

R = Ph, Me
R′ = cumyl, adamantyl



8

Fig. 11: Phenoxyimine catalyst **7** and titanatrane complex **8**

1.4. HOMOGENEOUS AND HETEROGENEOUS CATALYSIS

The desire to enhance the profitability of every process leads to an effort to apply the catalytic reaction. The proposed role of the catalyst is to accelerate the reaction by a mutual reaction of catalyst with a reactant. This so called activated intermediate, which can be sometimes isolated and characterised, can smoothly react with other reactant to a desired product. The simplified energetic model of the catalytic reaction is sketched in **Fig. 12**.

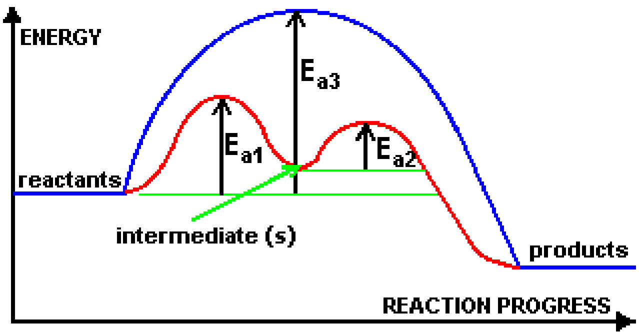


Fig. 12: Energy profile of catalytic reaction (**blue line** refers to non-catalysed reaction and **red line** refers to catalysed path)[38]

According to a number of phases, the catalysis is divided into a *homogeneous catalysis* and *heterogeneous catalysis*. The first one says that reactants and catalyst are presented in one phase, mainly liquid phase, and the second one refers that reactants and catalyst are separated in their own phase.

Homogeneous catalysis is common and widespread utilised in industrial processes, but a huge disadvantage is the separation of the catalyst after the reaction itself, because the separation, such as distillation or crystallization etc., significantly increases the cost of the all process. Nevertheless, advantages are mostly higher activities, yields, TOFs and overall faster reaction kinetics, because the reaction itself is not slowed by a transition between separated phases.

Nowadays, the subsequent separation of the catalyst causes sometimes a hardly soluble problem and for these reasons the *heterogeneous catalysis* is enforced instead of the homogeneous system, because the phases can be easily separated and then worked up.[39] A further great benefit of the heterogeneous catalysis is a recycling of the catalyst, because a simple separation causes an only negligible damage of it. Heterogeneous systems are generally immiscible liquid-liquid, solid-liquid, gas-solid and gas-liquid.

The principle of catalysis on supports can be simply described by a few key steps (**Fig. 13**). Reactants are transferred to the second phase, where the catalyst is presented. Then, the catalytic reaction proceeds and the product is released from the support.

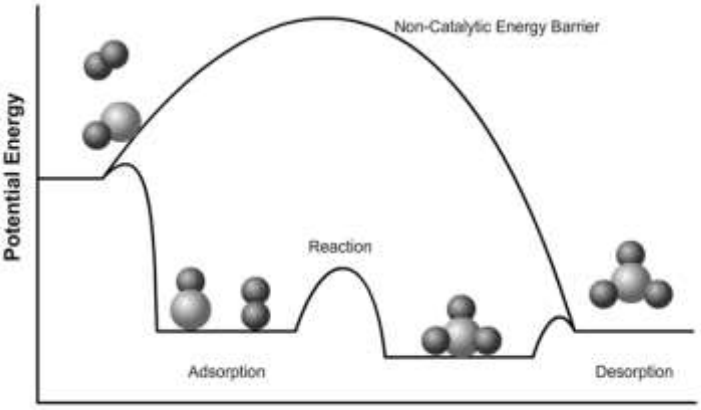
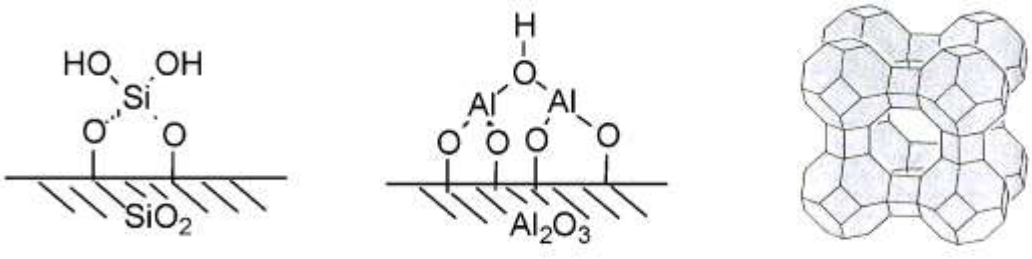


Fig. 13: Energy profile of heterogeneous catalytic reaction[40]

As a carrier of the catalyst are often used a porous material such as silica, alumina or zeolites (**Fig. 14**). These materials give an enormous stimulus to practical application, because the heterogenization of the catalytic active compounds on supports leads to their wide distribution due to their advantages. The porous materials are generally divided according to their porosity on – microporous (pore size up to 2 nm), mesoporous (pore size in range 2-50 nm) and macroporous materials (above 50 nm).

Silica, used as a carrier, is mostly used in its amorphous form, which includes anhydrous amorphous silica and surface-hydroxylated amorphous silica with a tuneable quantity of hydroxyl groups. Number of silanol group can be modified by thermal treatment. Up to 180 °C, only adsorbed water gradually evaporates and above this temperature, the silanol groups condensate to siloxane form.

Zeolites are crystalline aluminosilicates with a three-dimensional framework structure arranged to well-done defined pores suitable to adsorb organic molecules. These materials are preferably used in industry as an acidic catalyst *e.g.* for Friedel-Crafts reaction or as molecular sieves. Great pros of zeolites are price, easy recycling, relatively good thermal stability and high surface area in hundreds of $m^2 \cdot g^{-1}$.[39]

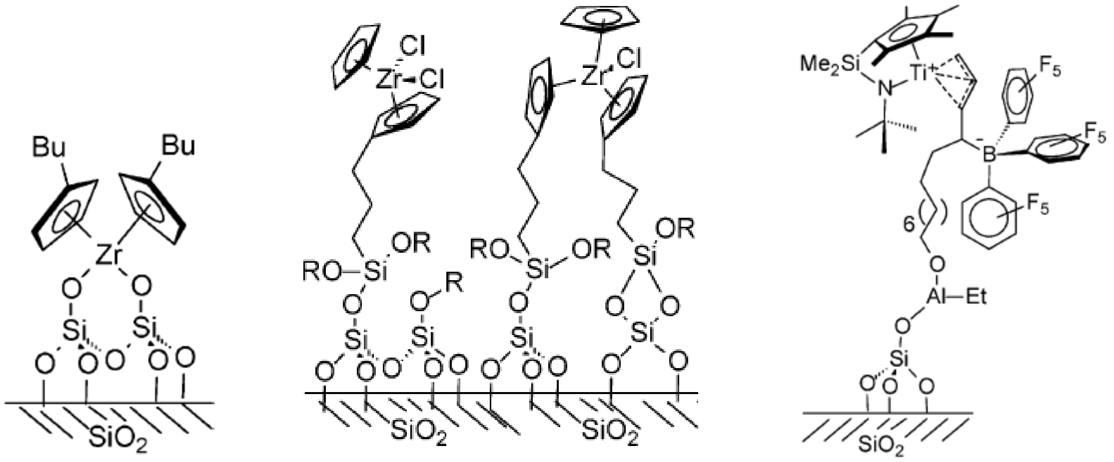


a **b** **c**

Fig. 14: Examples of supports – silica (**a**)[39], alumina (**b**)[39] and zeolite (**c**)[41]

The catalyst can be anchored to a heterogeneous system by various pathways (**Fig. 15**).[39] One option is the covalent bonding of the support to the central metal atom, where *e.g.* silica acts as a macroscopic silanolate ligand (**Fig. 15a**). The catalyst can be grafted to a carrier *e.g.* via acid-base reaction, when an acidic surface of carrier reacts with a catalyst, or classic nucleophilic substitution etc.[42] Typical example is grafting of zirconocene dichloride and its derivatives to a silica support. The products of this metathesis are preferable heterogeneous catalysts for olefin polymerization. In this case, the metal atom is directly bonded to silanol group and its flexibility is suppressed.[43]

Hence, other path was applied to anchor the catalyst to the carrier. Tethering a catalytic complex via a covalent link between the support and the pendant ligand of the catalyst is one representative of this anchoring (**Fig. 15b**).[44] The suitable conjunctions are silane, siloxane or borane groups that are introduced by hydrosilylation, hydroboration, transmetalation or even coordination.[45]



a **b** **c**

Fig. 15: Examples of anchored catalysts – the direct metal to support bonding (**a**), via the covalent link between the support and ligand (**b**) and the electrostatic interaction between cationic catalytic centrum and anionic ligand bounded to support (**c)**

Other important alternative is a co-catalyst supporting. This pre-catalyst supporting system is the result of reaction of surface (*e.g.* silanol groups) with a co-catalyst such as MAO or perfluoroaryl boranes. This solid is then treated with a catalytic precursor and it generates the catalytic active species that are hold by an electrostatic interaction between cationic catalytic centre and anionic ligand (**Fig. 15c**).[46]

It is obvious that the heterogenization of the catalyst is a difficult problem and it is necessary to optimize the conditions for a suitable catalytic procedure. As a modelling molecules for silica surface are often employed derivatives of silsesquioxanes (**Fig. 16**). Silsesquioxanes are organosilicon compounds that have cage-like structure and the form is varied, from cube to dodecagonal prism. Again, the models can be targeted on the various pathways of heterogenization. The catalytic active metallasilsesquioxanes of half-sandwich titanium catalysts were prepared and as an activation agent was used MAO.[47] Alternatively, tethering approach was tested as well. And finally, pre-catalyst prepared by the reaction of the open form of silsesquioxanes with MAO or perfluoroaryl boranes were prepared and studied too. .

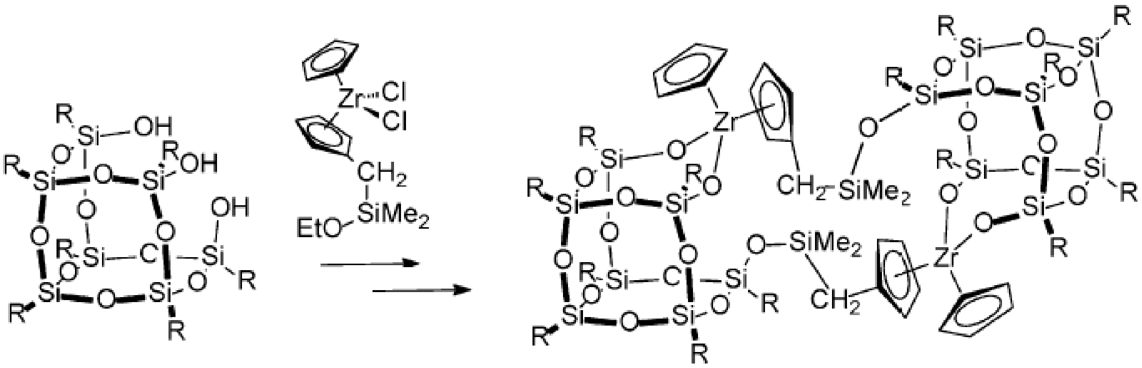


Fig. 16: Silsesquioxane used as models of silica-grafted catalysts[39]

It is surprising, that the only one study was done, which was focused on the trimerization catalysts immobilized on the supports. In 2005, Nenu et al. published their study of chromium-based heterogeneous trimerization catalysts. They found that the Phillips catalysts anchored to an amorphous silica carrier is a low active and the selectivity is strongly temperature dependant and higher amount of polyethylene was achieved.[48]

Major interest is focused on the catalysts derived from chromium and titanium. Across the last few decades, a large amount of pioneering work was done to find the correlation between the structure of the catalyst and the catalytic activity or selectivity. Partially, these efforts have been met, but many exceptions could be declared.

Inspired by these facts, we have decided to fill a gap among this pioneering work and focus on the synthesis and characterisation of new half-sandwich complexes of titanium with a various pendant tether. Furthermore, the effect of σ-bonding ligand on titanium was only marginally studied, but the electronic effects on the central atom might play a significant role during an initial stage of activation (*i.e.* alkylation). And finally, we shall use the prepared potential catalyst to anchoring to a specified surface for a purpose to get the active heterogeneous catalysts for the trimerization of ethylene to 1-hexene.

2. THESIS OBJECTIVES

Based on the previously described motivation, the goals of this thesis are to develop processes for supporting of cyclopentadienyl-arene titanium complexes onto solid supports and to evaluate catalytic properties of the obtained species in ethylene trimerization. The aim of the work can be divided into following issues:

1. Design and synthesis of half-sandwich complexes of titanium used for anchoring on supports and their utilisation for ethylene trimerization

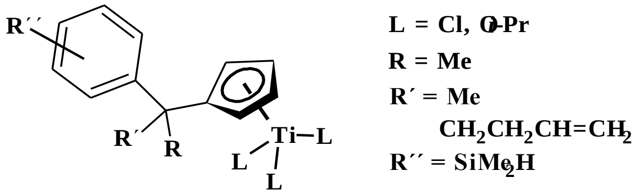


Fig. 17: Final derivatives with a various pendant group and σ-ligands

2. Design and synthesis of homogeneous models of surface species of anchored catalysts

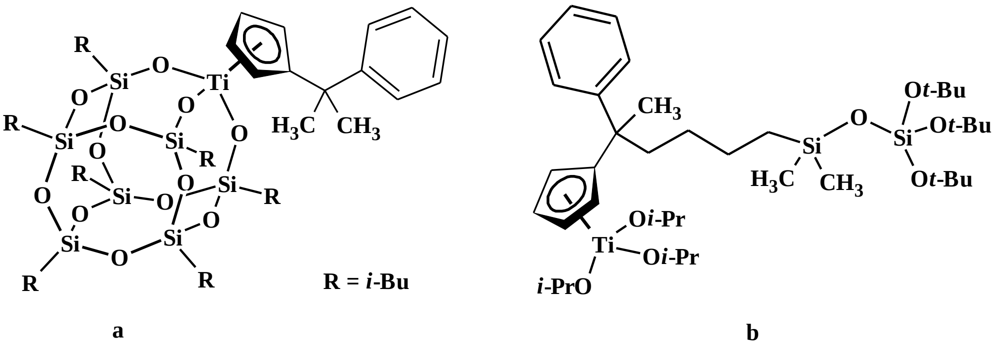


Fig. 18: Final model catalyst – direct anchoring (**a**) and by a flexible tether (**b**)

3. Heterogenization of selected complexes by different heterogenization strategies

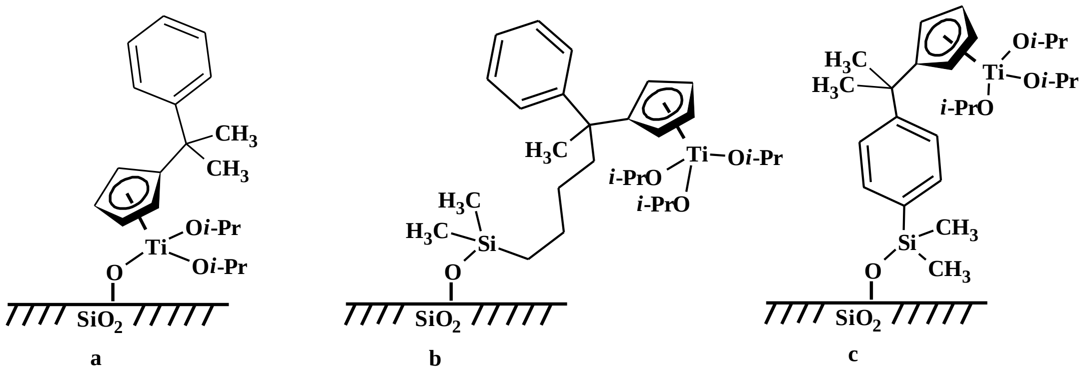


Fig. 19: Various heterogenization strategies – direct anchoring (**a**), via a flexible tether (**b**) and via a rigid tether (**c**)

4. Study the activity and selectivity of selected compounds in catalytic trimerization of ethylene to 1-hexene

3. THEORETICAL

Based on the experiences of Hessen and co-workers and other scientists, we have designed the half-sandwich complexes of titanium of general formula $[(\eta^5\text{-}C_5H_4CMeArR_1)Ti(L_3)]$, where Ar = phenyl or aryl, Me = methyl and R_1 refers to various substituents such as methyl, but-3-enyl and L means various ligands - Cl or O*i*-Pr. The design was subjected to further utilisation of proposed complexes for immobilization on various supports. Furthermore, as a model of immobilised surface species were used derivatives of formula $[(\eta^5\text{-}C_5H_4CMe_2Ph)Ti(POSS\text{-}O_3)]$, where σ-ligand $POSS\text{-}O_3$ = open silsesquioxane or $[(\eta^5\text{-}C_5H_4CMePhR_1)Ti(O\mathit{i}\text{-}Pr)_3]$, where R_1 is represented by $-(CH_2)_4SiMe_2OSi(O\mathit{t}\text{-}Bu)_3$.

3.1. IMMOBILIZATION STRATEGIES

This thesis is focus on the synthesis of anchored catalysts for ethylene trimerization. We designed two independent pathways to heterogenization of catalysts and these approaches are depicted in **Fig. 20**.

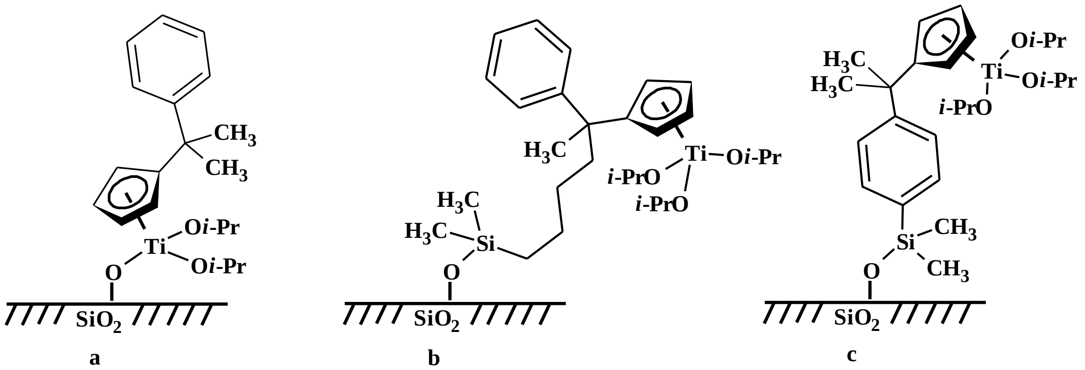
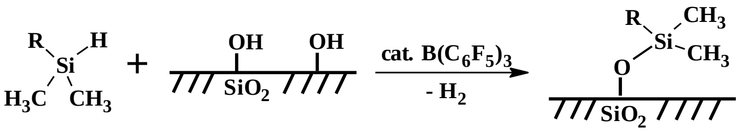


Fig. 20: Various heterogenization strategies – direct anchoring (**a**), via a flexible tether (**b**) and via a rigid tether (**c**)

The first possible immobilization (**Fig. 20a**) represents the direct bonding of Ti on supports through covalent Ti−O−Si bond via *e.g.* acid-base reaction or ligand-exchange reaction, because also a support surface (with free silanol groups on silica surface) can be considered as a ligand.[39]

In contrast with this approach, the second strategy considers free titanium complex bonded to the support through pendant tether attached to cyclopentadienyl ligand. Even these strategies could be divided to two variants. The first one counts with the terminal double bond on a flexible tether (**Fig. 20b**) that is attached to carrier via addition reactions such as hydrosilylation, hydroboration etc. In this thesis, we have decided to utilise the catalytic hydrosilylation reaction, which is commonly catalysed by platinum complexes.[49] The most utilised is Karstedt's catalyst, platinum(0)-1,3-divinyl-1,1,3,3-tetramethyl-disiloxane, but there are other choices − Speier's catalyst H_2PtCl_6, $[Rh(COD)_2]BF_4$, $[Rh(NBD)Cl]_2$ and many others.

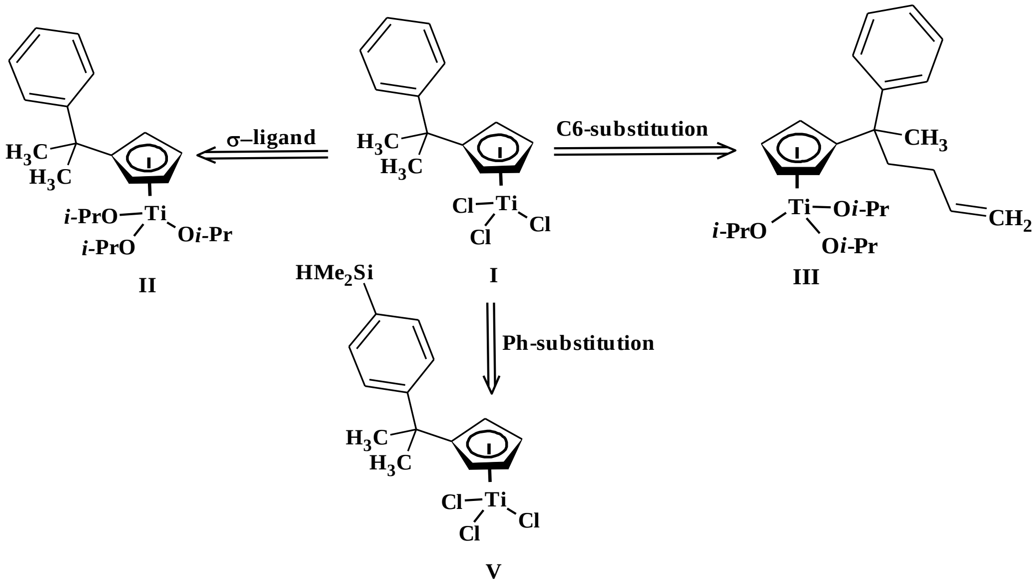
We assume that the activity could be influenced by the character of tether between the catalytic centre and the linkage. In the case, the pendant arm is long enough and flexible (**Fig. 20b**), the titanium could be in close contact with the surface as well and this contact could decrease the catalytic activity. Hence, we designed the third anchor strategy (**Fig. 20c**), when the complex is attached to the surface through a phenylene tether. Planned $-SiMe_2-$ linkage could be established by a reaction of hydrosilane with silanol group catalyzed with $B(C_6F_5)_3$ (**Scheme 2**).[50]



Scheme 2: Reaction of hydrosilane with silica surface silanol group catalysed with $B(C_6F_5)_3$

3.2. RETROSYNTHETIC ANALYSIS OF HALF-SANDWICH COMPLEXES

Following our goals, we had to create the suitable titanium complexes derived from Hessen's complex **I** (**Scheme 3**) .



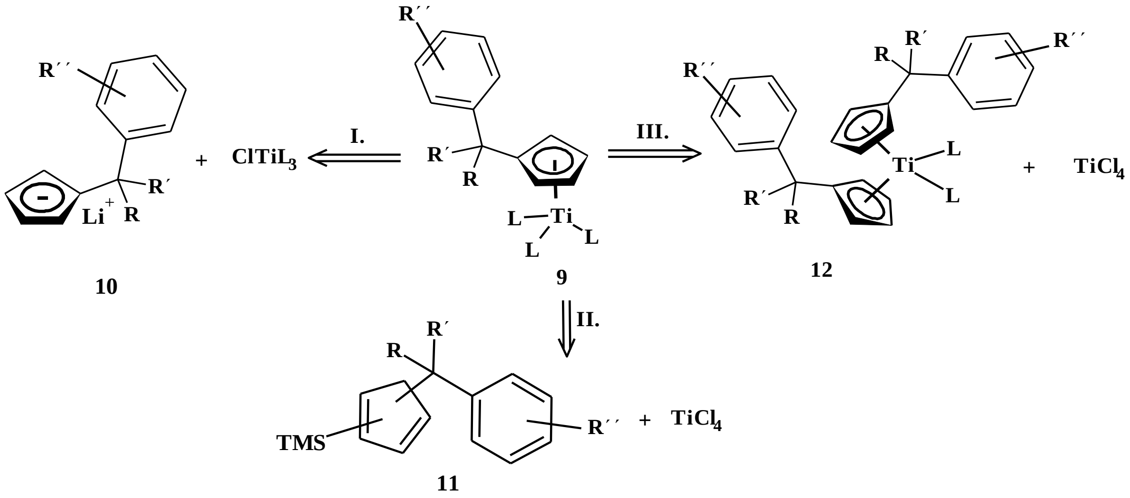
Scheme 3: Suggested modification of Hessen's complex **I**

We have modified Hessen's complex **I** by introduction of various σ-ligand (*i.e.* replacing of parent chloride with isopropoxide giving a complex **II**). Then substitution of cyclopentadienyl ligand at C6 was processed (*i.e.* formal replacing of methyl group with but-3-enyl group giving complexes **III** and **IV**). This pendant alkenyl group was selected for further anchoring on the $SiMe_2H$-modified silica by hydrosilylation. The last proposed modification was substitution on aromatic core (*i.e.* formal substitution of *para*-hydrogen with $SiMe_2H$ group to give a complex **V**), that will also utilised to anchoring on silica surface through $-SiMe_2-$ linkage.

Retrosynthetic analysis of the half-sandwich cyclopentadienyl-arene complexes of titanium **9** could be divided into three major pathways (**Scheme 4**). The first approach **I.** represents the selective synthesis from suitable lithium cyclopentadienide precursor. These complexes are often prepared via multi-step reaction that includes the transmetalation of lithium cyclopentadienide **10** with the source of titanium. The right choice of the titanium salt depends on the desired σ-ligand. For example, if the alkoxide is the ligand of choice, the direct transmetalation of lithium cyclopentadienide with $ClTi(OR)_3$ is possible and smoothly proceeds to the product. Despite, the trichloride derivative cannot be prepared by the direct transmetalation of lithium cyclopentadienide **10** with $TiCl_4$, because the major product would be the relevant titanocene dichloride instead of the proposed half-sandwich complex. It is caused by a higher reactivity of $TiCl_4$ in comparison to $Ti(Oi\text{-}Pr)_4$.

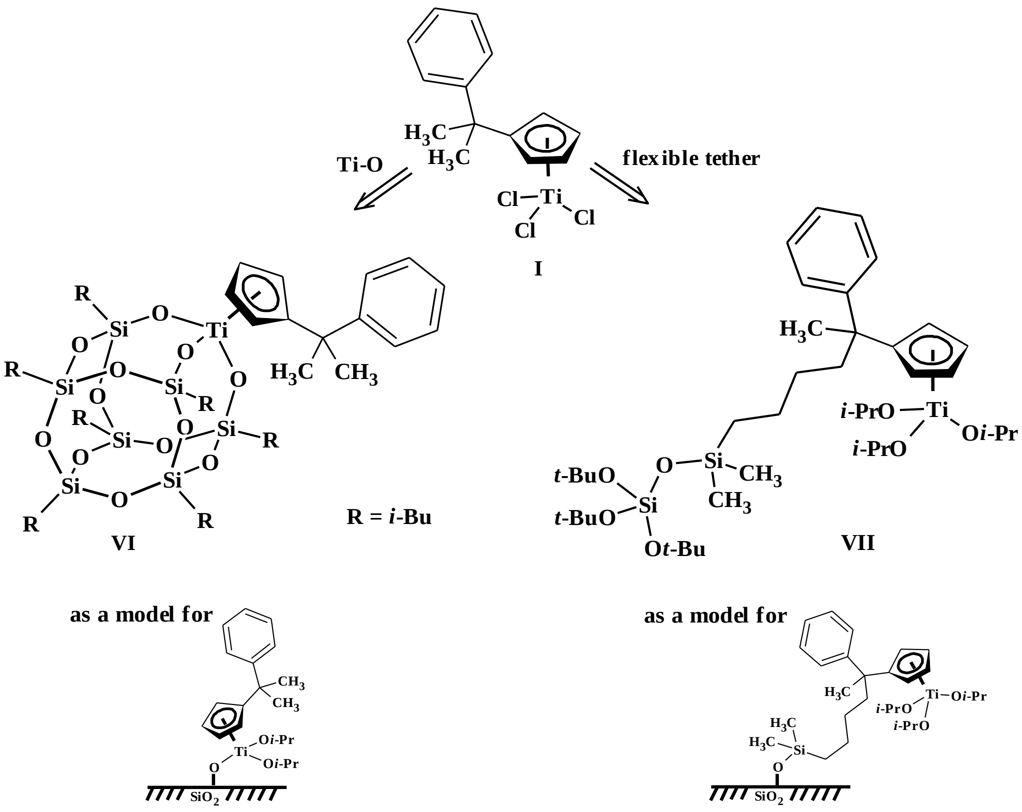
An elegant solution for preparation of $CpTiCl_3$ complexes is two-step reaction **II.** via silyl derivative **11** that is prepared by transmetalation of lithium cyclopentadienide **10** with trimethylsilyl chloride (TMSCl). The trimethylsilyl derivative is usually obtained as a mixture of all possible regioisomers. However, the reaction of this regioisomer mixture with $TiCl_4$ is selective and provides a half-sandwich cyclopentadienyl titanium complex **9** with three chloride σ-ligands as a main product and a volatile TMSCl as the only by-product.[51]

The last pathway **III.** is the redistribution reaction of equimolar mixture of a suitable titanocene dichloride **12** with $TiCl_4$ in boiling aromatic solvents. Unfortunately, this reaction strategy is hardly applicable for some derivatives due to the higher temperature.[52]



Scheme 4: Retrosynthetic analysis of the half-sandwich titanium complexes

Since the characterisation of heterogeneous systems is the challenge for many scientists and for these reasons, the model compounds are often designed that simulate particular surface species (**Scheme 5**).[53] We intended to prepare the model POSS derivative **VI** that illustrates the covalent bonding of Ti onto the support and the derivative **VII** that represents the anchoring through a flexible tether.



Scheme 5: Suggested models of surface species of anchored catalysts

4. RESULTS AND DISCUSSION

This chapter summarises the results of the synthetic part, characterisation of prepared compounds and the trimerization experiments of prepared promised catalysts as well.

4.1. SYNTHETIC STRATEGIES

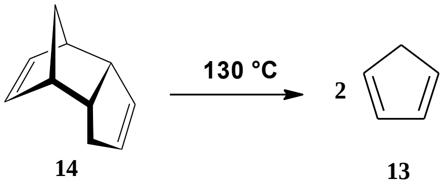
According to planned anchored strategy, the synthetic part could be divided into these independent parts – synthesis of homogeneous complexes **I-V**, model compounds **VI-VII** and anchored polymeric catalyst **III/PMHS**; and immobilization of selected compounds on surface carrier **II/SiO_2(200)**, **II/SiO_2(800)**, **II/SBA-15(200)** and **II/SBA-15(700)**, **III/SiO_2SiMe_2H** and **III/SiO_2SiMe_2H(90)**.

Homogeneous catalysts differ in the type of σ-ligand bonded directly on Ti, concretely **I**, **IV** and **V** bear chloride σ-ligands, **II**, **III**, **VII** and **III/PMHS** bear isopropoxy σ-ligands and the derivative **VI** contains tridentate POSS ligand. Furthermore, these compounds differ in the substitution of cyclopentadienyl ring, concretely **I**, **II** and **VI** bear CMe_2Ph substituent, **III** and **IV** contain unsaturated pendant arm $CMe[(CH_2)_2CH{=}CH_2]Ph$, the derivative **V** consists of $CMe_2(PhSiMe_2H)$ pendant substituent, the derivative **VII** contains $CMe[(CH_2)_4(SiMe_2)OSi(O\textit{t}\text{-Bu})_3]Ph$ pendant substituent and the substituent of the final homogeneous derivative **III/PMHS** can be illustrated as $\{CMePh[(CH_2)_4(SiMe)O]\}_n$.

4.1.1. SYNTHESIS OF HOMOGENEOUS HALF-SANDWICH COMPLEXES

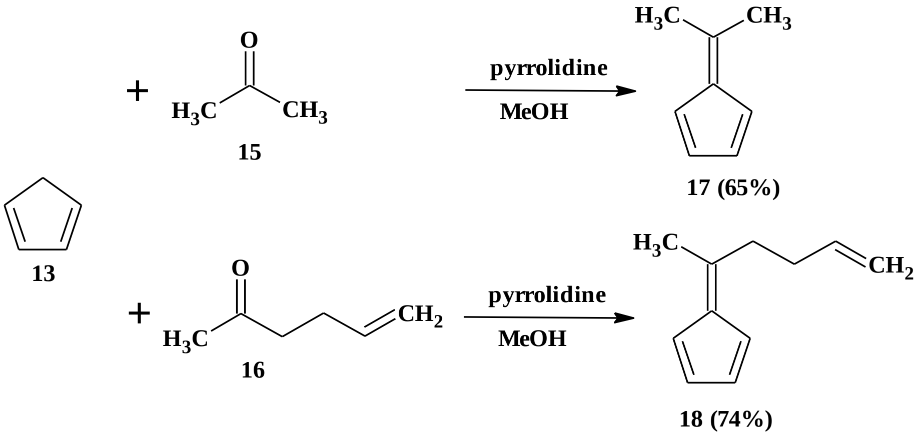
Synthetic strategy begins with a design of an appropriate precursor of cyclopentadienyl ligand. Modern synthesis counts with fulvenes, because these compounds are easily available from reaction of cyclopentadiene (**13**) with suitable carbonyl compounds, aldehyde or ketone, by base-catalysed condensation reaction.[54]

We have chosen this reaction pathway as well. First of all was necessary to prepare cyclopentadiene (**13**) by retro Diels-Alder reaction of dicyclopentadiene (**14**) (**Scheme 6**).



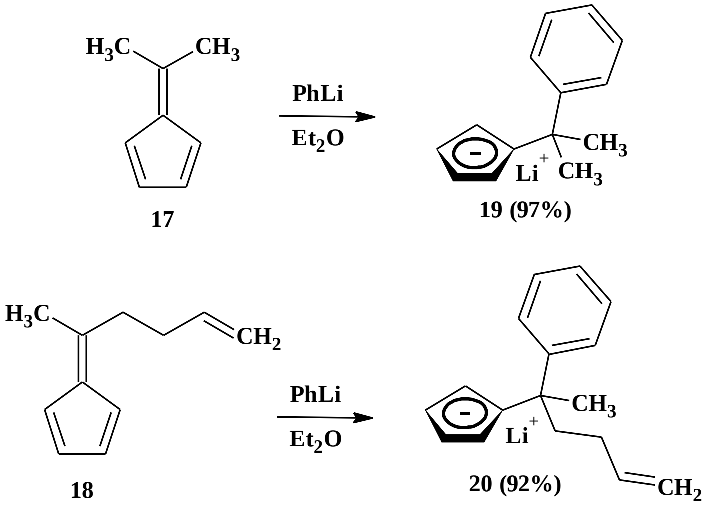
Scheme 6: Retro Diels-Alder reaction

The cracking of dicyclopentadiene (**14**) was done at 130 °C and the released cyclopentadiene (**13**) was continually distilled off. Freshly cracked cyclopentadiene (**14**) was then used in the condensation reaction with acetone (**15**) or 5-hexen-2-one (**16**) in MeOH and pyrrolidine was used as a base (**Scheme 7**). The corresponding fulvenes, 6,6-dimethylfulvene (**17**) and 6-(but-3-enyl)-6-methylfulvene (**18**) were obtained after a vacuum distillation in modest yields 65% and 74%, respectively.



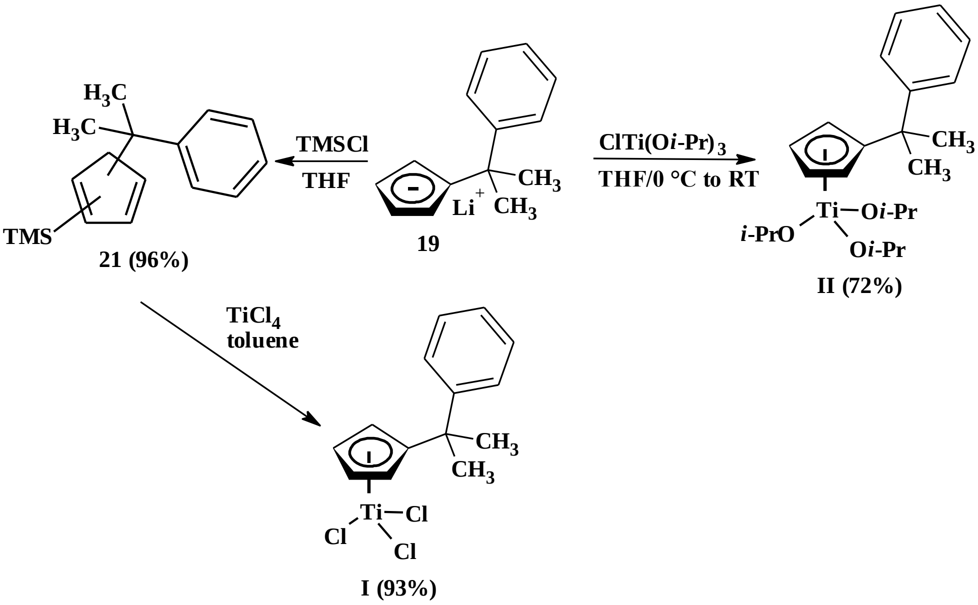
Scheme 7: Synthesis of fulvenes **17** and **18**

In the next step, the fulvenes **17** and **18** were transformed to the corresponding lithium cyclopentadienides **19** and **20** by a nucleophilic addition of phenyllithium with excellent yields 97% and 92% (**Scheme 8**). The regioselectivity of the addition is supported by the emergence of the stable cyclopentadienyl anion.



Scheme 8: Synthesis of lithium cyclopentadienide derivatives

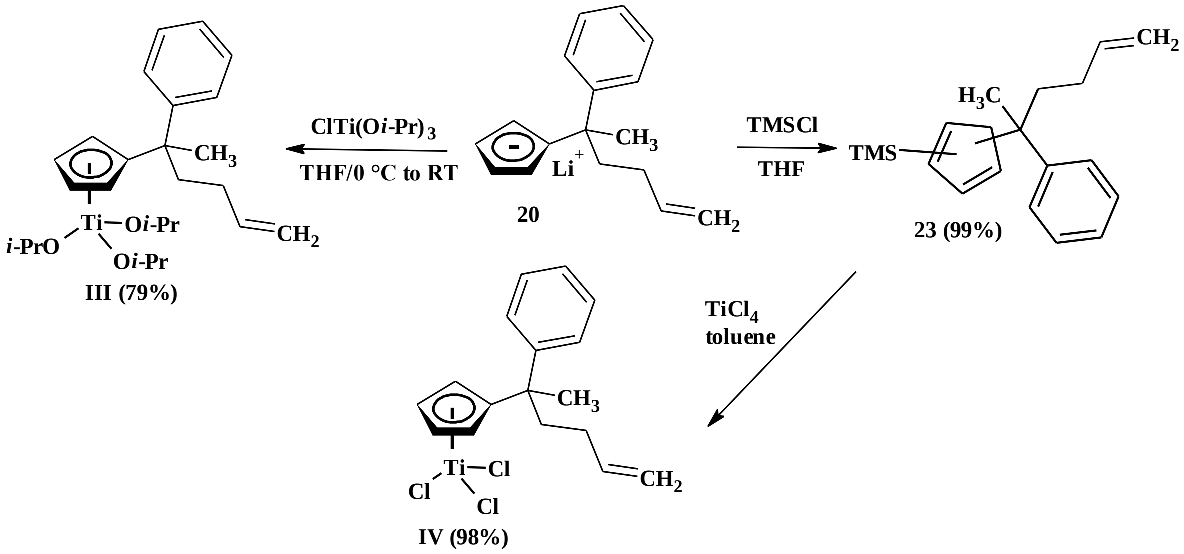
The lithium cyclopentadienide **19** was used to the synthesis of the final homogeneous catalysts with $PhMe_2C$ substituted cyclopentadienyl ring (**Scheme 9**).



Scheme 9: Synthesis of half-sandwich complexes **I** and **II**

As it was explained above, the complex **I** with chlorides as σ-ligands was prepared via the silyl derivative **21** by the reaction of lithium cyclopentadienide **19** with TMSCl. The reaction product was a statistic mixture of all possible regioisomers. Hessen's complex **I** was then prepared by exchange reaction of silyl **21** with $TiCl_4$ and after the purification was obtained with 93% yield.[27] This complex was necessary to prepare as a standard for the trimerization experiments. Furthermore, the half-sandwich complex **II** with pendant $PhMe_2C$ group and isopropoxy groups bonded to titanium was prepared by direct transmetalation of lithium cyclopentadienide **19** with ClTi(O*i*-Pr)$_3$ with an acceptable yield 72%.

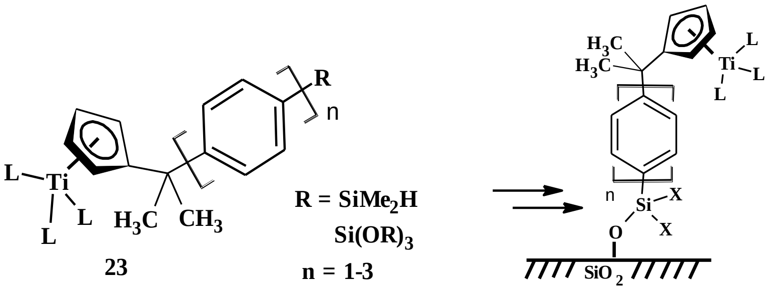
Analogously, the final homogeneous catalysts with $PhMe(CH_2{=}CHCH_2CH_2)C$ substituted cyclopentadienyl ring and isopropoxy ligands was provided by transmetalation of lithium cyclopentadienide **20** with ClTi(O*i*-Pr)$_3$ with a good yield 79% (**Scheme 10**). The titanium complex **IV** was also obtained through the silyl derivative **22** analogously to the complex **I**. The following reaction of **22** with $TiCl_4$ provided the desired complex **IV** with a pendant $PhMe(CH_2{=}CHCH_2CH_2)C$ group on cyclopentadienyl ring and chlorides as σ-ligands with an excellent yield 98%.



Scheme 10: Synthesis of half-sandwich complexes **III** and **IV**

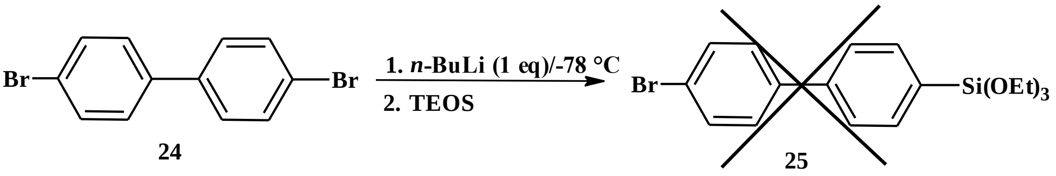
The complex **III** was designed with the proposal its anchoring via hydrosilylation onto $SiMe_2H$-modified silica. Hence, it represents an example for a flexible tethering.

In addition, we decided to design a new complex of general formula **23** (**Scheme 11**). We assume that the planar geometry of aromatic ring causes the inflexibility of titanium catalysts and prevents an active species deactivation by the interaction with the silica surface. The first system contains free $SiMe_2H$ group usable for anchoring to the surface of carrier. Next to it, the general strategy of anchoring by ligand-exchange reaction is also available and it motivated us to design the complex with terminal Si(OR)$_3$ group analogously to anchoring approach of Bek and co-workers.[55]



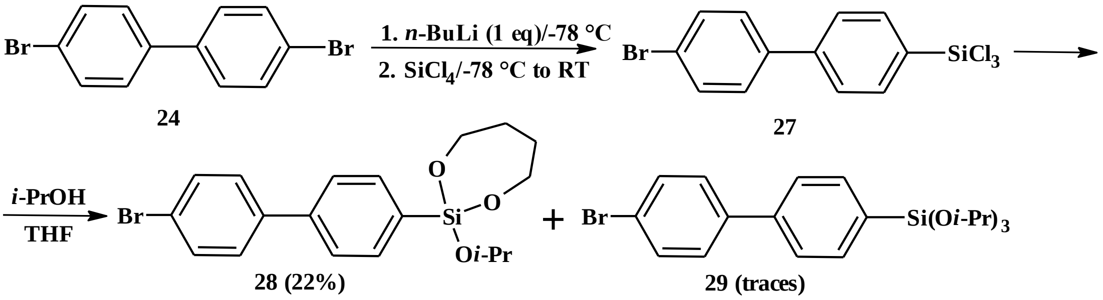
Scheme 11: General formula of complex **23** and assumed structure of anchored systems

First of all, we have started with a commercially available 4,4′-dibromobiphenyl (**24**), which was monolithiated at -78 °C by *n*-BuLi and this lithium salt was quenched with tetraethyl orthosilicate (TEOS) (**Scheme 12**) analogously to the published procedure.[56] Unfortunately, this reaction led to no product formation and as a most abundant by-product was product of debromination, *i.e.* 4-bromobiphenyl **26** (GC-MS (EI): m/z 232 ($[M]^{+\cdot}$)).



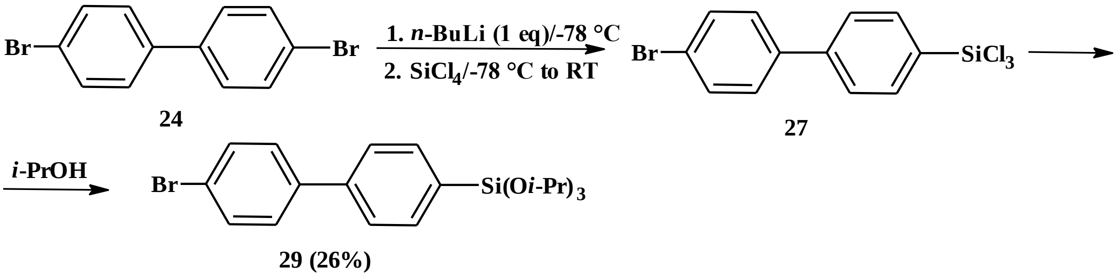
Scheme 12: Proposed synthesis of 4,4′-disubstituted biphenyl **25**

For these reason, we had to modify the synthesis. We suggested the reaction pathway through *in situ* prepared trichloro intermediate **27** following by alcoholysis (**Scheme 13**). 4,4′-Dibromobiphenyl (**24**) was again monolithiated with 1 eq of *n*-BuLi and it was quenched with $SiCl_4$ to yield trichloro intermediate **27** that was treated with *i*-PrOH and THF was added for better solubility of reagents. Surprisingly, the major product was biphenyl **28** with cyclic siloxane group instead of the desired trialkoxy product **29**. We assume that during the reaction period THF attacked trichloride **27**. THF circle is then cleaved by *i*-PrO ligand and chloride anion then attacked isopropyl group. Proposed driving force is the formation of cyclic structure of siloxane **28**, but no deeper study was done due to the sake of time. *i*-PrOH was used instead of EtOH, because ethoxy derivatives exhibit generally lower stability in comparison with more stable isopropoxy derivatives.



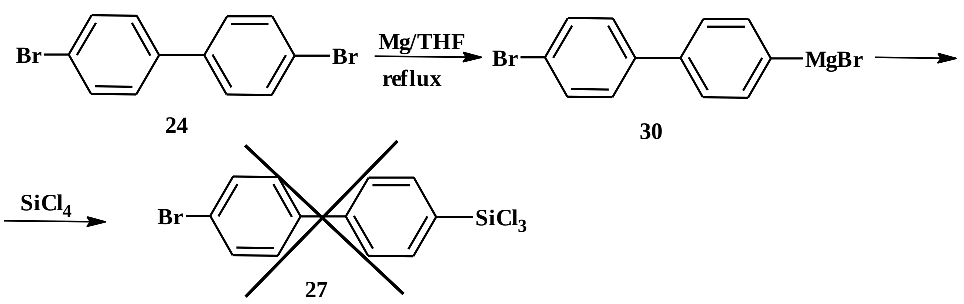
Scheme 13: Suggested synthesis of biphenyl **29**

Once more, we had to modified the synthesis of **29** (**Scheme 14**) and analogous reaction, this time without the presence of THF, provided the desired biphenyl **29**, however, in a low yield 26%.



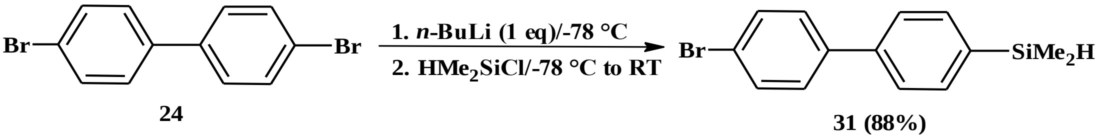
Scheme 14: Synthesis of biphenyl **29**

Because we were interested in the gram-scale (up to 10-20 g) synthesis of biphenyl **29**, we tried to avoid the lithiation step and to use a cheaper alternative through Grignard reagent **30** (**Scheme 15**). Unfortunately, the formation of Grignard reagent was unsuccessful, therefore we returned to the lithiation pathway.



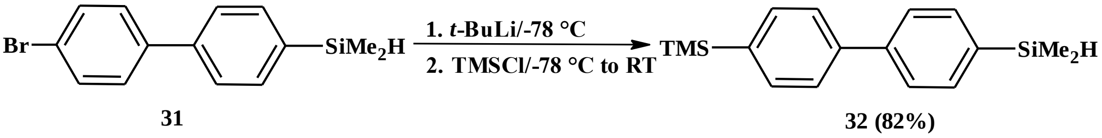
Scheme 15: Synthetic pathway through the Grignard reagent **30**

The introducing of $SiMe_2H$ group was processed analogously to the synthesis of siloxane **29** (**Scheme 16**). Monolithiated biphenyl was treated with chlorodimethylsilane to produce the biphenyl **31** in 88% yield.



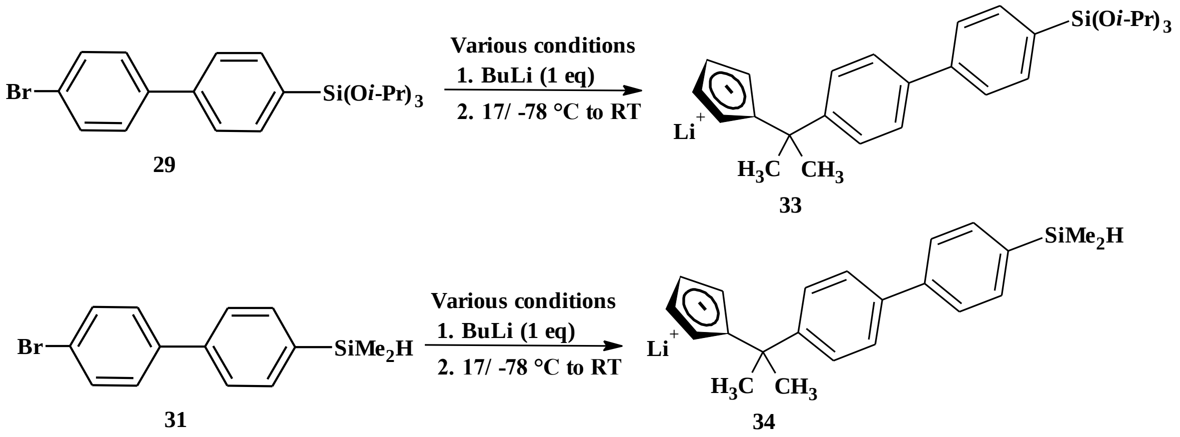
Scheme 16: Synthesis of $SiMe_2H$ modified biphenyl **31**

Before the crucial step, the nucleophilic addition of lithium salts of biphenyls **29** or **31** to 6,6-dimethylfulvene (**17**), we have decided to check the lithiation of these bromobiphenyls with BuLi at -78 °C (**Scheme 17**). As a model reaction was processed the reaction of bromobiphenyl **31** with *t*-BuLi and next treatment with TMSCl (an electrophile) produced the disubstituted biphenyl **32** in a good yield 82%.



Scheme 17: Synthesis of biphenyl **32**

The key step to the desired complexes was the addition of aryllithium salts based on biphenyls **29** or **31** to fulvene **17** (**Scheme 18**).



Scheme 18: Nucleophilic addition of lithium salts to 6,6-dimethylfulvene (**17**)

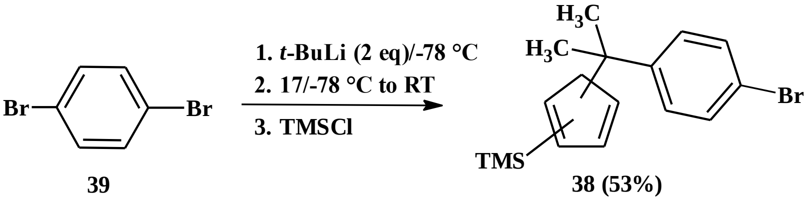
The lithiation of biphenyls **29** or **31** was done at -78 °C by 1 eq of BuLi and the success of this step was approved by GC-MS (after hydrolysis, the only products were debrominated biphenyls, (biphen-4-yl)triisopropoxysilane **35** (GC-MS (EI): m/z 359 ($[M]^{+\cdot}$)) and (biphen-4-yl)dimethylsilane **36** (GC-MS (EI): m/z 212 ($[M]^{+\cdot}$))). Further addition of fulvene **17** into the reaction and subsequent warming up to an ambient temperature led to color change of mixture from yellowish to dark red. Unfortunately, the GC-MS analyses of reaction mixtures confirmed that the addition failed and the only products were debrominated biphenyls **35** and **36**. The observed color change was probably the result of polymerization of fulvene **17** under the reaction conditions. Because this reaction step was crucial for our progress, we tried to optimize the reaction condition. Optimized parameters were – the lithiation agent, solvent and further additives (**Tab. 1**).

Tab. 1: Optimized condition for nucleophilic addition

Biphenyl	**Solvent**	**Li reagent**	**Additive**	**Product**	**Main by-product**
29 or **31**	Et_2O	*n*-BuLi (1 eq)	TMEDA (2 eq)	–	**35** or **36**
29 or **31**	THF	*n*-BuLi (1 eq)	TMEDA (2 eq)	–	**35** or **36**
29 or **31**	Et_2O	*t*-BuLi (1 eq)	–	–	**35** or **36**
29 or **31**	THF	*t*-BuLi (1 eq)	–	–	**35** or **36**
31	THF	*t*-BuLi (2 eq)	12-crown-4 (1.2 eq)	traces	**36**

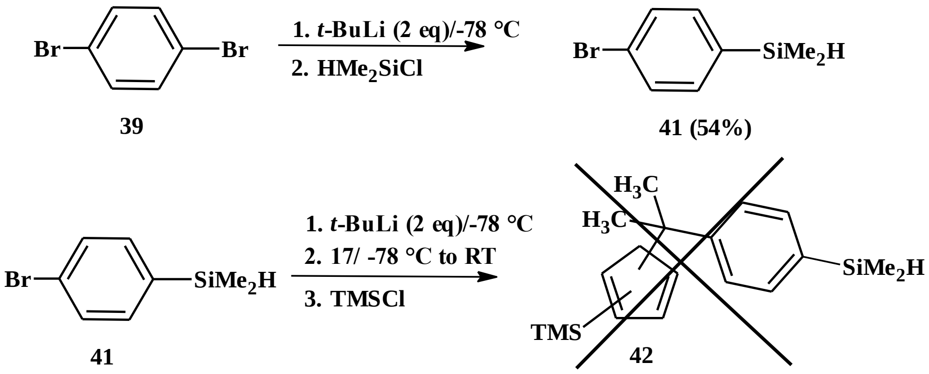
All reaction mixtures were analysed by GC-MS and as it is clearly obvious from the **Tab. 1**, the lithiation of the starting materials was independent on the organometallic agent, but instead of the desired adduct, the debrominated products **35** or **36** were observed only. Only the addition of 12-crown-4 ether to the reaction led to a detectable product formation, but for the synthesis this approach is unusable. The observation of product after the addition of crown ether testifies that the low nucleophilicity of aryllithium salts is the reason why the addition was not preferred.

Due to these results, we have applied a new synthetic strategy. According to literature, it is possible to add substituted benzene onto fulvenes and, as it was approved above, this ability strongly depends on the nucleophilicity of aryllithium salt, but no correlation between the structure and the nucleophilicity has been found for this reaction yet. Miller and co-workers published the nucleophilic addition of 4′-bromophenyllithium (**37**) onto 6,6-dimethylfulvene (**17**) with an excellent yield 92%.[57] We used the modified process (**Scheme 19**), without an isolation of the lithium salt **37**, that provided the silyl derivative **38** in a moderate yield.



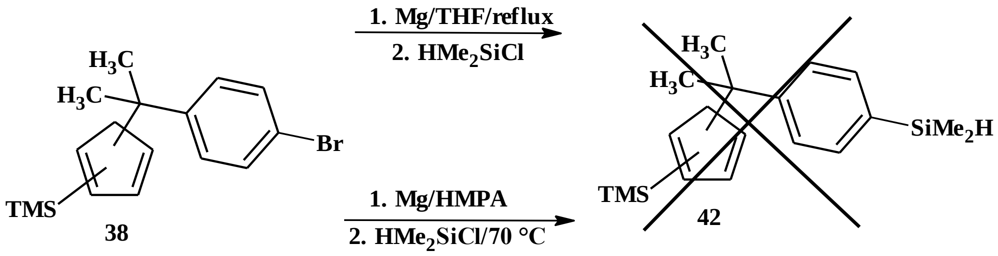
Scheme 19: Synthesis of silyl **38**

At first, we have deeply focused only on titanium complex **23** with pendant $SiMe_2H$ substituted phenyl group. Because the addition of 4-bromophenyllithium (**37**) onto fulvene **17** was successful, we analogously tried the addition of 4-(dimethylsilyl)phenyllithium (**40**) too (**Scheme 20**). First of all, we prepared 4-(dimethylsilyl)bromobenzene (**41**) through *in situ* prepared monolithiated salt **37** and its reaction with chlorodimethylsilane in a modest yield 54%.[58] The subsequent addition of lithium salt based on **41** was processed, but the desired adduct **42** was not observed even in the trace amount. It again directly confirmed that the addition onto fulvene strongly depends on the electronic properties of nucleophile and it is hard to predict the structure-nucleophilicity relationship for this type of reaction.



Scheme 20: Proposed synthesis of adduct **42**

Silyl **38** was then used for synthesis of derivatives with different length of aromatic arm terminated with $SiMe_2H$, namely phenyl, biphenyl and terphenyl. The silyl **42** with $SiMe_2H$ substituted phenyl group was designed through the Grignard reagent (**Scheme 21**). Unfortunately, the formation of the organomagnesium compound in THF was unsuccessful even with an addition of hexamethylphosphoramide (HMPA) that in general rapidly increases the reactivity of organometallic compounds.[59] The same reaction processed in a pure HMPA yielded to no product formation as well.



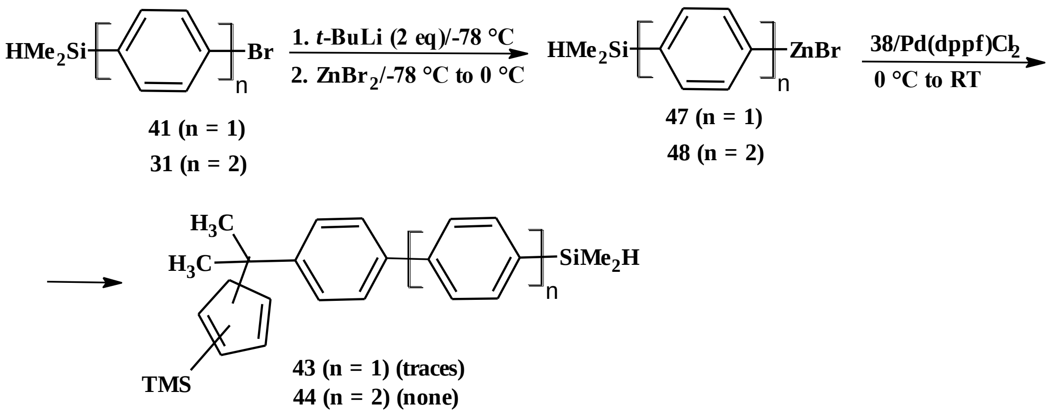
Scheme 21: Proposed synthesis of silyl **42**

Therefore, we abandoned this idea and followed the further synthesis of prolonged derivatives **43** and **44** utilising the palladium-catalysed Negishi cross-coupling reaction. First of all, we prepared the catalyst **45** (**Scheme 22**), [1,1′-bis(diphenylphosphino)-ferrocene]dichloropalladium(II) $Pd(dppf)Cl_2$, that is one of the most utilised and active Pd-catalyst in C−C coupling reactions. This catalyst was prepared according to literature from polymeric $(PdCl_2)_n$ that is heated in acetonitrile to produce quantitatively $Pd(CH_3CN)_2Cl_2$ (**46**). Following ligand-exchange reaction of **46** with 1,1′-bis(diphenyl-phosphino)ferrocene (dppf) in $CHCl_3$ yielded the desired catalyst.[60]

$$\underset{}{(PdCl_2)_n} \xrightarrow{CH_3CN} \underset{\textbf{46 (100\%)}}{Pd(CH_3CN)_2Cl_2} \xrightarrow[CHCl_3]{dppf} \underset{\textbf{45 (84\%)}}{Pd(dppf)Cl_2}$$

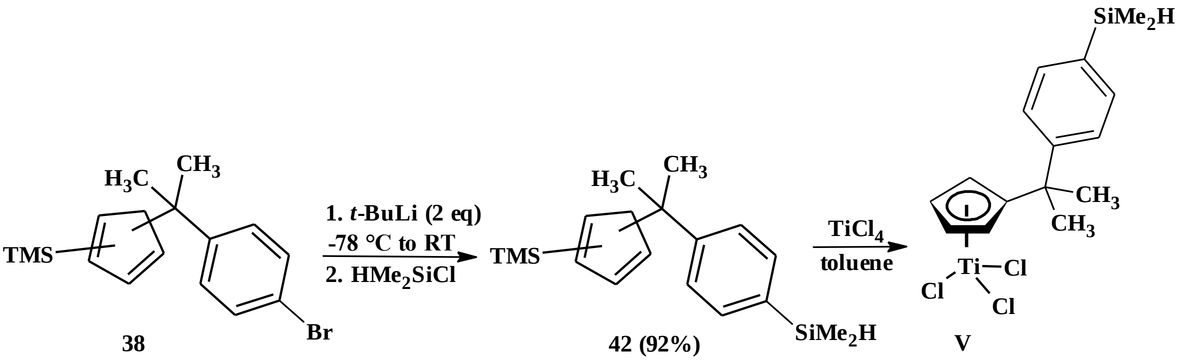
Scheme 22: Synthesis of Pd(dppf)Cl_2 (**45**)

Then, silyl derivative **38** was used in Negishi cross-coupling reaction with the corresponding organozinc reagents **47** or **48** (**Scheme 23**). The organozinc species were prepared from bromo derivatives **41** or **31** by reaction with 2 eq of *t*-BuLi at -78 °C following the transmetalation with freshly sublimed $ZnBr_2$. Next addition of silyl **38** with catalytic amount of Pd(dppf)Cl_2 (**45**) (5%$_{mol}$) led only to the negligible quantity of the desired coupled product **43** as was determined by GC-MS.



Scheme 23: Negishi cross-coupling reaction

Despite these problems, we expected that the $SiMe_2H$ functional group could be introduce also through the lithium salt derived from silyl compound **38** instead of the previously planned Grignard reagents (**Scheme 24**). Analogously to the other $SiMe_2H$ substituted derivatives was prepared the desired derivative **42** with an excellent yield 92%. Finally, the key half-sandwich complex **V** with terminal $SiMe_2H$ group was processed by verified transmetalation of TMS-intermediate **42** with $TiCl_4$ in toluene. For the sake of time, the complex **V** was not prepared with the sufficient purity for trimerization study and its utilization and immobilization will be the goal of the further study.

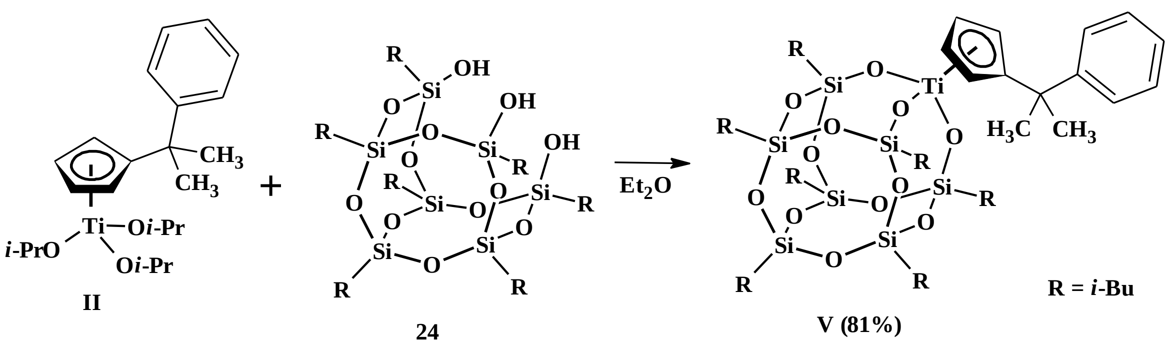


Scheme 24: Synthesis of half-sandwich complex **V**

4.1.2. SYNTHESIS OF HOMOGENEOUS MODELS OF SURFACE SPECIES OF ANCHORED CATALYSTS

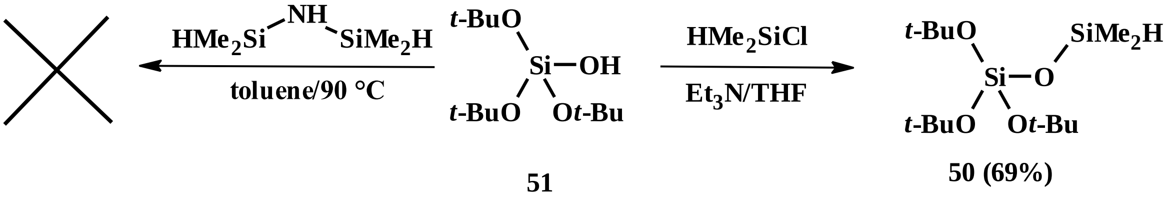
Prior to the preparation of the heterogeneous catalysts for the trimerization of ethylene to 1-hexene, we were interested in the design of model compounds that are the homogeneous models of heterogeneous catalysts.

Following our plans, we started with a model compound **VI**, which contains a silsesquioxane as a ligand, because the POSS derivatives are generally accepted as a model of silica surface (**Scheme 25**). This metallasilsesquioxane complex **VI** was prepared by a ligand-exchange reaction of the half-sandwich complex **II** with a commercially available POSS-$(OH)_3$ **49**. The product was yielded in 81% and the reaction is forced by the good leaving ability of isopropoxy group together with the higher acidity of silanol groups in the POSS derivative **49** in comparison to isopropanol hydroxyl group.



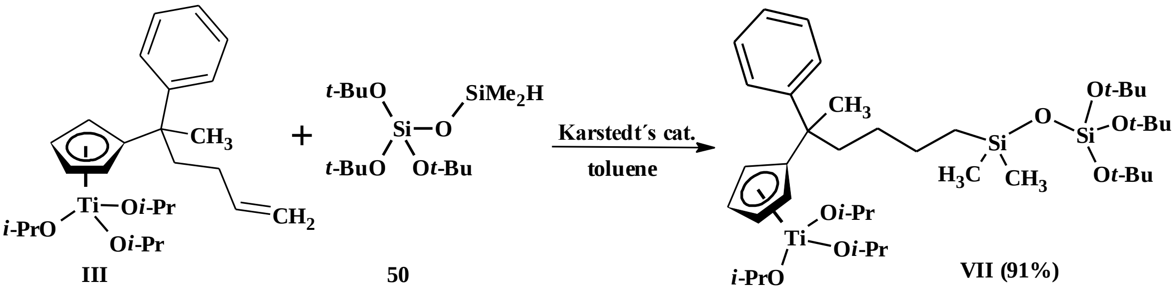
Scheme 25: Synthesis of titanium metallasilsesquioxane complex **VI**

As it was described above, the second possible approach includes the addition of Si−H on alkene by hydrosilylation reaction. Before the reaction, the $SiMe_2H$-modified siloxane **50**, which is a simple model of surface with $-OSiMe_2H$ group in $SiMe_2H$-modified silica, was necessary to prepare (**Scheme 26**). We tested two independent pathways based on nucleophilic substitution of tri(*t*-butoxy)silanol (**51**). According to literature, the silica surface can be simply modified with $SiMe_2H$ group by a reaction with 1,1,3,3-tetramethyldisilazane[61], but in our case, no product formation was observed in the mixture of silanol **51** with 1,1,3,3-tetramethyldisilazane, even after heating at 90 °C. We assumed that a low reactivity of **51**, in comparison to silica surface silanol groups, is due to a lower acidity of hydroxyl group of tri(*t*-butoxy)silanol (**51**). Hence, we attempted a reaction of silanol **51** with chlorodimethylsilane and Et_3N was used as a scavenger of the evolved HCl. This approach led to the desired simple model of $SiMe_2H$-modified silica **50**.



Scheme 26: Synthesis of simple model of $SiMe_2H$-modified silica **50**

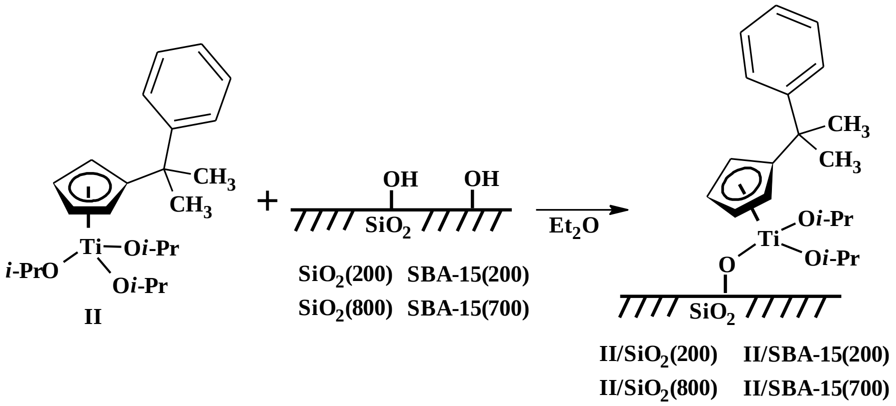
Then, the hydrosilylation reaction of siloxane **50** with terminal $SiMe_2H$ group and titanium complex **III** was proceed at the presence of catalytic amount of Karstedt's catalyst (**Scheme 27**). This reaction provided the desired homogeneous model of anchored catalyst **VII** with 91% yield.



Scheme 27: Synthesis of titanium model catalyst **VII**

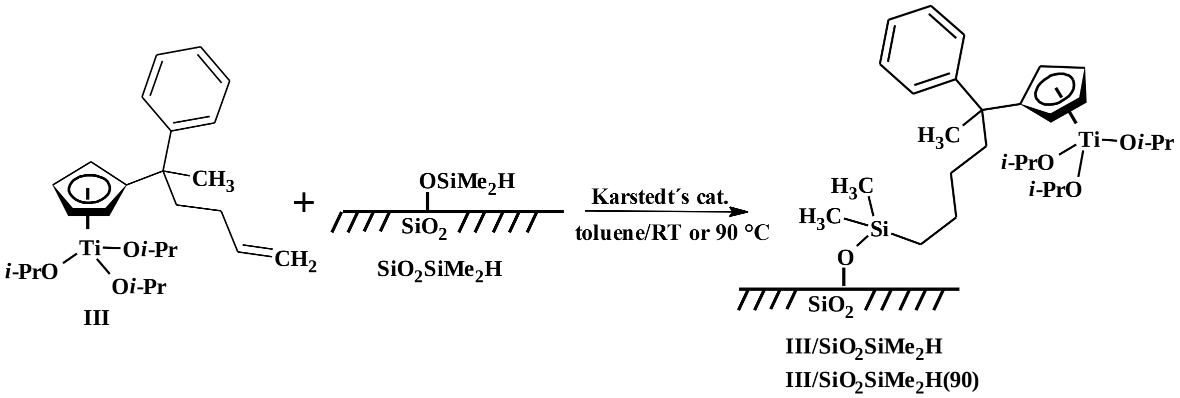
4.1.3. IMMOBILISED COMPLEXES FOR TRIMERIZATION OF ETHYLENE

The final synthetic target of this thesis was the heterogenization of prepared complexes. The titanium complex **II** was used to the direct immobilization on support surface via ligand-exchange reaction (**Scheme 28**). The selected siliceous supports were SiO_2(200), SiO_2(800), SBA-15(200) and SBA-15(700), where the number in brackets refers to the temperature of calcination. The immobilization was manufactured at Et_2O and after 12 h the liquid phase was filtrated off and tested on the presence of *i*-PrOH. The determination of *i*-PrOH in the filtrate was achieved by GC-MS analysis and its presence approved the immobilization of catalyst by ligand-exchange reaction.



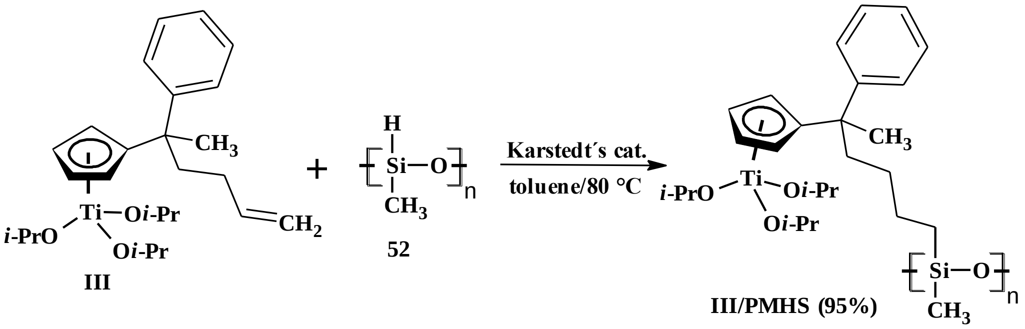
Scheme 28: The immobilization of **II** on the support surface

Then, the verified hydrosilylation procedure of synthesis of **VII** was applied for the anchoring of complex **III** on the commercially available $SiMe_2H$-modified silica support (**Scheme 29**). The reaction at room temperature or at 90 °C provided **III/SiO_2SiMe_2H** and **III/SiO_2SiMe_2H(90)** containing 1.45 and 1.67$\%_{wt}$ of Ti (determined by ICP-OES), respectively.



Scheme 29: The immobilization of **III** by hydrosilylation reaction

Polymethylhydrosiloxane (PMHS) is also commonly used as a polymer support for catalyst grafting.[62] The hydrosilylation procedure was also utilised for the synthesis of immobilized complex **III** on PMHS **(III/PMHS**) with an excellent yield 95% (**Scheme 30**).



Scheme 30: Synthesis of **III/PMHS** complex

4.2. CHARACTERIZATION OF MATERIALS

Characterization details of homogeneous systems

The identity of prepared homogeneous complexes and anchored models was verified by ^{1}H, ^{13}C NMR, ESI-MS and IR spectroscopy. The NMR spectra showed an expected pattern for all complexes.

The main characterization method of the complexes was chosen IR spectroscopy, because it would be further helpful for the description of heterogeneous species. The absorption band found at 1021 cm^{-1} in POSS derivative **VI** corresponds to a Ti−O−Si valence vibration which gives a persuasive evidence for the formation of Ti−O−Si bond.

An absorption region bellow 1300 cm^{-1} is the result of superposition of silica and Halooil 700 in heterogeneous samples, therefore other bands had to be used to the analysis of species. Valence C−H vibrations were found as a suitable probe of evidence, while they could be assigned as two weak absorption bands in the range 3077-3087 cm^{-1} and 3057-3062 cm^{-1} for aromatic units and as three strong to medium bands (2954-2972 cm^{-1}, 2929-2930 cm^{-1}, 2860-2870 cm^{-1}) for aliphatic units for all studied materials. The presence of pendant alkenyl group C=C in **III** could be revealed as a weak band at 1641 cm^{-1} as well as a medium band at 909 cm^{-1} that corresponds to =C−H out-of-plane bending vibration.

In addition, the ESI mass spectra of homogeneous complexes show the characteristic ion peak $[M + Na]^+$ at *m/z* 431 for **II**, 471 for **III**, 1041 for **VI** and 793 for **VII** and the fragmentation peak of isopropoxide derivatives [M-O*i*-Pr]$^+$ at *m/z* 349 for **II**, 389 for **III** and 711 for **VII**.

Characterization details of immobilized systems

Characterization of the directly anchored complexes on siliceous supports

The immobilization of the corresponding complexes on siliceous support was performed by direct reaction of them with the corresponding siliceous material. The immobilized complexes were characterized by ICP-OES (titanium loading analysis), IR, TGA and textural parameters were evaluated as well. The content of titanium in supported catalysts is proportional to the amount of free silanol groups of supports. Thus, supports dried at lower temperature (200 ºC) accommodated a higher amount of Ti (2.67$\%_{wt}$ in **II/SBA-15(200)** and 2.55$\%_{wt}$ in **II/SiO_2(200)**) and those calcinated at high temperatures (700 and 800 ºC) accommodated a lower amount of Ti (1.35$\%_{wt}$ in **II/SBA-15(700)** and 1.83$\%_{wt}$ in **II/SiO_2(800)**) with only a marginal influence of the support used.

The textural parameters of SiO_2, SBA-15 and modified systems were determined from nitrogen adsorption/desorption isotherms (**Fig. 21**; isotherms of SBA-15 materials) at -196 ºC and the results are summarized in **Tab. 2**. All immobilized materials showed a significant decrease in BET area from 593 m^2/g for SiO_2 to 383 m^2/g for **II/SiO_2(200)** and 337 m^2/g for **II/SiO_2(800)** and from 827 m^2/g for SBA-15 to 495 m^2/g for **II/SBA-15(200)** and 524 m^2/g for **II/SBA-15(700)**. A reduced pore volume (from 0.78 cm^3/g for SiO_2 to 0.47 cm^3/g for **II/SiO_2(200)** and 0.40 cm^3/g for **II/SiO_2(800)** and from 0.86 cm^3/g for

SBA-15 to 0.59 cm^3/g for **II/SBA-15(200)** and 0.66 cm^3/g for **II/SBA-15(700)**) as well as reduced average pore size (reduced about 0.6 nm for **II/SiO$_2$(200)**, 0.7 nm for **II/SiO$_2$(800)**, 1.6 nm for **II/SBA-15(200)** and 1.4 nm for **II/SBA-15(700)**) in comparison to parent materials gives evidence of efficient immobilization of **II** inside the mesopores.

Tab. 2: Textural properties and Ti loading for used supports with **II**

Modified support	**Ti loading**[a] [%$_{wt}$] (mmol/g)	**S$_{BET}$**[b] [m^2/g]	**Pore volume** [cm^3/g]	**Pore diameter** [nm]
SiO$_2$	–	593	0.78	5.2
II/SiO$_2$(200)	2.55 (0.53)	383	0.47	4.6
II/SiO$_2$(800)	1.83 (0.38)	337	0.40	4.5
SBA-15	–	827	0.86	6.8
II/SBA-15(200)	2.67 (0.55)	495	0.59	5.2
II/SBA-15(700)	1.35 (0.28)	524	0.66	5.4

[a] determined by ICP-OES

[b] BET area

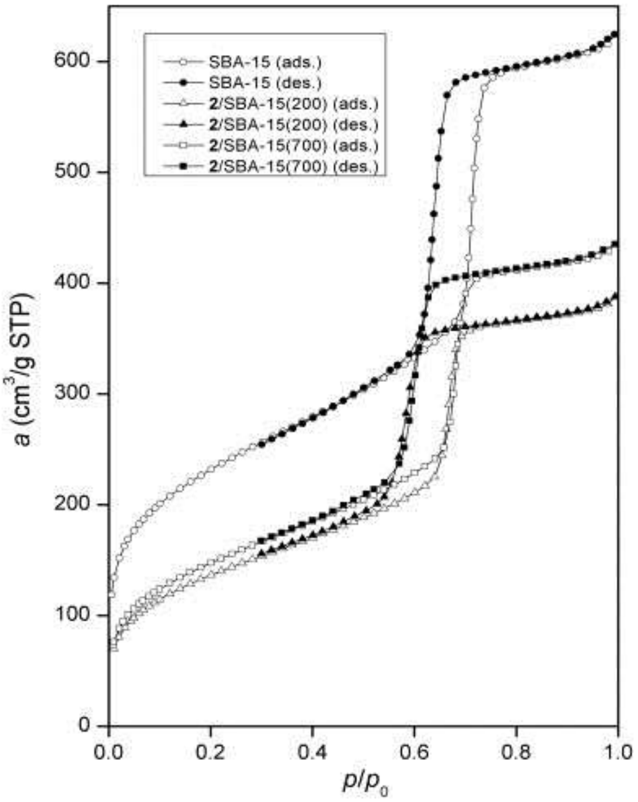


Fig. 21: Nitrogen adsorption/desorption isotherms for SBA-15 (○/●), **II/SBA-15(200)** (Δ/▲) and **II/SBA-15(700)** (□/■)

The X-ray powder diffraction (XRD) patterns (**Fig. 22**) of all the SBA-15 based materials (SBA-15, **II/SBA-15(200)** and **II/SBA-15(700)**) showed a typical three-peak pattern at low angle region characteristic for mesopores. The hexagonal structure was retained after grafting the titanium complex due to the well resolved peaks in **II/SBA-15** materials.

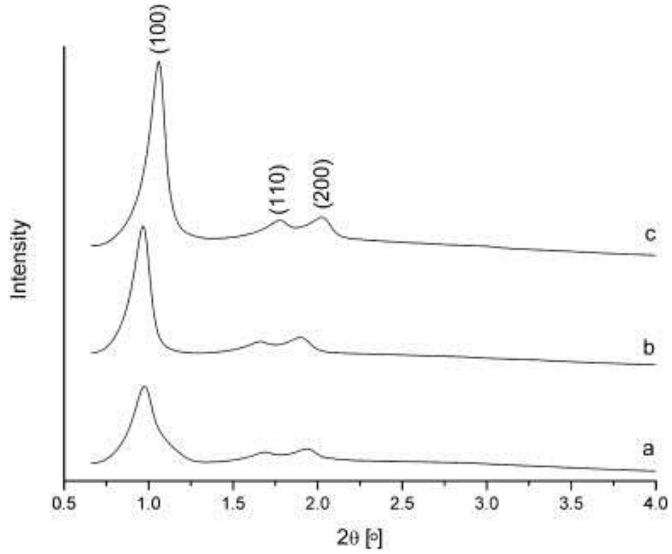


Fig. 22: XRD patterns for SBA-15 (**a**), **II/SBA-15(200)** (**b**) and **II/SBA-15(700)** (**c**)

The ^{13}C CP MAS NMR spectrum of **II/SBA-15(700)** is comparable to the spectrum of pure **II** in solution (**Fig. 23**), with the following signals: 24 ppm (a) (OCHMe_2); 29 ppm (f) (CMe_2); 41 ppm (e) (CMe$_2$); 82 ppm (b) (OCHMe$_2$); 115 ppm (c) (C_5H$_4$, CH); 126 ppm, 127 ppm (h) (C_6H$_5$, CH); 147 ppm (g,d) (C_{ipso}). The formal substitution of isopropoxy group or groups in the starting **II** by a surface silanol group affects the electronic properties of central atom. The NMR chemical shifts of the *C*H carbon (e) in O*C*HMe2 and the Cp carbons (c) are the most sensitive to this substitution, shifting about 5 ppm downfield (77 to 82 ppm for (e); 110 and 112 to 115 ppm for (c)). This implies the proposed immobilization of **II** to SBA-15 by formation of at least one Si−O−Ti bond. The signals at 13 and 66 ppm are assigned to Et$_2$O that was not removed under vacuum.

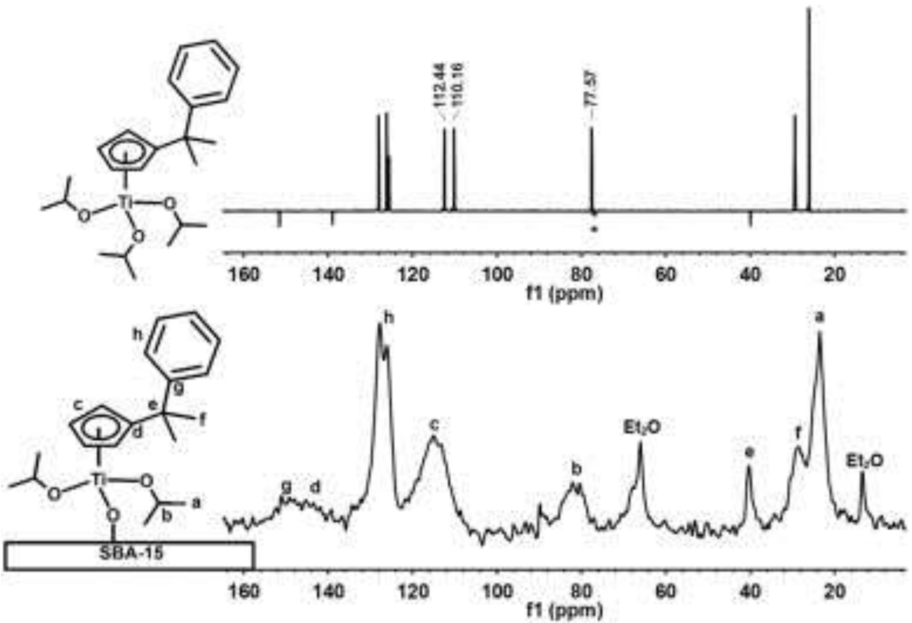


Fig. 23: ^{13}C NMR (APT) spectrum of **II** in $CDCl_3$ (**a**) and ^{13}C CP MAS NMR spectrum of **II/SBA-15(700)** (**b**)

IR spectra of the starting materials SiO_2(200) (**a**), SiO_2(800) (**b**), the complex **II** (**c**) and the immobilized complexes **II/SiO_2(200)** (**d**) and **II/SiO_2(800)** (**e**) between 2750-4000 cm^{-1} are sketched in **Fig. 24**. The observed band corresponds to surface terminal silanol groups of the supports (centered at 3712 cm^{-1} for SiO_2(200) and at 3716 cm^{-1} for SiO_2(800)) is absent in both immobilized systems **II/SiO_2(200)** and **II/SiO_2(800)** and that indicates preferential reaction of titanium with terminal silanols.

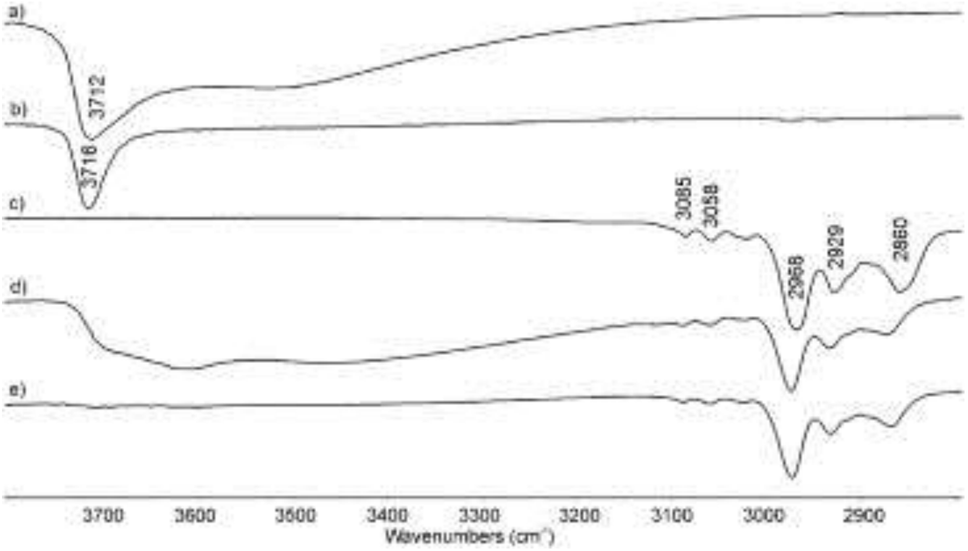


Fig. 24: Expanded regions of IR spectra for SiO_2(200) (**a**), SiO_2(800) (**b**), **II** (**c**) **II/SiO_2(200)** (**d**) and **II/SiO_2(800)** (**e**)

Similar situation was observed for complexes immobilized onto SBA-15 as shown in **Fig. 25**. However, the band at 3715 cm^{-1} corresponding to terminal silanols is still relatively populated in **II/SBA-15(700)** (**Fig. 25e**). We assume that it is a result of lower than stoichiometric amount (with respect to the silanol group concentration) of **II** used for preparation of the desired material (concretely 155 mg, 0.38 mmol of **II** and 1.4 g of SBA-15(700)). Absorption bands characteristic for titanium ligand skeleton (particularly: 3085-3089 cm^{-1} and 3057-3059 cm^{-1} for valence C−H vibration of phenyl ring and 2973-2976 cm^{-1}, 2930-2930 cm^{-1}, 2868-2864 cm^{-1} for valence C−H vibration of methyl group) are preserved in IR spectra of all **II**/**support** materials and it indicates the stability of η^5-coordination of the cyclopentadienyl ring during immobilization process.

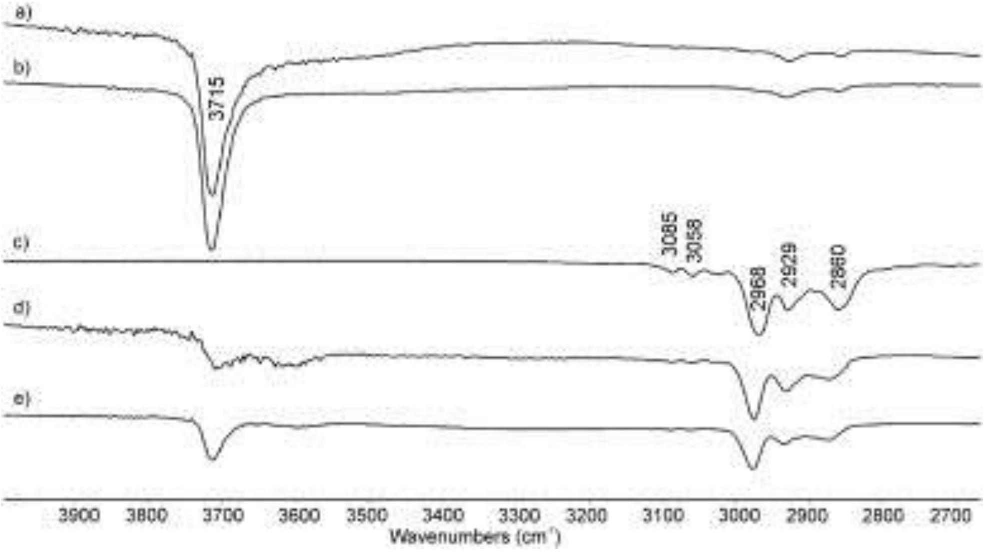


Fig. 25: Expanded regions of IR spectra for SBA-15(200) (**a**), SBA-15(700) (**b**), **II** (**c**), **II/SBA-15(200)** (**d**) and **II/SBA-15(700)** (**e**)

TGA curves of the immobilized complexes **II/SiO$_2$(200)**; **II/SiO$_2$(800)**; **II/SBA-15(200)**; **II/SBA-15(700)** are shown in **Fig. 26**. The weight loss between 300 and 400 ºC could be assigned to the breakdown of substituted cyclopentadienyl ligand and isopropyl group. The weight loss above 400 ºC most probably corresponds to the condensation of residual silanol groups, as it is more pronounced in materials pretreated at low temperature (**II/SiO$_2$(200)** and **II/SBA-15(200)**).

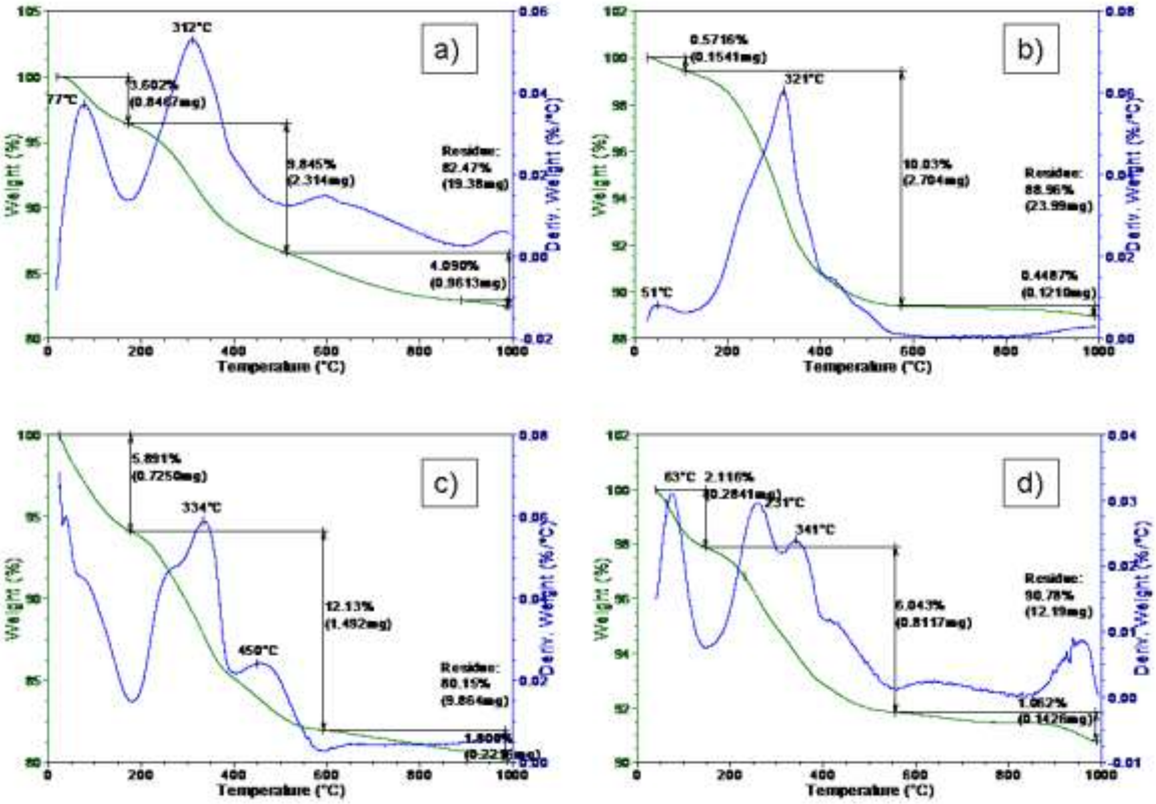


Fig. 26: TGA curves of **II/SiO$_2$(200)** (**a**); **II/SiO$_2$(800)** (**b**); **II/SBA-15(200)** (**c**) and **II/SBA-15(700)** (**d**)

Characterization of the immobilized complexes on $\mathit{SiMe_2H}$ modified silica

The complex **III** with pendant terminal double bond was immobilized on $SiMe_2H$-modified silica (1.59 mmol of $–SiMe_2H$ group·g^{-1}). The titanium loading analysis (determined by ICP-OES) of **III/SiO$_2$SiMe$_2$H** and **III/SiO$_2$SiMe$_2$H(90)**) reveals the content of Ti 1.45 and 1.67 %$_{wt}$, respectively.

The ^{13}C CP MAS NMR spectrum (**Fig. 27**) of **III/SiO$_2$SiMe$_2$H(90)** corresponds to the proposed surface species. The complete signal assignment is follows: -1 ppm (m) ($\mathrm{Si}\mathit{Me}_2$); 10 ppm (l) ($\mathrm{SiMe_2}\mathit{C}\mathrm{H_2}$); 25 ppm (a, f, j, k) ($\mathrm{SiMe_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2}\mathit{C}\mathrm{H_2}$, $\mathrm{C}\mathit{Me}\mathrm{CH_2}$, $\mathrm{OCH}\mathit{Me}_2$); 43 ppm (e,i) ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CMe}$, $\mathit{C}\mathrm{Me}\mathit{C}\mathrm{H_2}$); 79 (b) ($\mathrm{O}\mathit{C}\mathrm{HMe_2}$); 113 ppm (c) ($\mathit{C}_5\mathrm{H}_4$, $\mathit{C}\mathrm{H}$); 127 ppm (h) ($\mathit{C}_6\mathrm{H}_5$, $\mathit{C}\mathrm{H}$); 138 (d), 146 ppm (g) (C_{ipso}). Methine signals (b) and (c) ($\mathrm{C}\mathit{H}\mathrm{Me_2}$ and $\mathit{C}\mathrm{H}$ in Cp) of **III/SiO$_2$SiMe$_2$H(90)** were barely different (1-2 ppm downfield) from those of **VII** in solution. It indicates that there are three isopropoxy ligands on titanium. Interestingly, signal l (from methylene $\mathrm{SiMe_2}\mathit{C}\mathrm{H_2}$ group) of the supported catalyst occurs at 18 ppm, 8 ppm upfield from the same carbon in **VII** (10 ppm). This shielding could be caused by the proximal silica surface.

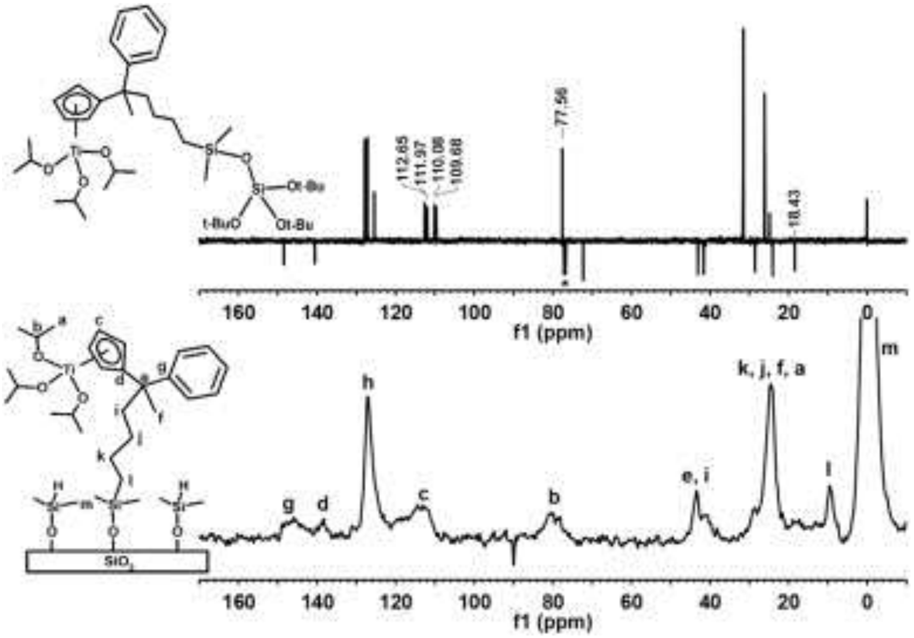


Fig. 27: ^{13}C NMR (APT) spectrum of **VII** in $CDCl_3$ (**a**) and ^{13}C CP MAS NMR spectrum of **III/SiO$_2$SiMe$_2$H(90)** (**b**)

IR spectra of starting materials (**III** (**a**) and SiO_2SiMe_2H (**c**)), both immobilized complexes (**III/SiO$_2$SiMe$_2$H** (**d**) and **III/SiO$_2$SiMe$_2$H(90)** (**e**)) and model compound **VII** (**b**) are shown in **Fig. 28**. The band at 1641 cm^{-1}, characteristic for C=C vibration, in **III** (**Fig. 28a**) is absent in the spectrum of model compoud **VII** (**Fig. 28b**) and strongly reduced in **III/SiO$_2$SiMe$_2$H** (**Fig. 28d**) and **III/SiO$_2$SiMe$_2$H(90)** (**Fig. 28e**). The characteristic valence C−H vibration of phenyl groups could be found at 3089 and 3065 cm^{-1} in **III/SiO$_2$SiMe$_2$H** and at 3089 and 3062 cm^{-1} in **III/SiO$_2$SiMe$_2$H(90)**. The bands characteristic for vicinal and geminal silanol groups (centered at 3676 and ca 3500 cm^{-1}) in SiO_2SiMe_2H remained almost untouched in **III/SiO$_2$SiMe$_2$H** (3650 and ca 3500 cm^{-1}) and **III/SiO$_2$SiMe$_2$H(90)** (3648 and ca 3500 cm^{-1}). These observations prove that **III** is immobilized onto the surface preferentially via the $-(CH_2)_4SiMe_2-$ tether. However, many of $SiMe_2H$ groups on the support remained unmodified in the immobilized species as could be envisaged by the presence of strong band of Si−H vibration (2146 cm^{-1} in SiO_2SiMe_2H; 2144 cm^{-1} in **III/SiO$_2$SiMe$_2$H** and 2145 cm^{-1} in **III/SiO$_2$SiMe$_2$H(90)**).

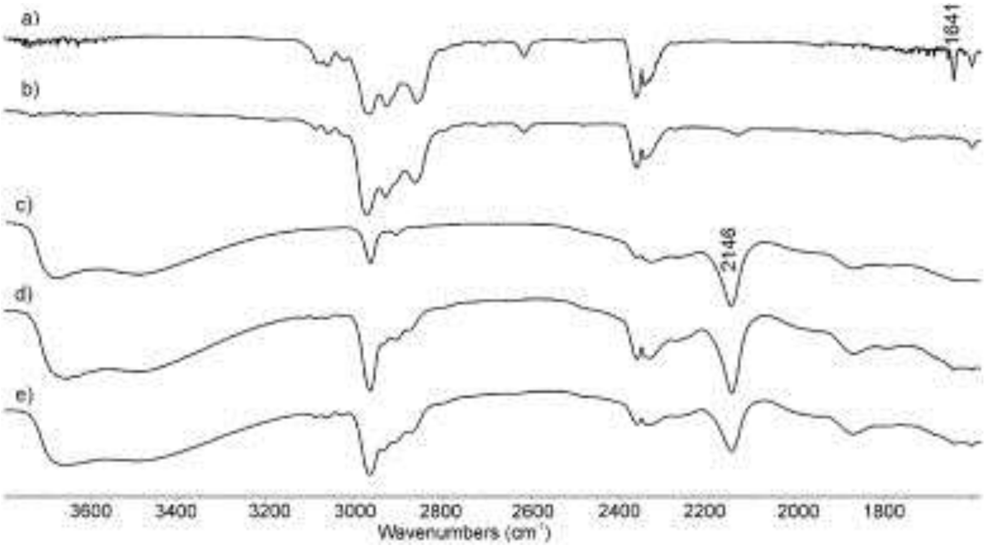


Fig. 28: Expanded regions of IR spectra for **III** (**a**), **VII** (**b**), SiO_2SiMe_2H (**c**) **III/**$\mathbf{SiO_2SiMe_2H}$ (**d**) and **III/**$\mathbf{SiO_2SiMe_2H}$**(90)** (**e**)

TGA curves of SiO_2SiMe_2H (**a**), **III/**$\mathbf{SiO_2SiMe_2H}$ (**b**) and **III/**$\mathbf{SiO_2SiMe_2H}$**(90)** (**c**) are shown in **Fig. 29**. Two main (partially overlapped) processes are proposed: decomposition of ligands positioned at titanium, which occurred between 200-450 ºC and elimination of silyl species (*i.e.* $SiMe_2H$ and $SiMe_2$ tethered **III**) from the surface proceeding between 300-550 ºC and the condensation of residual silanol groups above 400 °C.

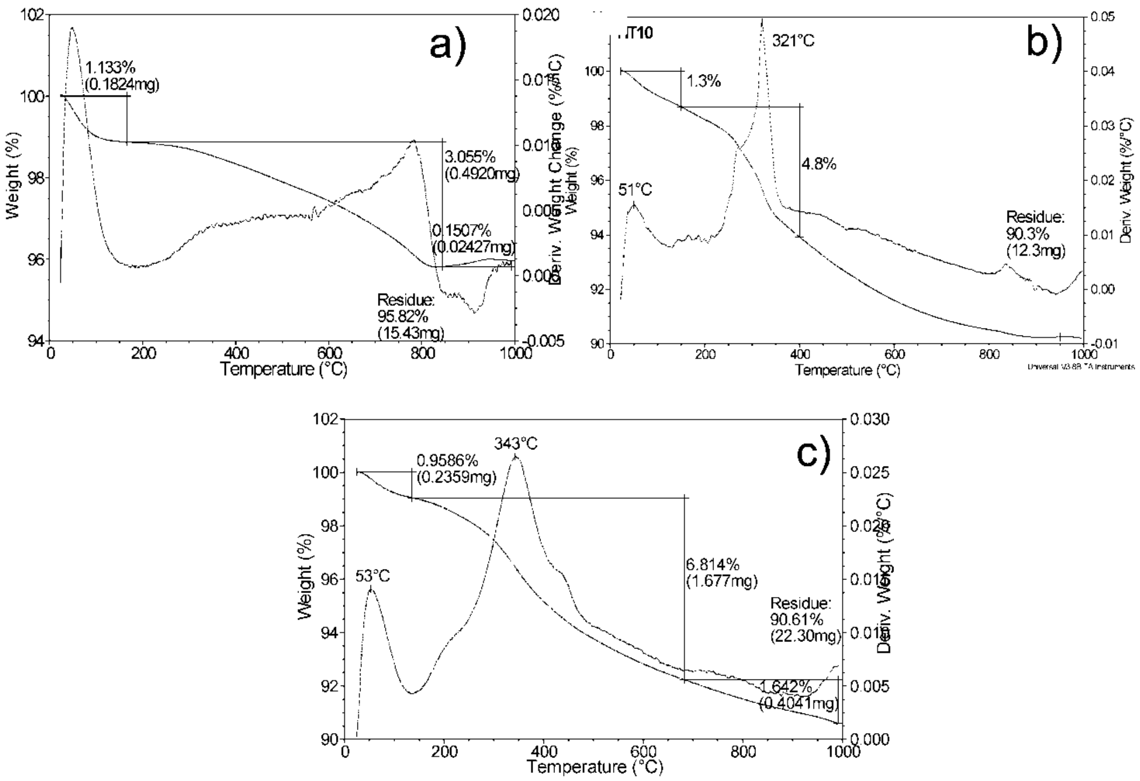


Fig. 29: TGA curves of SiO_2SiMe_2H (**a**) **III/SiO_2SiMe_2H** (**b**) and **III/SiO_2SiMe_2H(90)** (**c**)

Furthermore, the complex **III** with pendant terminal double bond was immobilized on a commercially available PMHS. IR spectra of starting materials (**III** (**a**) and PMHS (**b**)) and immobilized complex **III/PMHS** (**c**) are sketched in **Fig. 30**. The band at 1639 cm^{-1}, characteristic for C=C vibration, in **III** (**Fig. 30a**) is almost absent in **III/PMHS** (**Fig. 30c**) and its presence in **III/PMHS** verified the negligible amount of unreacted complex **III**. The characteristic valence C−H vibration of phenyl groups could be found at 3086 and 3058 cm^{-1} in **III/PMHS**. The bands characteristic for Si−H valence vibration (centered at 2166 cm^{-1}) in PMHS fully disappeared in **III/PMHS**. These observations testifies that **III** is anchored via the $-(CH_2)_4SiMe_2-$ tether analogously to **III/SiO_2SiMe_2H** and **III/SiO_2SiMe_2H(90)**).

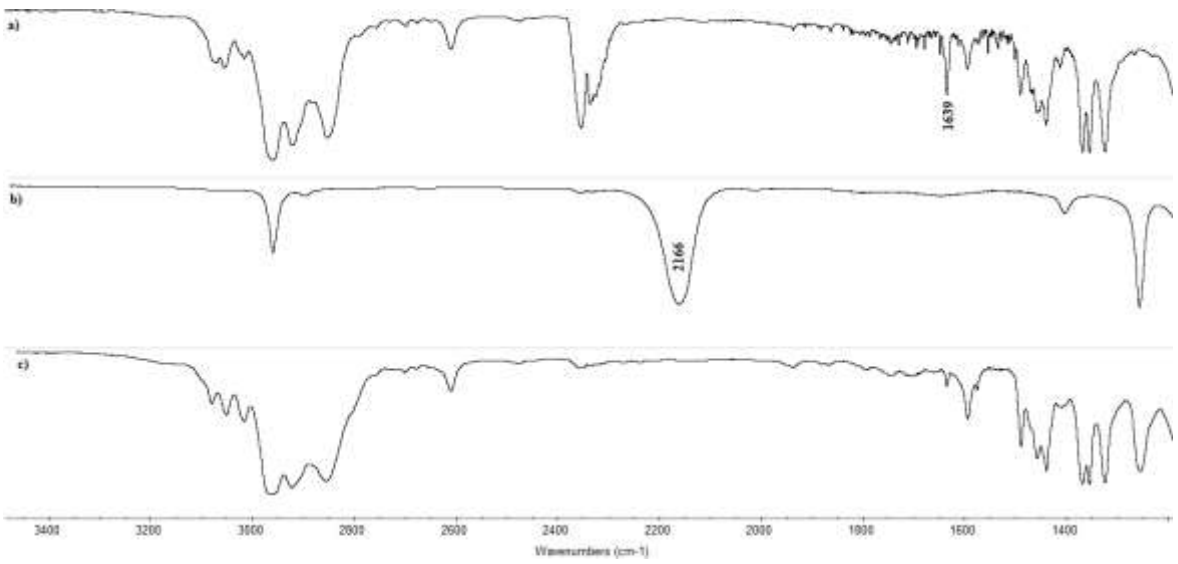


Fig. 30: Expanded regions of IR spectra for **III** (**a**), PMHS (**b**) and **III/PMHS** (**c**)

4.3. TRIMERIZATION REACTION

The trimerization experiments could be divided to two independent parts – the trimerization experiments of homogeneous systems **I-VII** and the trimerization experiments of immobilized systems **II/SiO$_2$(200)**, **II/SiO$_2$(800)**, **II/SBA-15(200)**, **II/SBA-15(700)**, **III/SiO$_2$SiMe$_2$H**, **III/SiO$_2$SiMe$_2$H(90)** and **III/PMHS**.

Ethylene trimerization of homogeneous systems

The homogeneous complexes **I-VII** were activated by a huge excess of MAO (Ti/Al = 1/1000) and their activity and selectivity in trimerization of ethylene to 1-hexene were evaluated. The measured results are clearly summarized in **Tab. 3**. The comparison of catalytic activity was divided into two parts dealing with – complexes bearing the same η^5-ligand, but different σ-ligands (*e.g.* Cl, O*i*-Pr etc.) and complexes bearing different pendant substituent at η^5-cyclopentadienyl ring (*e.g.* Me, but-3-enyl).

Tab. 3: Trimerization of ethylene catalyzed by homogeneous systems[a]

Run	**Cat.**	**A**[b]	**S**[c]	**1-hexene** [g] ($\%_{wt}$)[d]	**C_{10}**[e] [g] ($\%_{wt}$)[d]	**PE** [g] ($\%_{wt}$)[d]
Blank[f]	**MAO**	–	–	–	–	traces
1	**I**	330	85	3.096 (85)	0.472 (13)	0.081 (2)
2	**II**	46	91	0.431 (91)	0.010 (2)	0.034 (7)
3	**II**[g]	57	95	0.538 (95)	0.013 (2)	0.017 (3)
4	**III**	55	93	0.516 (93)	0.012 (2)	0.024 (5)
5	**IV**	272	87	2.554 (87)	0.296 (10)	0.102 (3)
6	**VI**	309	86	2.886 (86)	0.401 (12)	0.052 (2)
7	**VII**	44	92	0.412 (92)	0.008 (2)	0.025 (6)

[a] Reaction conditions: n_{Ti} = 3.75 μmol; Ti/Al = 1/1000; 30 °C; 5 bar of ethylene; rpm 800
[b] Activity in production of 1-hexene [$kg_{1\text{-}hexene}/mol_{Ti} \cdot bar \cdot h$]
[c] Selectivity to 1-hexene ($\%_{wt}$ of 1-hexene from total mass of reaction products)
[d] $\%_{wt}$ from total mass of reaction products
[e] C_{10} fraction that contents products of co-trimerization of 1-hexene with 2 molecules of ethylene
[f] Blank refers to Ti-free catalytic system, when only MAO is used
[g] Ti/Al = 1/3000

The order of activity **I**/MAO ≈ **VI**/MAO >> **II**/MAO could be attributed to electron-withdrawing properties of the corresponding σ-ligand: Cl > POSS-$(O)_3$ >> O*i*-Pr. Similar behavior of chloro and silsesquioxane ligand under activation with MAO was recently observed in polymerization of ethylene catalyzed with $[(\eta^5\text{-}C_5H_5)ZrL_2]$/MAO systems (L = Cl, silsequioxane).[63] Systems **I**/MAO and **VI**/MAO produced considerably lower amount of PE in comparison with **II**/MAO, which is probably caused by faster generation of catalytic species active in trimerization during the initial phase of oligomerization.[23] It should be noted, that lower selectivity towards 1-hexene over **I**/MAO, **IV**/MAO and **VI**/MAO in comparison with **II**/MAO is probably a consequence of a semi-batch technology used for oligomerization, where high amount of 1-hexene formed compete with ethylene in the trimerization process and form C_{10} products.

The effect of substitution on cyclopentadienyl ring in complexes was studied by comparison of catalysts **II**, **III** and **VII**. However, only negligible effect was found either for activity (ranging from 44 to 55 $kg_{1\text{-}hexene}/mol_{Ti} \cdot bar \cdot h$) or selectivity (ranging from

91-93%$_{wt}$ of 1-hexene).

Ethylene trimerization of immobilized systems

Immobilized complexes **II/support** and **III/support** were activated with a huge excess of MAO and evaluated in catalytic trimerization of ethylene (**Tab. 4**).

Tab. 4: Trimerization of ethylene catalyzed by immobilized systems[a]

Run	**Supported catalyst**	n_{Ti} **[μmol]**	**A**[b]	**S**[c]	**1-hexene** [g] (%$_{wt}$)[d]	**C$_{10}$**[e] [g] (%$_{wt}$)[d]	**PE** [g] (%$_{wt}$)[d]
1	**II/SiO$_2$(200)**	5.2	4	77	0.055 (77)	–	0.016 (23)
2	**II/SiO$_2$(800)**	3.1	35	87	0.272 (87)	0.005 (2)	0.037 (11)
3	**II/SBA-15(200)**	3.8	26	92	0.248 (92)	0.003 (1)	0.020 (7)
4	**II/SBA-15(700)**	3.9	34	93	0.334 (93)	0.005 (1)	0.019 (5)
5	**III/SiO$_2$SiMe$_2$H**	3.3	0.2	n.d.	0.002 (-)	–	–
6	**III/SiO$_2$SiMe$_2$H(90)**	3.7	0.3	n.d.	0.003 (-)	–	–
7	**III/PMHS**	4.7	18	53	0.209 (53)	0.003 (1)	0.186 (46)

[a] Reaction conditions: Ti/Al = 1/1000; 30 °C; 5 bar of ethylene; rpm 800; V_{tot} = 50 ml
[b] Activity in production of 1-hexene [kg$_{1\text{-hexene}}$/mol$_{Ti}$·bar·h]
[c] Selectivity to 1-hexene (%$_{wt}$ of 1-hexene from total mass of reaction products)
[d] %$_{wt}$ from total mass of reaction products
[e] C$_{10}$ fraction that contents products of co-trimerization of 1-hexene with 2 molecules of ethylene
[f] Ti/Al = 1/3000

The activity decreases in the order: **II/SiO$_2$(800)/MAO** ≈ **II/SBA-15(700)/MAO** > **II/SBA-15(200)/MAO** > **II/SiO$_2$(200)/MAO** > **III/SiO$_2$SiMe$_2$H/MAO** ≈ **III/SiO$_2$SiMe$_2$H(90)/MAO**. In the case of **II/support/MAO**, the decreasing order of activities corresponds to the increasing amount of residual surface silanol groups in the **II/support** (calculated as a difference between the amount of −SiOH in the support used and amount of titanium grafted on support): 0.0 mmol·g^{-1} for **II/SiO$_2$(800)** ≈ 0.1 mmol·g^{-1} for **II/SBA-15(700)** < 1.7 mmol·g^{-1} for **II/SBA-15(200)** < 3.1 mmol·g^{-1} for **II/SiO$_2$(200)**. The high selectivity observed in homogeneous **II/MAO** was retained in complexes immobilized on SBA-15 (92-93%$_{wt}$ of 1-hexene), whereas complexes supported on conventional SiO$_2$ suffer from lowering the selectivity (77-87%$_{wt}$ of 1-hexene).

Significantly low activity of **III/SiO_2SiMe_2H/MAO** and **III/SiO_2SiMe_2H(90)/MAO** could be the result of tight bonding of catalysts to the support through a flexible $-(CH_2)_3CHSiMe_2-$ tether. The tether does not allow efficient releasing of titanium center to homogeneous phase. The strongly electrophilic active center Ti(II), formed upon MAO activation, maintained in close proximity to surface would interact with either residual silanol groups or even with surface siloxane units Si−O−Si which could act as a Lewis base. This interaction would efficiently compete with coordination of ethylene and consequently, suppress trimerization. Similar interaction of surface siloxane unit to an electrophilic ruthenium tethered to silica via flexible spacer was published too.[64]

In contrast, the immobilized system **III/PMHS** was soluble under trimerization conditions, but revealed the catalytic activity (18 $kg_{1\text{-hexene}}/mol_{Ti}\cdot bar\cdot h$) and selectivity (53$\%_{wt}$ of 1-hexene) between the directly bonded supported catalysts on SiO_2 or SBA-15 and supported catalyst with a flexible $-(CH_2)_3CHSiMe_2-$ tether. Surprisingly, this catalytic system shown a higher production of polyethylene (46$\%_{wt}$).

5. EXPERIMENTAL

Characterization Methods

Melting points of all substances were determined using a Koffler block.

^{1}H (300.0 MHz), ^{13}C (75.0 MHz) and ^{29}Si (59.6 MHz) NMR spectra were recorded using either Varian-Gemini 300 HC or Varian Mercury 300 spectrometer at 25 °C. NMR measurements were performed in $CDCl_3$ or other deuterated solvents (namely benzene-d_6, THF-d_8, toluene-d_8). Chemical shifts (δ/ppm) are given relative either to solvent signals (C_6D_6: δ_H 7.15 ppm, δ_C 128.00 ppm; $CDCl_3$: δ_H 7.26 ppm, δ_C 77.16 ppm; C_7D_8: δ_H 2.08, 6.97, 7.01, 7.09 ppm, δ_C 20.43, 125.13, 127.96, 128.87, 137.48 ppm) or to the internal standard tetramethylsilane. Coupling constants *J* are given in Hz. ^{13}C NMR and ^{29}Si NMR spectra were recorded with ^{1}H decoupling. Abbreviations used for the description of multiplicity are: s – singlet, d – doublet, t – triplet, dd – doublet of doublets, dt – doublet of triplets, q – quartet, m – multiplet, bs – broad singlet.

Infrared spectra were recorded on a Nicolet Avatar FTIR spectrometer over the range 400-4000 cm^{-1} using air-tight cuvettes. Samples were prepared in a glovebox Labmaster 130 (mBraun) under purified nitrogen and measured either neat or KBr pellets. Heterogeneous materials were measured in Halocarbon 700 oil mulls between KBr plates.

Electrospray mass spectra (ESI-MS) were measured with a Bruker Esquire 3000 instrument for the complexes dissolved in dichloromethane/acetonitrile.

Elemental analyses were carried out on a FLASH EA1112 CHN-O Automatic Elemental Analyzer (Thermo Scientific).

The titanium content was determined by Inductively Coupled Plasma-Optical Emission Spectrometry ICP-OES IRIS Interpid II XDL (2004).

Thermal analyses were performed with a TGA Q500 (TA Instruments, USA) under nitrogen flow (60 ml·min^{-1}) using a gradient of 20 ºC·min^{-1}. The initial weight loss up to ca 175 °C can be attributed to the removal of physisorbed water.

MAS NMR spectra were collected with a Bruker ASX-300 using air-tight rotors packed in a glove box under N_2 atmosphere to prevent exposure to humidity and air. ^{13}C MAS spectra were recorder at 75.0 MHz under ^{1}H–^{13}C cross polarization with 67.0 kHz ^{13}C power, 5 ms contact time, 2 s delay, mlev-16 decoupling, 4 mm rotors spinning at 12.0 kHz and shifts referenced to tetramethylsilane (0 ppm) via adamantane (at 38.5 and 29.4 ppm).

X-ray powder diffraction (XRD) data were collected on a Bruker AXS D8 Advance diffractometer with a Vantec-1 detector in the Bragg−Brentano geometry using Cu Kα (λ = 0.154178 nm) radiation.

Adsorption isotherms of nitrogen at -196 ºC were recorded using an ASAP 2020 volumetric instrument. SBA-15 was degassed up to 110 ºC (temperature ramp of 0.5 $ºC\cdot min^{-1}$) until a residual pressure of 1.33 Pa was attained. After further heating at 110 ºC for 1 h the temperature was increased (temperature ramp of 1 $ºC\cdot min^{-1}$) to 250 ºC. Degassing was continued at this temperature under turbomolecular pump vacuum for 12 h. The samples **II/SBA-15(200)** and **II/SBA-15(700)** were degassed at 100 ºC (temperature ramp of 0.5 $ºC\cdot min^{-1}$) under turbomolecular pump vacuum for 24 h. The BET surface area was calculated from the isotherm in the range of relative pressures 0.05 - 0.25. Pore size distribution was calculated from the desorption isotherm using the BJH method.[65]

Combined gas chromatography-mass spectrometry GC-MS analyses were performed by GC-MS with a Thermo Focus DSQ instrument using a capillary column Thermo TR-5MS (15 m × 0.25 mm ID × 0.25 μm) and mass detection technique with electron impact ionization. The oligomerized product was examined by high-resolution GC-FID Agilent 6890 with a DB-5 column (length: 50 m, inner diameter: 320 μm, stationary phase thickness: 1 μm) with decane used as an internal standard.

Materials

The reactions were monitored by thin layer chromatography using glass plates with a layer of silica gel Kieselgel GF_{254} (Merck) and suitable eluents. Results of thin layer chromatography were determined under ultraviolet light (λ = 254 nm, λ = 366 nm) or by carbonisation after spraying with 1% solution of diammonium cerium(IV) nitrate in 10% aqueous solution of sulfuric acid.

Column chromatography was performed on silica gel Kieselgel 60 (Merck), 0.063-0.100 mm.

All used solvents were dried and deoxygenated before use by refluxing over sodium benzophenone ketyl and stored over molecular sieves (4 Å). Chlorinated solvents were dried by refluxing over CaH_2, distilled and stored over molecular sieve 3 Å.

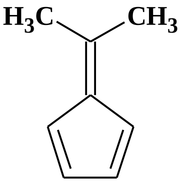
1,3,5,7,9,11,14-heptaisobutyltricyclo[7.3.3.15,11]heptasiloxane-endo-3,7,14-triol

(POSS-(OH)$_3$), ClTi(O*i*-Pr)$_3$ (1 M solution in hexane), Karstedt's catalyst (Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane) solution in xylene ($w_{Pt} \approx 2\%_{wt}$), methylaluminoxane (MAO, $10\%_{wt}$ solution in toluene) and polymethylhydrosiloxane (M_n = 1700-3200 g·mol^{-1}) were used as received from Aldrich.

Conventional silica (Whatman, Purasil 60 A, 70-230 mesh, BET surface area 539 m^2·g^{-1}, pore volume 0.8 cm^3·g^{-1} and average pore diameter 5.2 nm) was heated under dynamic vacuum (10^{-1} mbar) at 200 ºC (denoted SiO_2(200) with 3.6 mmol –OH groups·g^{-1}) or at 800 ºC (denoted SiO_2(800) with 0.4 mmol –OH groups·g^{-1}). Purely siliceous mesoporous sieve SBA-15 (BET surface area 828 m^2·g^{-1}, pore volume 0.9 cm^3·g^{-1} and average pore diameter 6.8 nm) was synthesized by a recently published procedure and heated under dynamic vacuum (10^{-1} mbar) at 200 ºC (denoted SBA-15(200) with 2.3 mmol –OH groups·g^{-1}) or at 700 ºC (denoted SBA-15(700) with 0.4 mmol –OH groups·g^{-1} of material).[66] Silanol density was determined by the weight loss from TGA according to literature.[67] $SiMe_2H$ substituted silica (denoted SiO_2SiMe_2H) contained 1.59 mmol –$SiMe_2H$ groups·g^{-1} was purchased from Aldrich and dried for 8 h at 100 ºC in vacuum prior to use.

All other chemicals and reagents were obtained from commercial sources and were used without additional purification.

6,6-Dimethylfulvene (17)[54]



To a cold solution (0 °C) of acetone (**15**; 23.8 ml; 324 mmol) and freshly cracked cyclopentadiene (**13**; 30.0 ml; 357 mmol) in methanol (150 ml); pyrrolidine (40.2 ml; 486 mmol) was added dropwise. After 30 min the reaction was quenched with acetic acid (30.0 ml; 527 mmol). The mixture was washed with water to neutral pH and the aqueous fraction was extracted with Et_2O (2 × 50 ml). The combined organic fractions were washed with brine (50 ml) and dried over anhydrous $MgSO_4$. After filtration of the drying agent the filtrate was evaporated on a rotary evaporator. The crude reaction product was purified by distillation under reduced pressure (main fraction: 58 °C at 38 Torr). The desired product **17** was obtained as orange liquid (22.3 g; 65%).

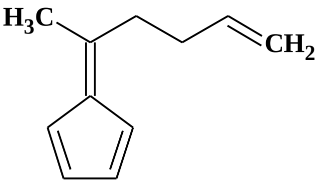
^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): 2.21 (s, 6H, $\mathrm{C}\mathit{Me}_2$); 6.46-6.57 (m, 4H, $\mathrm{C_5}\mathit{H}_4$).

^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): 23.34 ($\mathrm{C}\mathit{Me}_2$); 120.72, 130.83 ($\mathit{C}_5\mathrm{H}_4$, *C*H); 142.54 (*C*Me); 150.37 ($\mathit{C}_5\mathrm{H}_4$, $\mathit{C}_{\mathrm{ipso}}$).

IR (neat, cm^{-1}): 3103 (m), 3072 (m), 2995 (m), 2931 (m), 2907 (m), 2851 (w), 2724 (w), 1994 (w), 1807 (w), 1712 (w). 1639 (s), 1623 (s), 1522 (w), 1471 (s), 1438 (m), 1370 (s) 1253 (w), 1148 (w), 1087 (m), 996 (m), 923 (m), 857 (m), 812 (m), 765 (s), 624 (s), 570 (w), 535 (m), 526 (m), 519 (w), 517 (w).

GC-MS (EI): m/z 106 ($[\mathrm{M}]^{+\cdot}$); 91 ($[\mathrm{M{-}Me}]^{+}$).

6-(But-3-enyl)-6-methylfulvene (18)[68]



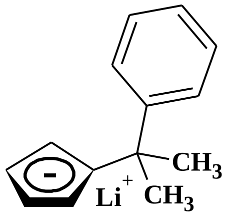
The fulvene **18** was prepared analogously to fulvene **17** from a commercial 5-hexen-2-one (**16**; 4.0 ml; 34.5 mmol), cyclopentadiene (**13**; 3.2 ml; 38 mmol) and pyrrolidine (4.3 ml; 58 mmol) in methanol (50 ml). The crude reaction product was purified by distillation under reduced pressure (main fraction: 97-102 °C at 19 Torr). The desired product **18** was obtained as orange liquid (2.5 g; 74%).

^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): 2.27 (s, 3H, C*Me*); 2.37 (m, 2H, $\mathrm{CH_2C}\mathit{H}_2\mathrm{CH{=}CH_2}$); 2.70 (t, $^{3}J_{\mathrm{HH}}$ = 7.7 Hz, 2H,$\mathrm{C}\mathit{H}_2\mathrm{CH_2CH{=}CH_2}$); 5.04-5.18 (m, 2H, $\mathrm{CH_2CH_2CH{=}C}\mathit{H}_2$); 5.83-5.97 (m, 1H, $\mathrm{CH_2CH_2C}\mathit{H}\mathrm{{=}CH_2}$); 6.54-6.59 (m, 4H, $\mathrm{C_5}\mathit{H}_4$).

^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): 21.00 (C*Me*); 33.33 ($\mathrm{CH_2}\mathit{C}\mathrm{H_2CH{=}CH_2}$); 36.36 ($\mathit{C}\mathrm{H_2CH_2CH{=}CH_2}$); 115.37 ($\mathrm{CH_2CH_2CH{=}}\mathit{C}\mathrm{H_2}$); 120.44, 120.81, 130.84, 131.04 ($\mathit{C}_5\mathrm{H}_4$, *C*H); 137.63 ($\mathrm{CH_2CH_2}\mathit{C}\mathrm{H{=}CH_2}$); 142.92 (*C*Me); 152.97 ($\mathit{C}_5\mathrm{H}_4$, $\mathit{C}_{\mathrm{ipso}}$).

GC-MS (EI): m/z 146 ($[\mathrm{M}]^{+\cdot}$); 131 ($[\mathrm{M{-}Me}]^{+}$); 91 ($[\mathrm{M{-}C_4H_7}]^{+}$).

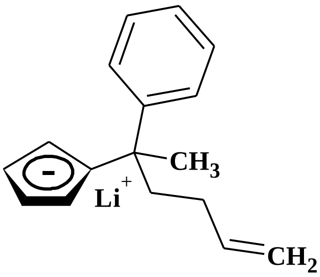
Lithium (2-phenylisopropyl)cyclopentadienide (19)



To a cold solution (0 °C) of fulvene **17** (3.64 g; 34.3 mmol) in $\mathrm{Et_2O}$ (20 ml); PhLi (20 ml of 1.8 M solution in $\mathrm{Et_2O}$; 36 mmol) was gradually dropped, which caused immediate formation of a precipitate. The reaction mixture was stirred overnight and the solvent was filtered off. The precipitate was washed with $\mathrm{Et_2O}$ (2 × 20 ml) and dried in vacuum to canstant weight. The pure product **19** was obtained as a white solid (6.31 g; 97%).

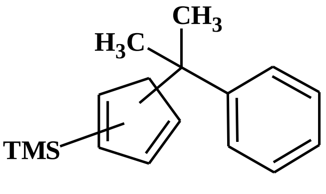
^{1}H NMR (300 MHz, THF-d_8): 1.61 (s, 6H, $\mathrm{C}Me_2$); 5.72 (s, 4H, $\mathrm{C_5}H_4$); 6.92-6.97 (m, 1H, $\mathrm{C_6}H_5$); 7.05-7.11 (m, 2H, $\mathrm{C_6}H_5$); 7.27-7.33 (d, $^3J_{\mathrm{HH}}$ = 7.8 Hz, 2H, $\mathrm{C_6}H_5$).
^{13}C NMR (75 MHz, THF-d_8): 32.45 ($\mathrm{C}Me_2$); 39.92 ($C\mathrm{Me_2}$); 101.80, 101.86 ($C_5\mathrm{H_4}$, CH); 124.59, 126.85, 127.69 ($C_6\mathrm{H_5}$, CH); 130.05 ($C_5\mathrm{H_4}$, C_{ipso}); 155.42 ($C_6\mathrm{H_5}$, C_{ipso}).

Lithium (2-phenylhex-5-en-2-yl)cyclopentadienide (20)



To a cold solution (0 °C) of fulvene **18** (5.02 g; 34.3 mmol) in $\mathrm{Et_2O}$ (20 ml); PhLi (20 ml of 1.8 M solution in $\mathrm{Et_2O}$; 36 mmol) was gradually dropped. The precipitate was observed immediately. The reaction mixture was stirred overnight at ambient temperature and then heated under reflux for 3 hours. The solvent was filtered off. The precipitate was washed with $\mathrm{Et_2O}$ (2 × 20 ml). The pure product **20** was dried in vacuum and obtained as a white solid (7.25 g; 92%).
^{1}H NMR (300 MHz, THF-d_8): 1.61 (s, 3H, $\mathrm{C}Me$); 1.79-1.89 (m, 1H, $\mathrm{CH_2C}H_2\mathrm{CH{=}CH_2}$); 1.94-2.03 (m, 1H, $\mathrm{CH_2C}H_2\mathrm{CH{=}CH_2}$); 2.05-2.13 (m, 2H, $\mathrm{C}H_2\mathrm{CH_2CH{=}CH_2}$); 4.79-4.94 (m, 2H, $\mathrm{CH_2CH_2CH{=}C}H_2$); 5.57 (s, 4H, $\mathrm{C_5}H_4$); 5.75-5.85 (m, 1H, $\mathrm{CH_2CH_2C}H\mathrm{{=}CH_2}$); 6.95-7.00 (m, 1H, $\mathrm{C_6}H_5$); 7.10-7.15 (m, 2H, $\mathrm{C_6}H_5$); 7.33-7.36 (d, $^3J_{\mathrm{HH}}$ = 8.1 Hz, 2H, $\mathrm{C_6}H_5$).
^{13}C NMR (75 MHz, THF-d_8): 28.09 ($\mathrm{C}Me$); 30.66 ($\mathrm{CH_2}C\mathrm{H_2CH{=}CH_2}$); 43.25 ($C\mathrm{Me}$); 43.95 ($C\mathrm{H_2CH_2CH{=}CH_2}$); 101.83, 102.12 ($C_5\mathrm{H_4}$, CH); 113.22 ($\mathrm{CH_2CH_2CH{=}}C\mathrm{H_2}$); 124.70, 127.26, 127.84 ($C_6\mathrm{H_5}$, CH); 129.32 ($C_5\mathrm{H_4}$, C_{ipso}); 141.03 ($\mathrm{CH_2CH_2}C\mathrm{H{=}CH_2}$); 154.03 ($C_6\mathrm{H_5}$, C_{ipso}).

($\mathrm{C_5H_4CMe_2Ph}$)$\mathrm{SiMe_3}$ (21); a mixture of isomers



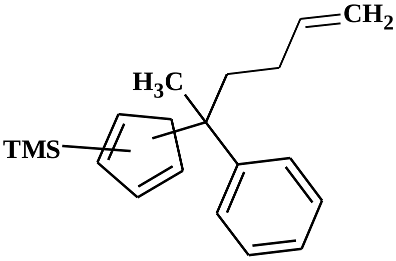
To a solution of lithium cyclopentadienide **19** (2.0 g; 10.5 mmol) in THF (20 ml); TMSCl (2.1 ml; 16.3 mmol) was added dropwise. The reaction mixture was stirred overnight and then the volatiles were evaporated in vacuum. The purity was evaluated by GC-MS and NMR. The product **21** was yielded as a yellow-greenish liquid (2.6 g; 96%). The ^{1}H NMR spectroscopy revealed presence of several regioisomers.
^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$, main isomer): 0.06 (s, 9H, $\mathrm{Si}Me_3$); 1.53 (s, 6H, $\mathrm{C}Me_2$); 3.22

(s, 1H, $C_5\mathit{H_5}$); 6.13 (s, 1H, $C_5\mathit{H_5}$); 6.28 (m, 1H, $C_5\mathit{H_5}$); 6.35 (m, 1H, $C_5\mathit{H_5}$); 7.13-7.30 (m, 5H, $C_6\mathit{H_5}$).

^{13}C NMR (75 MHz, $CDCl_3$, main isomer): -1.72 ($Si\mathit{Me_3}$); 30.12 ($C\mathit{Me_2}$); 40.15 ($\mathit{C}Me_2$); 50.37, 125.51, 131.39, 133.84 (C_5H_4, $\mathit{C}H$); 125.64, 126.58, 128.02 (C_6H_5, $\mathit{C}H$); 149.75 (C_5H_4, $\mathit{C_q}$); 154.60 (C_6H_5, C_{ipso}).

GC-MS (EI): m/z 256 ($[M]^{+\cdot}$); 241 ($[M–Me]^+$); 119 ($[M–C_5H_4SiMe_3]^+$); 73 ($[SiMe_3]^+$).

($C_5H_4\{CMePh(CH_2)_2CH{=}CH_2Ph\}$)$SiMe_3$ (22); a mixture of isomers



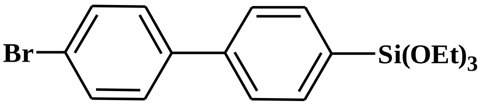
To a solution of lithium cyclopentadienide **20** (1.2 g; 5.1 mmol) in THF (20 ml); TMSCl (1.0 ml; 7.9 mmol) was added dropwise. The reaction mixture was stirred overnight and then the volatiles were evaporated in vacuum. The purity was evaluated by GC-MS and NMR. The product **22** was obtained as a yellow-greenish liquid (1.5 g; 99%).

^{1}H NMR (300 MHz, $CDCl_3$, main isomer): 0.13 (s, 9H, $Si\mathit{Me_3}$); 1.68 (d, 3H, $C\mathit{Me}$); 1.96-2.25 (m, 4H, $C\mathit{H_2}C\mathit{H_2}CH{=}CH_2$); 3.40 (m, 1H, $C_5\mathit{H_5}$); 5.03-5.14 (m, 2H, $CH_2CH_2CH{=}C\mathit{H_2}$); 5.90-5.99 (m, 1H, $CH_2CH_2C\mathit{H}{=}CH_2$); 6.34 (s, 1H, $C_5\mathit{H_5}$); 6.43 (m, 1H, $C_5\mathit{H_5}$); 6.55 (m, 1H, $C_5\mathit{H_5}$); 7.31-7.43 (m, 5H, $C_6\mathit{H_5}$).

^{13}C NMR (75 MHz, $CDCl_3$): -1.63 ($Si\mathit{Me_3}$); 26.50 ($C\mathit{Me}$); 29.29 ($CH_2\mathit{C}H_2CH{=}CH_2$); 40.79 ($\mathit{C}H_2CH_2CH{=}CH_2$); 43.44 ($\mathit{C}Me$); 50.38, 126.19, 131.52, 133.74 (C_5H_4, $\mathit{C}H$); 114.08 ($CH_2CH_2CH{=}\mathit{C}H_2$); 125.69, 126.70, 127.13 (C_6H_5, $\mathit{C}H$); 139.53 ($CH_2CH_2\mathit{C}H{=}CH_2$); 148.27 ($\mathit{C}_5H_4$, $\mathit{C_q}$); 153.46 (C_6H_5, C_{ipso}).

GC-MS (EI): m/z 296 ($[M]^{+\cdot}$); 281 ($[M–Me]^+$); 241 ($[M–C_4H_7]^+$); 73 ($[SiMe_3]^+$).

Attempted synthesis of (4´-bromobiphen-4-yl)triethoxysilane (25)



To a cold suspension (-78 °C) of a commercial 4,4´-dibromobiphenyl (**24**; 10 g; 32 mmol) in Et_2O (160 ml); *n*-BuLi (12.8 ml of 2.5 M solution in hexane; 32 mmol) was carefully added dropwise. The mixture was stirred at -78 °C for 2.5 h and then it was dropped to a solution of tetraethyl orthosilicate (15 ml; 67 mmol) in Et_2O (20 ml) at ambient temperature. The solution was stirred at ambient temperature for

2 h and then the reaction was quenched with TMSCl (5 ml; 40 mmol). Nevertheless, the GC-MS analysis of the reaction mixture revealed only mainly starting materials, 4-bromobiphenyl **26** (MS (EI): m/z 232 ($[M]^{+\cdot}$)) and only traces of the desired product formation could be detected.

GC-MS (EI): m/z 394 ($[M]^{+\cdot}$); 271; 147.

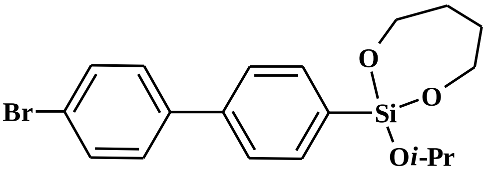
(4′-Bromobiphen-4-yl)triisopropoxysilane (29)

Method A:

To an activated magnesium chips (78 mg; 3.2 mmol) in THF (10 ml); a solution of 4,4′-dibromobiphenyl (**24**; 1.0 g; 3.2 mmol) in THF (12 ml) at ambient temperature was added gradually. No reaction was observed during 10 min and the reaction was initiated with a few drops of bromine, followed by heating under reflux. After 30 min, the reaction mixture was dropped to a solution of $SiCl_4$ (800 µl; 6.4 mmol) in THF (5 ml) and heated under reflux for 6 h. The volatiles were evaporated in vacuum and the residue was mixed with *i*-PrOH (10 ml). Nevertheless, the GC-MS analysis of the reaction mixture revealed only mainly starting materials, 4-bromobiphenyl **26** (MS (EI): m/z 232 ($[M]^{+\cdot}$)) and no proposed product formation could be detected.

Method B:

To a cold solution (-78 °C) of a commercial 4,4′-dibromobiphenyl (**24**; 10 g; 32 mmol) in THF (160 ml); *n*-BuLi (12.8 ml of 2.5 M solution in hexane; 32 mmol) was carefully added dropwise. The mixture was stirred at -78 °C for 10 min and then it was dropped to a solution of $SiCl_4$ (7.2 ml; 64 mmol) in THF (20 ml) at ambient temperature. The solution was stirred at ambient temperature overnight and then the volatiles were evaporated in vacuum and the residue was dissolved in a mixture of *i*-PrOH (50 ml) and THF (150 ml) and stirred for 20 h. All volatiles were evaporated under reduced pressure. The crude reaction product was purified by column chromatography (eluent hexane/toluene, 1/2, v/v) to yield the desired products **29** as a colorless liquid (only traces; 150 mg). The main product was the oily product of transalkylation, **28** (2.87 g; 22%), due to the presence of THF during reaction with *i*-PrOH.



28: ^{1}H NMR (300 MHz, $CDCl_3$): 1.23 (d, $^3J_{HH}$ = 6.1 Hz, 3H, $OCHMe_2$); 1.25 (d, $^3J_{HH}$ = 6.1 Hz, 3H, $OCHMe_2$); 1.75 (m, 2H, $OCH_2(CH_2)_2CH_2O$); 1.90

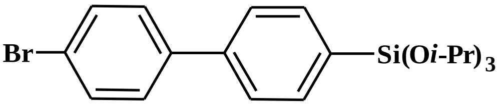
(m, 2H, $\mathrm{OCH_2(C}\mathit{H_2}\mathrm{)_2CH_2O}$); 3.57 (t, $^3J_{\mathrm{HH}}$ = 6.5 Hz, 2H, $\mathrm{OC}\mathit{H_2}\mathrm{(CH_2)_2C}\mathit{H_2}\mathrm{O}$); 3.85 (m, 2H, $\mathrm{OC}\mathit{H_2}\mathrm{(CH_2)_2C}\mathit{H_2}\mathrm{O}$); 4.29 (sept, $^3J_{\mathrm{HH}}$ = 6.1 Hz, 1H, $\mathrm{OC}\mathit{H}\mathrm{Me_2}$); 7.47 (d, $^3J_{\mathrm{HH}}$ = 8.6 Hz, 2H, $\mathrm{BrC_6}\mathit{H_4}\mathrm{C_6}\mathit{H_4}\mathrm{Si}$); 7.54-7.61 (m, 4H, $\mathrm{BrC_6}\mathit{H_4}\mathrm{C_6}\mathit{H_4}\mathrm{Si}$); 7.72 (d, $^3J_{\mathrm{HH}}$ = 8.1 Hz, 2H, $\mathrm{BrC_6}\mathit{H_4}\mathrm{C_6}\mathit{H_4}\mathrm{Si}$).

^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): 25.66 ($\mathrm{CH}\mathit{Me_2}$); 25.68 ($\mathrm{CH}\mathit{Me_2}$); 29.25, 29.77 ($\mathrm{OCH_2(}\mathit{C}\mathrm{H_2)_2CH_2O}$); 62.30, 62.47 ($\mathrm{O}\mathit{C}\mathrm{H_2(CH_2)_2}\mathit{C}\mathrm{H_2O}$); 65.99 ($\mathit{C}\mathrm{HMe_2}$); 126.54, 128.90, 132.08, 135.51 ($\mathrm{Br}\mathit{C_6}\mathrm{H_4}\mathit{C_6}\mathrm{H_4Si}$, $\mathit{C}\mathrm{H}$); 126.42, 126.66, 132.05, 135.57 ($\mathrm{Br}\mathit{C_6}\mathrm{H_4}\mathit{C_6}\mathrm{H_4Si}$, C_q).

GC-MS (EI): m/z 407 ($[\mathrm{M}]^{+\cdot}$).

Method C:

To a cold solution (-78 °C) of a commercial 4,4′-dibromobiphenyl (**24**; 3.0 g; 9.6 mmol) in THF (50 ml); *n*-BuLi (6.0 ml of 2.5 M solution in hexane; 9.6 mmol) was carefully dropped. The mixture was stirred at -78 °C for 30 min and then it was dropped to a solution of $\mathrm{SiCl_4}$ (2.2 ml; 19.2 mmol) in THF (8 ml) at ambient temperature. The solution was stirred at ambient temperature 1 h and then the volatiles were evaporated and the residue was dried in vacuum. The residue was mixed with *i*-PrOH (20 ml). The volatiles were evaporated under reduced pressure and the crude reaction product was purified by column chromatography (eluent hexane/toluene, 2/1, v/v) to yield the desired product **29** as a colorless liquid (1.1 g; 26%).



^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): 1.26 (d, $^3J_{\mathrm{HH}}$ = 6.2 Hz, 18H, $\mathrm{OCH}\mathit{Me_2}$); 4.32 (sept, $^3J_{\mathrm{HH}}$ = 6.2 Hz, 3H, $\mathrm{OC}\mathit{H}\mathrm{Me_2}$); 7.48 (d, $^3J_{\mathrm{HH}}$ = 8.8 Hz, 2H, $\mathrm{BrC_6}\mathit{H_4}\mathrm{C_6}\mathit{H_4}\mathrm{Si}$); 7.55 (d, $^3J_{\mathrm{HH}}$ = 8.2 Hz, 2H, $\mathrm{BrC_6}\mathit{H_4}\mathrm{C_6}\mathit{H_4}\mathrm{Si}$); 7.58 (d, $^3J_{\mathrm{HH}}$ = 8.8 Hz, 2H, $\mathrm{BrC_6}\mathit{H_4}\mathrm{C_6}\mathit{H_4}\mathrm{Si}$); 7.78 (d, $^3J_{\mathrm{HH}}$ = 8.2 Hz, 2H, $\mathrm{BrC_6}\mathit{H_4}\mathrm{C_6}\mathit{H_4}\mathrm{Si}$).

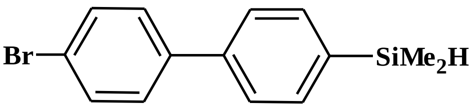
^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): 25.68 ($\mathrm{OCH}\mathit{Me_2}$); 65.63 ($\mathrm{O}\mathit{C}\mathrm{HMe_2}$); 126.28, 128.89, 132.02, 135.66 ($\mathrm{Br}\mathit{C_6}\mathrm{H_4}\mathit{C_6}\mathrm{H_4Si}$, $\mathit{C}\mathrm{H}$); 121.84, 132.36, 140.15, 141.41 ($\mathrm{Br}\mathit{C_6}\mathrm{H_4}\mathit{C_6}\mathrm{H_4O}$, C_q).

^{29}Si NMR (59.6 MHz, $\mathrm{CDCl_3}$): -62.06 ($\mathrm{C_6H_4}\mathit{Si}\mathrm{O_3}$).

IR (neat, cm^{-1}): 3394 (br, m), 3067 (w), 3022 (w), 2972 (s), 2931 (m), 2885 (m), 2644 (vw), 2148 (vw), 1901 (vw), 1793 (vw), 1657 (m), 1632 (m), 1601 (m), 1481 (m), 1467 (m), 1458 (m), 1382 (sh, s), 1369 (sh, s), 1173 (s), 1126 (s), 1040 (s), 1002 (s), 889 (m), 846 (w), 809 (s), 773 (s), 627 (m), 563 (m), 539 (s), 512 (s).

GC-MS (EI): m/z 438 ($[\mathrm{M}]^{+\cdot}$); 293 ($[\mathrm{M-Si(O}\mathit{i}\mathrm{\text{-}Pr)_2}]^+$); 214 ($[\mathrm{M-Br, Si(O}\mathit{i}\mathrm{\text{-}Pr)_2}]^+$); 204 ($[\mathrm{Si(O}\mathit{i}\mathrm{\text{-}Pr)_3}]^+$); 189.

(4´-Bromobiphen-4-yl)dimethylsilane (31)



To a cold solution (-78 °C) of a commercial 4,4´-dibromobiphenyl (**24**; 10 g; 32 mmol) in THF (200 ml); *n*-BuLi (21 ml of 1.6 M solution in hexane; 33.6 mmol) was gradually added dropwise. The mixture was stirred at -78 °C for 1 h and then HMe_2SiCl (5.0 ml; 44.9 mmol) was added at -78 °C. The reaction mixture was stirred at ambient temperature overnight and then the volatiles were evaporated in vacuum. The residue was purified by column chromatography (eluent hexane/CH_2Cl_2, 5/1, v/v) to yield the desired product **31** as a white solid (8.3 g; 88%).

M.p. 86-88 °C.

^{1}H NMR (300 MHz, $CDCl_3$): 0.37 (d, $^{3}J_{HH}$ = 4.2 Hz, 6H, SiH*Me*$_2$); 4.47 (sept, $^{3}J_{HH}$ = 4.2 Hz, 1H, Si*H*Me$_2$); 7.46 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, $BrC_6H_4C_6H_4Si$); 7.54 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, $BrC_6H_4C_6H_4Si$); 7.57 (d, $^{3}J_{HH}$ = 8.2 Hz, 2H, $BrC_6H_4C_6H_4Si$); 7.62 (d, $^{3}J_{HH}$ = 7.9 Hz, 2H, $BrC_6H_4C_6H_4Si$).

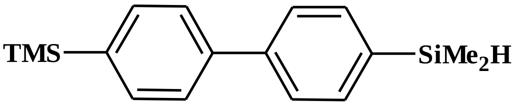
^{13}C NMR (75 MHz, $CDCl_3$): -3.61 (Si*Me*$_2$H); 126.51, 128.88, 132.05, 134.79 ($BrC_6H_4C_6H_4Si$, *C*H); 121.86, 136.95, 140.10, 140.89 ($BrC_6H_4C_6H_4Si$, C_q).

^{29}Si NMR (59.6 MHz, $CDCl_3$): -17.06 (*Si*Me$_2$H).

IR (neat, cm^{-1}): 3072 (w), 3021 (w), 2951 (m), 2901 (w), 2116 (s), 1922 (w), 1905 (w), 1595 (w), 1540 (w), 1476 (w), 1419 (w), 1379 (m), 1343 (w), 1246 (m), 1112 (w), 1071 (m), 998 (m), 880 (s), 831 (m), 805 (s), 758 (s), 695 (m), 652 (w), 624 (w), 510 (w), 478 (m), 419 (m).

GC-MS (EI): m/z 290 ($[M]^{+\cdot}$); 275 ($[M–Me]^{+}$); 211 ($[M–Br]^{+}$).

Dimethyl(4´-trimethylsilylbiphen-4-yl)silane (32)

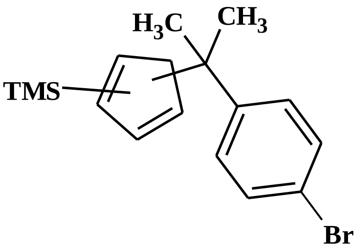


To a cold solution (-78 °C) of (4´-bromobiphen-4-yl)dimethylsilane (**31**; 100 mg; 0.34 mmol) in THF (10 ml); *t*-BuLi (202 µl of 1.7 M solution in pentane; 0.34 mmol) was added dropwise. The mixture was stirred at -78 °C for 20 min and then cold (-78 °C) TMSCl (200 µl; 1.66 mmol) was added. The solution was stirred at ambient temperature overnight and then the mixture was evaporated in vacuum. The residue was purified by column chromatography (eluent hexane/CH_2Cl_2, 5/1, v/v) to yield the desired product **32** as a white precipitate (80 mg; 82%).

^{1}H NMR (300 MHz, CDCl$_3$): 0.39 (s, 9H, Si*Me*$_3$); 0.45 (d, $^3J_{HH}$ = 4.2 Hz, 6H, SiH*Me*$_2$); 4.56 (sept, $^3J_{HH}$ = 4.2 Hz, 1H, Si*H*Me$_2$); 7.64-7.75 (m, 8H, Me$_2$HSiC$_6$*H*$_4$C$_6$*H*$_4$SiMe$_3$).

GC-MS (EI): m/z 284 ([M]$^{+\cdot}$); 269 ([M–Me]$^+$); 211 ([M–SiMe$_3$]$^+$); 73 ([SiMe$_3$]$^+$); 59 ([SiMe$_2$H]$^+$).

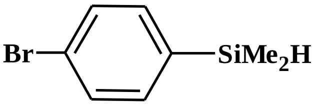
(C$_5$H$_4${CMe$_2$(PhBr)})SiMe$_3$ (38); a mixture of isomers



To a cold solution (-78 °C) of 1,4-dibromobenzene (**39**; 7.50 g; 31.8 mmol) in THF (100 ml); *t*-BuLi (38.4 ml of 1.7 M solution in pentane; 65.2 mmol) was added dropwise. The reaction mixture was stirred 2 h at -78 °C and then the solution of fulvene **17** (3.40 g; 31.8 mmol) in Et$_2$O (4 ml) was added. The reaction mixture was allowed to heat to ambient temperature and stirred overnight. Next day, the reaction was quenched with TMSCl (8.0 ml; 63 mmol) and stirred at ambient temperature overnight. The volatiles were removed in vacuum and the residue was purified by column chromatography (eluent hexane/CH$_2$Cl$_2$, 5/1, v/v) to yield a mixture of trimethyl silyl regioisomers **38** as a yellow liquid (5.57 g; 52%).

GC-MS (EI): m/z 334 ([M]$^{+\cdot}$); 196 ([M–C$_5$H$_4$SiMe$_3$]$^+$); 73 ([SiMe$_3$]$^+$).

(4-Bromophenyl)dimethylsilane (41)[58]



To a cold solution (-78 °C) of a commercial 1,4-dibromobenzene (**39**; 5 g; 21.2 mmol) in THF (40 ml); *t*-BuLi (13.7 ml of 1.7 M solution in pentane; 23.3 mmol) was added dropwise. The mixture was stirred at -78 °C for 1 h and then HMe$_2$SiCl (3.5 ml; 31.8 mmol) was added at -78 °C. The mixture was allowed to heat to ambient temperature and stirred overnight. The volatiles were evaporated in vacuum and the residue was purified by distillation (main fraction: 81-82 ºC at 6.2 Torr) to yield the desired product **41** as a colorless liquid (2.6 g; 54%).

^{1}H NMR (300 MHz, CDCl$_3$): 0.34 (d, $^3J_{HH}$ = 3.8 Hz, 6H, SiH*Me*$_2$); 4.41 (sept, $^3J_{HH}$ = 3.8 Hz, 1H, Si*H*Me$_2$); 7.40 (d, $^3J_{HH}$ = 8.1 Hz, 2H, BrC$_6$*H*$_4$Si); 7.50 (d, $^3J_{HH}$ = 8.1 Hz, 2H, BrC$_6$*H*$_4$Si).

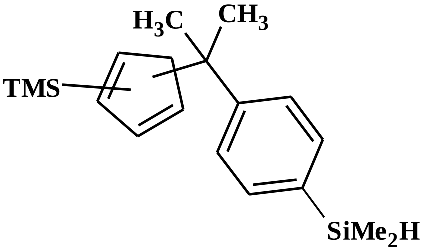
^{13}C NMR (75 MHz, CDCl$_3$): -3.71 (Si*Me*$_2$H); 131.15, 135.72 (Br*C*$_6$H$_4$Si, *C*H); 124.15, 136.35 (BrC_6H_4Si, C_q).

^{29}Si NMR (59.6 MHz, $CDCl_3$): -16.70 ($SiMe_2H$)

IR (neat, cm^{-1}): 3070 (w), 3032 (w), 3013 (w), 2959 (m), 2901 (w), 2123 (s), 1904 (w), 1575 (m), 1498 (w), 1479 (m). 1468 (m), 1424 (w), 1379 (m), 1251 (m), 1107 (m), 1067 (s) 1012 (m), 1005 (m), 878 (s), 837 (m), 810 (s), 765 (m), 740 (m), 722 (m), 627 (w), 481 (m), 429.

GC-MS (EI): m/z 214 ($[M]^{+\cdot}$); 199 ($[M–Me]^+$); 135 ($[M–Br]^+$).

$(C_5H_4CMe_2(PhSiMe_2H))SiMe_3]$ (42); a mixture of isomers



To a cold solution (-78 °C) of silyl derivative **38** (3.0 g; 9.0 mmol) in THF (30 ml); *t*-BuLi (10.8 ml of 1.7 M solution in pentane; 18.3 mmol) was added dropwise. The reaction mixture was stirred 1.5 h at -78 °C and then HMe_2SiCl (5.0 g; 45.0 mmol) was added. The reaction mixture was allowed to heat to ambient temperature and stirred overnight. Next day, the volatiles were evaporated and the crude product was extracted with hexane (3 × 15 ml). The volatiles were removed in vacuum and the residue was purified by column chromatography (eluent hexane/CH_2Cl_2, 8/1, v/v) to yield a mixture of trimethylsilyl regiomers **42** as a yellow liquid (2.6 g; 92%).

GC-MS (EI): m/z 314 ($[M]^{+\cdot}$); 225; 195; 135 ($[M–Me_2C(C_5H_4)SiMe_3]^+$); 73 ($[SiMe_3]^+$); 59 ($[SiMe_2H]^+$).

General method for attempted synthesis of derivatives 43 and 44 (Negishi coupling)

All glassware was purified, flame-dried and allowed to cool down to ambient temperature in a vacuum and stored under an argon atmosphere before use.

To a cold solution (-78 °C) of biphenyl **41** or **31** (1 eq) in dry Et_2O (20 ml), *t*-BuLi (2.1 eq of 1.7 M solution in pentane) was added dropwise. The suspension was stirred at -78 °C for 1 h and then freshly sublimed $ZnBr_2$ (1 eq) in dry THF (10 ml) was added. The reaction mixture was stirred for 15 min, allowed to heat up to 0 °C and stirred for 15 min. To the resulting solution of arylzinc bromide, a solution of silyl derivative **38** (0.5 eq) with Pd catalyst **45** ($5\%_{mol}$) in dry THF (10 ml) was added dropwise. The reaction mixture was allowed to warm to ambient temperature or heated at 50 °C and stirred overnight. The reaction progress was monitored by TLC (eluent hexane/ethyl acetate, 8/1) and quenched with brine (20 ml). The mixture was extracted with Et_2O (2 × 20 ml). The combined organic solution was washed with brine (30 ml) and dried over anhydrous $MgSO_4$. The drying agent was filtered off and the filtrate was evaporated under reduced pressure. The crude product was checked by GC-MS. Despite the conditions used, no product formation was detected.

$(C_5H_4CMe_2(PhPhSiMe_2H))SiMe_3$ (43)

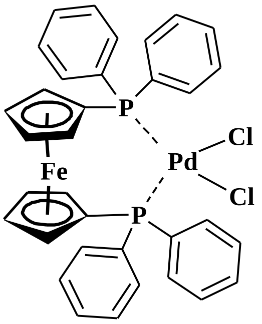
The title compound was determined only in trace amount by GC-MS.

GC-MS (EI): m/z 390 ($[M]^{+\cdot}$); 253 ($[M–C_5H_4SiMe_3]^+$); 73 ($[SiMe_3]^+$); 59 ($[SiMe_2H]^+$).

$(C_5H_4CMe_2(PhPhPhSiMe_2H))SiMe_3$ (44)

The title compound was not determined even in trace amount by GC-MS.

[1,1´-bis(diphenylphosphino)ferrocene]palladium(II) chloride (45)

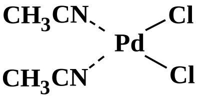


A solution of palladium(II) complex **46** (276 mg; 1.06 mmol) and 1,1´-bis(diphenylphosphino)ferrocene (619 mg; 1.12 mmol) in $CHCl_3$ (50 ml) was heated at 50 °C overnight. The solution was allowed to cool down and the precipitate was formed. The solid was filtered off and dried in vacuum to yield the complex **45** as a red crystalline solid (652 mg; 84%).

M.p.257-259 °C, ref.[69] 260 °C.

^1H NMR (300 MHz, $CDCl_3$): 4.19 (s, 2 × 2H, C_5H_4); 4.39 (s, 2 × 2H, C_5H_4); 7.39 (m, 4 × 2H, C_6H_5); 7.48 (m, 4 × 1H, C_6H_5); 7.89 (m, 4 × 2H, C_6H_5).

Bis(acetonitrile)palladium(II) chloride (46)



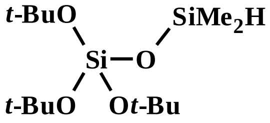
A suspension of $PdCl_2$ (504 mg; 2.84 mmol) in acetonitrile (60 ml) was heated under reflux for 2 h. The homogeneous solution was allowed to cool down and evaporated on a rotary evaporator. The complex **46** was yielded as a yellow crystalline solid (737 mg; 100%).

M.p.128-130 °C, ref.[70] 129-131 °C.

^{1}H NMR (300 MHz, $CDCl_3$): 2.40 (s, 2 × 3H, CH_3CN).

Tri(*t*-butyl)dimethylsilyl orthosilicate (50)

Method A:



A mixture of tris(*t*-butoxy)silanol (**51**; 3.34 g; 10.7 mmol) and an excess of $(HMe_2Si)_2NH$ (1.7 ml; 9.8 mmol) in toluene (20 ml) was heated at 90 ºC for 8 h. Nevertheless, the ^{1}H NMR analysis of the mixture revealed only starting materials and no product formation could be detected.

Method B:

To a solution of tris(*t*-butoxy)silanol (**51**; 2.85 g; 9.1 mmol) and HMe_2SiCl (1.1 ml, 10 mmol) in THF (20 ml); triethylamine (1.5 ml; 11 mmol) was added. The precipitate of ammonium salt was observed immediately. The mixture was stirred for 1 h and then the volatiles were removed in vacuum. The residue was extracted with heptane (15 ml) and after the evaporation of the solvent the product **50** was obtain as colorless oily liquid (3.38 g; 69%).

^{1}H NMR (300 MHz, $CDCl_3$): 0.22 (d, $^3J_{HH}$ = 6.0 Hz, 6H, Si*Me*$_2$); 1.29 (s, 27H, OC*Me*$_3$); 4.73 (sept, $^3J_{HH}$ = 6.0 Hz, 1H, Si*H*).

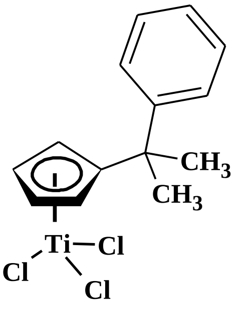
^{13}C NMR (75 MHz, $CDCl_3$): 0.61 (Si*Me*$_2$); 31.50 (OC*Me*$_3$); 72.51 (O*C*Me$_3$).

^{29}Si NMR (59.6 MHz, $CDCl_3$): -6.55 (*Si*Me$_2$H); -99.53 (*Si*O$_4$).

IR (neat, cm^{-1}): 2976 (s), 2931 (w), 2873 (vw), 2131 (m), 1473 (sh, w), 1389 (m), 1356 (m), 1251 (m), 1243 (m), 1194 (s), 1067 (vs), 1028 (m), 907 (s), 833 (m), 807 (w), 770 (sh, m), 703 (m), 645 (w), 627 (vw), 572 (vw), 502 (w), 479 (w), 431 (w).

Elemental analysis calculated for $C_{14}H_{34}O_4Si_2$ (322.59): C, 52.12; H, 10.62%. Found: C, 52.27; H, 10.81%.

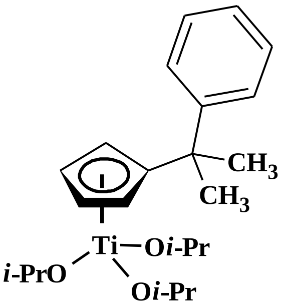
Preparation of [(η^5-$C_5H_4CMe_2Ph$)$TiCl_3$] (I)



To a solution of trimethylsilyl derivative **21** (2.5 g; 10 mmol) in toluene (25 ml); a solution of $TiCl_4$ (10 ml of 1 M solution in toluene; 10 mmol) was added with vigorous stirring. The reaction mixture changed its color from bright yellow to dark red and was stirred overnight at ambient temperature. The volatiles were evaporated in vacuum and the residue was purified by distillation and precipitation from mixture of CH_2Cl_2 and hexane. The product [(η^5-$C_5H_4CMe_2Ph$)$TiCl_3$] **I** was obtained as a dark red oily liquid (3.0 g; 93%). The spectral characterization corresponded with a literature.[27]

^{1}H NMR (300 MHz, $CDCl_3$): 1.86 (s, 6H, C*Me*$_2$); 6.88, 7.04 (2 × pseudo t, 2 × 2H, C_5*H*$_4$); 7.28-7.36 (m, 5H, C_6*H*$_5$).

Preparation of [(η^5-$C_5H_4CMe_2Ph$)Ti(O*i*-Pr)$_3$] (II)



To a solution of lithium cyclopentadienide ($C_5H_4CMe_2Ph$)Li (**19**; 3.12 g; 16.4 mmol) in THF (20 ml); ClTi(O*i*-Pr)$_3$ (15 ml of 1 M solution in hexane; 15.0 mmol) was added dropwise. The reaction mixture changed its color from red to yellow. Next day, the volatiles were removed in vacuum and the residue was extracted with hexane (20 ml). After evaporation of solvents, the crude product was purified by vacuum distillation (main fraction: 124-134 ºC at 0.11 Torr). The complex [(η^5-$C_5H_4CMe_2Ph$)Ti(O*i*-Pr)$_3$] **II** was obtained as a yellow-greenish liquid (4.42 g; 72%).

^{1}H NMR (300 MHz, $CDCl_3$): 1.21 (d, $^3J_{HH}$ = 6.0 Hz, 18H, CH*Me*$_2$); 1.84 (s, 6H, C*Me*$_2$); 4.61 (sept, $^3J_{HH}$ = 6.0 Hz, 3H, C*H*Me$_2$); 6.18, 6.31 (2 × pseudo t, 2 × 2H, C_5*H*$_4$); 7.12-7.20 (m, 1H, C_6*H*$_5$); 7.26-7.30 (m, 4H, C_6*H*$_5$).

^{1}H NMR (300 MHz, C_6D_6): 1.17 (d, $^3J_{HH}$ = 6.1 Hz, 18H, CH*Me*$_2$); 1.85 (s, 6H, C*Me*$_2$); 4.52 (sept, $^3J_{HH}$ = 6.1 Hz, 3H, C*H*Me$_2$); 6.01, 6.20 (2 × pseudo t, 2 × 2H, C_5*H*$_4$); 7.00-7.07 (m, 1H, C_6*H*$_5$); 7.11-7.19 (m, 2H, C_6*H*$_5$); 7.24-7.29 (m, 2H, C_6*H*$_5$).

^{13}C NMR (75 MHz, $CDCl_3$): 26.12 (CH*Me*$_2$); 29.37 (C*Me*$_2$); 39.94 (*C*Me$_2$); 77.57 (*C*HMe$_2$); 110.16, 112.45 (*C*$_5$H$_4$, *C*H); 125.57, 126.11, 128.01 (*C*$_6$H$_5$, *C*H); 138.96 (*C*$_5$H$_4$, C_{ipso}); 151.58 (*C*$_6$H$_5$, C_{ipso}).

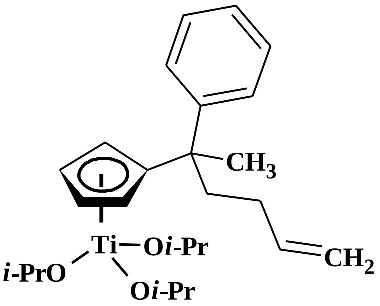
^{13}C NMR (75 MHz, C_6D_6) 26.17 (CH*Me*$_2$); 29.56 (C*Me*$_2$); 40.14 (*C*Me$_2$); 77.53 (*C*HMe$_2$); 110.26, 112.78 (*C*$_5$H$_4$, *C*H); 125.79, 126.43, 128.24 (*C*$_6$H$_5$, *C*H); 139.21 (*C*$_5$H$_4$, C_{ipso}); 151.75 (*C*$_6$H$_5$, C_{ipso}).

IR (neat, cm^{-1}): 3085 (vw), 3058 (vw), 3021 (vw), 2968 (s), 2929 (m), 2860 (m), 2616 (vw), 1599 (sh, w), 1494 (w), 1463 (w), 1445 (w), 1373 (m), 1360 (m), 1329 (m), 1261 (vw), 1222 (vw), 1167 (s), 1124 (sh, vs), 1017 (s), 1004 (vs), 891 (vw), 849 (m), 799 (m), 763 (w), 699 (m) 597 (sh, s), 552 (w), 462 (m).

MS (ESI$^+$): m/z 431 ($[M+Na]^+$); 349 ($[M–OCHMe_2]^+$).

Elemental analysis calculated for $C_{23}H_{36}O_3Ti$ (408.42): C, 67.63; H, 8.89%. Found: C, 67.85; H, 8.93%.

Preparation of [(η^5-C_5H_4\{CMe(CH_2)$_2$CH=CH_2Ph\})Ti(O*i*-Pr)$_3$] (III)



The complex **III** was prepared from ClTi(O*i*-Pr)$_3$ (8.1 ml of 1 M solution in hexane; 8.1 mmol) and (2-phenylhex-5-en-2-yl)cyclopentadienyllithium (**20**; 1.96 g, 8.5 mmol) by the same manner as described above for complex **II**. The crude complex **III** was purified by distillation (main fraction: 143-146 ºC at 0.11 Torr) and obtained as a yellow-greenish liquid (2.86 g; 79%).

^{1}H NMR (300 MHz, $CDCl_3$): 1.17, 1.18 (2 × d, 2 × $^3J_{HH}$ = 6.0 Hz, 2 × 9H, CH*Me*$_2$); 1.66-1.81 (m, 1H, CH_2C*H*$_2$CH=CH_2); 1.84 (s, 3H, C*Me*); 2.00-2.15 (m, 1H, CH_2C*H*$_2$CH=CH_2); 2.26-2.46 (m, 2H, C*H*$_2$$CH_2$CH=$CH_2$); 4.56 (sept, $^3J_{HH}$ = 6.0 Hz, 3H, C*H*Me$_2$); 4.89-5.04 (m, 2H, CH_2CH_2CH=C*H*$_2$); 5.74-5.90 (m, 1H, CH_2CH_2C*H*=CH_2); 6.02-6.07, 6.12-6.16, 6.16-6.20, 6.36-6.41 (4 × m, 4 × 1H, C_5*H*$_4$); 7.14-7.20 (m, 1H, C_6*H*$_5$); 7.25-7.38 (m, 4H, C_6*H*$_5$).

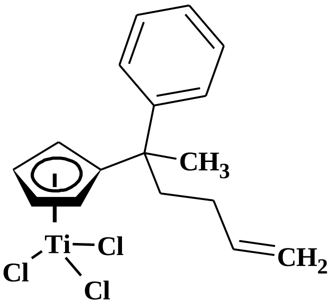
^{13}C NMR (75 MHz, $CDCl_3$): 24.73 (C*Me*); 26.01, 26.04 (CH*Me*$_2$); 29.06 (CH_2*C*H$_2$CH=CH_2); 40.74 (*C*H$_2$$CH_2$CH=$CH_2$); 42.98 (*C*Me); 77.58 (*C*HMe$_2$); 109.68, 110.14, 111.92, 112.55 (*C*$_5$H$_4$, *C*H); 114.01 (CH_2CH_2CH=*C*H$_2$); 125.64, 127.09, 127.97 (*C*$_6$H$_5$, *C*H); 139.32 (CH_2CH_2*C*H=CH_2); 139.87 (*C*$_5$H$_4$, *C*$_{ipso}$); 147.97 (*C*$_6$H$_5$, *C*$_{ipso}$).

IR (neat, cm^{-1}): 3077 (vw), 3062 (vw), 3022 (vw), 2967 (s), 2929 (m), 2860 (m), 2615 (vw), 1641 (w), 1600 (vw), 1496 (w), 1464 (sh, w), 1445 (m), 1374 (m), 1360 (m), 1329 (m), 1166 (s), 1126 (vs), 1070 (w), 1005 (sh, s), 909 (m), 849 (s), 798 (s), 766 (w), 700 (s), 684 (w), 597 (s), 462 (m).

MS (ESI$^+$): m/z 471 ($[M+Na]^+$); 389 ($[M–OCHMe_2]^+$).

Elemental analysis calculated for $C_{26}H_{40}O_3Ti$ (448.48): C, 69.63; H, 8.99%. Found: C, 69.55; H, 9.06%.

Preparation of $[(\eta^5\text{-}C_5H_4\{CMe(CH_2)_2CH=CH_2Ph\})TiCl_3]$ (IV)

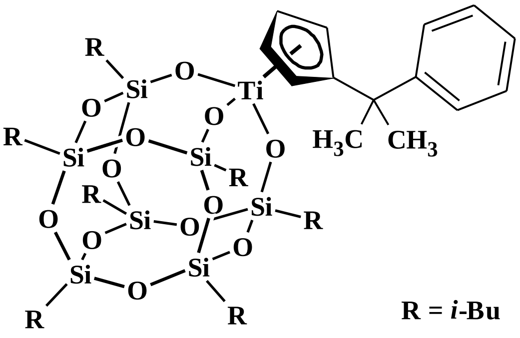


The complex **IV** was prepared from trimethylsilyl derivative **22** (1.5 g; 5 mmol) and $TiCl_4$ (5.25 ml of 1 M solution in toluene; 5.25 mmol) in toluene (10 ml) by the same manner as described above for complex **I**. The crude complex **IV** was purified by precipitation from mixture of CH_2Cl_2 and hexane and obtained as a dark red oily liquid (1.8 g; 98%).

^{1}H NMR (300 MHz, $CDCl_3$): 1.62-1.77 (m, 1H, $CH_2C\mathit{H}_2CH=CH_2$); 1.84 (s, 3H, $C\mathit{Me}$); 1.95-2.11 (m, 1H, $CH_2C\mathit{H}_2CH=CH_2$); 2.28-2.45 (m, 2H, $C\mathit{H}_2CH_2CH=CH_2$); 4.91-5.03 (m, 2H, $CH_2CH_2CH=C\mathit{H}_2$); 5.69-5.87 (m, 1H, $CH_2CH_2C\mathit{H}=CH_2$); 6.73-6.77, 6.83-6.87, 6.90-6.95, 7.13-7.18 (4 × m, 4 × 1H, $C_5\mathit{H}_4$); 7.21-7.29 (m, 3H, $C_6\mathit{H}_5$); 7.29-7.37 (m, 2H, $C_6\mathit{H}_5$).

^{13}C NMR (75 MHz, $CDCl_3$): 24.51 ($C\mathit{Me}$); 28.59 ($CH_2\mathit{C}H_2CH=CH_2$); 40.42 ($\mathit{C}H_2CH_2CH=CH_2$); 44.32 ($\mathit{C}Me$); 120.89, 122.49, 123.28, 123.77 (C_5H_4, $\mathit{C}H$); 114.98 ($CH_2CH_2CH=\mathit{C}H_2$); 126.98, 128.15, 128.77 (C_6H_5, $\mathit{C}H$); 138.08 ($CH_2CH_2\mathit{C}H=CH_2$); 144.38 (C_5H_4, C_{ipso}); 155.49 (C_6H_5, C_{ipso}).

Preparation of $[(\eta^5\text{-}C_5H_4CMe_2Ph)Ti(POSS\text{-}O_3)]$ (VI)



To a solution of POSS-$(OH)_3$ (**49**; 1.13 g; 1.42 mmol) in Et_2O (60 ml); complex $[(\eta^5\text{-}C_5H_4\{CMe_2Ph\}Ti(O\mathit{i}\text{-}Pr)_3]$ (**II**; 465 mg, 1.04 mmol) in Et_2O (15 ml) was added dropwise. The reaction mixture was stirred overnight. Acetonitrile (15 ml) was added and the mixture was concentrated in vacuum to precipitate of white solid. The crude product was washed with acetonitrile (2 × 4 ml) and dried in vacuum. The complex $[(\eta^5\text{-}C_5H_4CMe_2Ph)Ti(POSS\text{-}O_3)]$ **VI** was obtained as a white solid (1.17 g; 81%).

M.p. 118 ºC.

^{1}H NMR (300 MHz, $CDCl_3$): 0.52-0.60 (m, 14H, $C\mathit{H}_2$, *i*-Bu); 0.93-1.02 (m, 42H, $CH\mathit{Me}_2$, *i*-Bu); 1.77-1.94 partially overlapped (m, 7H, $C\mathit{H}Me_2$, *i*-Bu); 1.78 (s, 6H, $C\mathit{Me}_2$); 6.37, 6.44

(2 × pseudo t, 2 × 2H, C_5H_4); 7.13-7.30 (m, 5H, C_6H_5).

^{1}H NMR (300 MHz, Toluene-D_8): 0.75-0.83 (m, 14H, CH_2, *i*-Bu); 1.03-1.15 (m, 42H, CH*Me*$_2$, *i*-Bu); 1.78 (s, 6H, C*Me*$_2$); 1.98-2.17 partially overlapped with solvent signal (m, 7H, C*H*Me$_2$, *i*-Bu); 6.21, 6.34 (2 × pseudo t, 2 × 2H, C_5H_4); 6.98-7.04 partially overlapped with solvent signal (m, 1H, C_6H_5); 7.11-7.14 (m, 4H, C_6H_5).

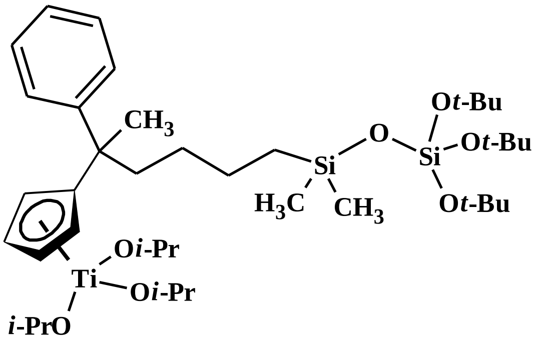
^{13}C NMR (75 MHz, $CDCl_3$): 22.74 (4C), 22.94 (3C) (*C*H$_2$, *i*-Bu); 24.07 (1C), 24.16 (3C), 24.31 (3C) (*C*HMe$_2$, *i*-Bu); 25.87 (2C), 25.91 (6C), 26.07 (6C) (CH*Me*$_2$, *i*-Bu); 29.67 (C*Me*$_2$); 40.02 (*C*Me$_2$); 114.82, 116.52 (*C*$_5$H$_4$, *C*H); 125.97, 126.12, 128.27 (*C*$_6$H$_5$, *C*H); 141.24 (*C*$_5$H$_4$, *C*$_{ipso}$); 150.48 (*C*$_6$H$_5$, *C*$_{ipso}$).

^{29}Si NMR (60 MHz, $CDCl_3$): -68.8 (3Si); -65.1 (4Si).

IR (KBr, cm^{-1}): 3087 (vw), 3058 (vw), 3022 (vw), 2954 (s), 2929 (m), 2905 (m), 2870 (m), 1495 (vw), 1465 (m), 1402 (vw), 1383 (vw),1366 (w), 1331 (w), 1228 (m), 1168 (m), 1097 (Si−O-Si, vs), 1038 (s), 1021 (Si−O−Ti, s), 954 (vw), 898 (m), 836 (w), 809 (m), 741 (m), 698 (w), 473 (m), 429 (w), 417 (w).

Elemental analysis calculated for $C_{42}H_{78}O_{12}Si_7Ti$ (1019.57): C, 49.47; H, 7.71%. Found: C, 49.12; H, 7.60%.

Preparation of $[(\eta^5\text{-}C_5H_4\{CMePh(CH_2)_4SiMe_2OSi(OtBu)_3\})Ti(Oi\text{-}Pr)_3]$ (VII)



To a solution of siloxane **50** (407 mg; 1.1 mmol) and complex $[(\eta^5\text{-}C_5H_4\{CMePh(CH_2)_2CH{=}CH_2Ph\})Ti(Oi\text{-}Pr)_3]$ (**III**; 465 mg, 1.04 mmol) in toluene (10 ml); a catalytic amount of Karstedt's catalyst in xylene (few drops) was added. The mixture was stirred at ambient temperature for 2.5 h. The ^{1}H NMR analysis showed complete consumption of **III** and formation of $[(\eta^5\text{-}C_5H_4\{CMePh(CH_2)_4SiMe_2OSi(OtBu)_3\})Ti(Oi\text{-}Pr)_3]$. The volatiles were removed in vacuum and the oily product was dried in vacuum (4 h at room temperature and then 5 h at 100 ºC). The pure product **VII** was obtained as a slightly yellow oily liquid (777 mg; 91%).

^{1}H NMR (300 MHz, $CDCl_3$): 0.04 (Si*Me*$_2$); 0.46-0.57 (m, 2H, SiMe$_2$C*H*$_2$); 0.851.01 (m, 2H, C*H*$_2$); 1.12, 1.14 (2 × d, 2 × $^3J_{HH}$ = 6.0 Hz, 2 × 9H, CH*Me*$_2$); 1.21-1.36 partially overlapped (m, 2H, C*H*$_2$); 1.25 (s, 27H, OC*Me*$_3$); 1.76 (s, 3H, C*Me*); 2.08-2.29 (m, 2H, CMeC*H*$_2$); 4.50 (sept, $^3J_{HH}$ = 6.0 Hz, 3H, C*H*Me$_2$); 5.95-6.01, 6.04-6.08, 6.08-6.14, 6.30-6.35 (4 × m, 4 × 1H, C$_5$*H*$_4$); 7.07-7.15 (m, 1H, C$_6$*H*$_5$); 7.18-7.32 (m, 4H, C$_6$*H*$_5$).

^{13}C NMR (75 MHz, CDCl$_3$): 0.04 (Si*Me*$_2$); 18.43 (Si*C*H$_2$); 24.01, 28.48 (SiCH$_2$*C*H$_2$*C*H$_2$); 24.79 (C*Me*); 26.08 (CH*Me*$_2$); 31.51 (OC*Me*$_3$); 41.58 (*C*H$_2$CMe); 43.04 (*C*Me); 72.24 (O*C*Me$_3$); 77.56 (*C*HMe$_2$); 109.68, 110.08, 111.97, 112.65 (*C*$_5$H$_4$, *C*H); 125.45, 127.14, 127.87 (*C*$_6$H$_5$, *C*H); 140.53 (*C*$_5$H$_4$, *C*$_{ipso}$); 148.45 (*C*$_6$H$_5$, *C*$_{ipso}$).

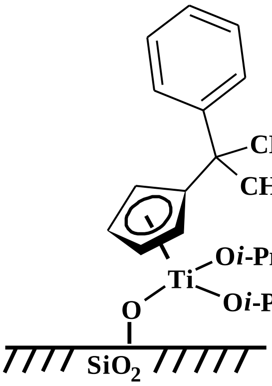
^{29}Si{^{1}H} NMR (CDCl$_3$): -99.4 (*Si*O$_4$); 8.4 (*Si*Me$_2$CH$_2$).

IR (neat, cm^{-1}): 3088 (vw), 3059 (vw), 2973 (s), 2930 (m), 2863 (m), 1600 (vw), 1496 (vw), 1473 (sh, w), 1446 (w), 1388 (m), 1364 (sh, s), 1329 (m), 1248 (m), 1193 (s), 1168 (s), 1125 (s), 1064 (vs), 1027 (s), 1003 (s), 908 (w), 843 (sh, m), 798 (m), 700 (m), 597 (sh, m), 480 (sh, m), 432 (w).

MS (ESI$^+$): m/z 809 ([M+K]$^+$); 793 ([M+Na]$^+$); 711 ([M−OCHMe$_2$]$^+$).

Elemental analysis calculated for C40H74O7Si2Ti (771.07): C, 62.30; H, 9.67%. Found: C, 62.48; H, 9.75%.

General method for immobilization of complex II on supports



To a suspension of support in Et$_2$O (40 ml); a solution of complex [(η^5-C$_5$H$_4${CMe$_2$Ph}Ti(O*i*-Pr)$_3$] **II** in Et$_2$O (10 ml) was added dropwise. The mixture was stirred for 12 h at ambient temperature. The solution was filtered off and the solid was washed with Et$_2$O (3 × 20 ml). The pure product was dried in vacuum to yield immobilised complex as slightly yellow solids. The solutions and washings were collected and checked by GC-FID and GC-MS to determine the presence of *i*-PrOH.

Tab. 5: Experimental conditions for immobilization of **II**

Supported catalyst	m_{Ti}[a] [g]	n_{Ti}[b] [mmol]	$m_{Support}$[c] [g]	$m_{Product}$[d] [g]
II/SiO$_2$(200)	0.523	1.28	1.068	1.295
II/SiO$_2$(800)	0.387	0.95	1.013	1.156
II/SBA-15(200)	0.450	1.10	1.510	1.937
II/SBA-15(700)	0.155	0.38	1.389	1.540

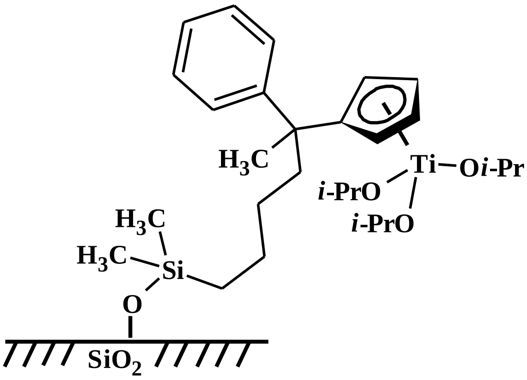
[a] m_{Ti} refers to mass of Ti complex

[b] n_{Ti} refers to molar amount of Ti complex

[c] $m_{Support}$ refers to mass of used support

[d] $m_{Product}$ refers to mass of observed product

General method for immobilization of complex III on supports



To a suspension of $SiMe_2H$-modified silica (1 eq that refers to $SiMe_2H$ group) and a commercial Karstedt's catalyst in xylene (5 drops; $w_{Pt} \approx 2\%$) in toluene (10 ml); $[(\eta^5\text{-}C_5H_4\{CMePh(CH_2)_2CH{=}CH_2Ph\})Ti(Oi\text{-}Pr)_3]$ **III** (1.1 eq) in toluene (5 ml) was added dropwise. The mixture was stirred for 5 h at ambient temperature or at 90 °C. The solution was filtered off and the solid was washed with toluene (5 × 5 ml). The pure product was dried in vacuum to afford immobilised complex as slightly yellow solids.

Tab. 6: Experimental conditions for immobilization of **III**

Supported catalyst	m_{Ti}[a] [g]	n_{Ti}[b] [mmol]	m_{Support}[c] [g]	n_{SiMe2H}[d] [mmol]	m_{Product}[e] [g]
III/SiO$_2$SiMe$_2$H	0.458	1.02	0.58	0.93	0.617
III/SiO$_2$SiMe$_2$H(90)	0.458	1.02	0.58	0.93	0.716

[a] m_{Ti} refers to mass of Ti complex

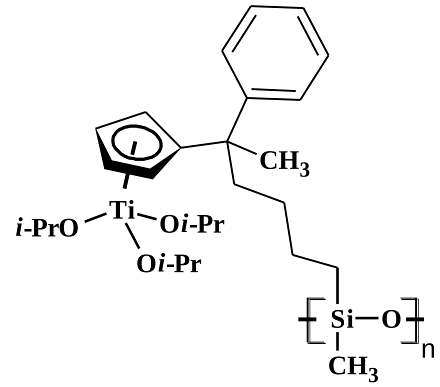
[b] n_{Ti} refers to molar amount of Ti complex

[c] m_{Support} refers to mass of used support

[d] n_{SiMe2H} refers to molar amount of present SiMe$_2$H groups

[e] m_{Product} refers to mass of observed product

General method for grafting complex III on PMHS (III/PMHS)



To a solution of polymethylhydrosiloxane (60 µl; 1 mmol) and complex [(η^5-C$_5$H$_4${CMePh(CH$_2$)$_2$CH=CH$_2$Ph})Ti(O*i*-Pr)$_3$] (**III**; 446 mg; 1 mmol) in toluene (10 ml); a commercial Karstedt's catalyst in xylene (few drops) was added dropwise. The reaction mixture was heated for 20 h at 80 °C. The volatiles were evaporated in vacuum and the unreacted titanium complex **III** (21 mg; 47 µmol) was distilled off under reduced pressure (bath temperature: 170 °C at 0.15 Torr). The product **III/PMHS** was yielded as a dark greenish oil (485 mg; 95%).

^{1}H NMR (300 MHz, CDCl$_3$): -0.16-0.27 (bs, Si*Me*); 0.32-0.55 (bs, SiMeC*H*$_2$); 0.76-1.03 (m, 2H, C*H*$_2$); 1.07-1.25 (m, CH*Me*$_2$); 1.47-1.59 (m, 2H, C*H*$_2$); 1.72 (s, 3H, C*Me*); 1.95-2.24 (m, CMeC*H*$_2$); 4.39-4.59 (m, C*H*Me$_2$); 5.92-6.54 (bs, C$_5$*H*$_4$); 7.05-7.43 (m, C$_6$*H*$_5$).

IR (neat, cm^{-1}): 3086 (vw), 3058 (vw), 3022 (w), 2967 (s), 2930 (s), 2862 (s), 2616 (w), 1599 (m), 1581 (w), 1494 (m), 1463 (sh, m), 1444 (m), 1415 (w), 1373 (s), 1360 (sh, s), 1329 (s), 1259 (m), 1124 (s), 1019 (s), 851 (m), 799 (m), 763 (m), 699 (sh, m), 599 (sh, m), 463 (m).

General procedure for ethylene trimerization

Ethylene trimerization experiments were carried out at constant ethylene pressure (5 bar) and temperature (30 ºC) in a 250 ml Büchi glass double-jacketed autoclave equipped with a magnetic stirrer (at 800 rpm). The hot autoclave was evacuated twice and filled with argon, charged with toluene, and a solution of MAO (molar ratio Al/Ti = 1000). After 15 min of stirring at the appropriate pressure of ethylene and temperature, the reactor was vented and the reaction was started by injecting the desired amount of catalyst precursor (stock solution of the homogeneous complex or a suspension of the heterogeneous material in toluene) under a stream of ethylene and immediately pressurized to 5 bar. The final volume of the oligomerization solution was 50 ml for all experiments. The autoclave temperature was kept constant during the reaction. The consumption of ethylene was followed with a calibrated mass flow meter (Bronkhorst, EL-FLOW). After 30 min, the reactor was vented and the reaction was quenched by the addition of methanol (5 ml). A sample of the reaction mixture was taken to analyse and quantify the soluble components by GC-FID. The residual mixture in the autoclave was finally quenched with 80 ml of a 10% solution of HCl in ethanol. The precipitated PE was stirred for 1 h, filtered off, rinsed repeatedly with ethanol and acetone, and dried under vacuum to constant weight.

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6. CONCLUSION

In this thesis, we suggested two independent pathways for immobilization of titanium complexes through direct Ti−O bond on the support surface and through a pendant tether by various strategies. The first one was anchoring through the flexible $-(CH_2)_4SiMe_2-$ tether and the second one was utilization of rigid tether based on aromatic unit.

Firstly, the titanium complexes suitable for anchoring to siliceous materials were prepared and characterized by spectroscopic methods (NMR, IR, MS) and elemental analysis. Subsequently, the heterogeneous systems were designed and prepared by either ligand-exchange reaction or hydrosilylation reaction. These heterogeneous systems were deeply characterized by spectroscopic methods (IR, ICP-OES, MAS NMR), thermal analysis (TGA) and the textural parameters were evaluated as well.

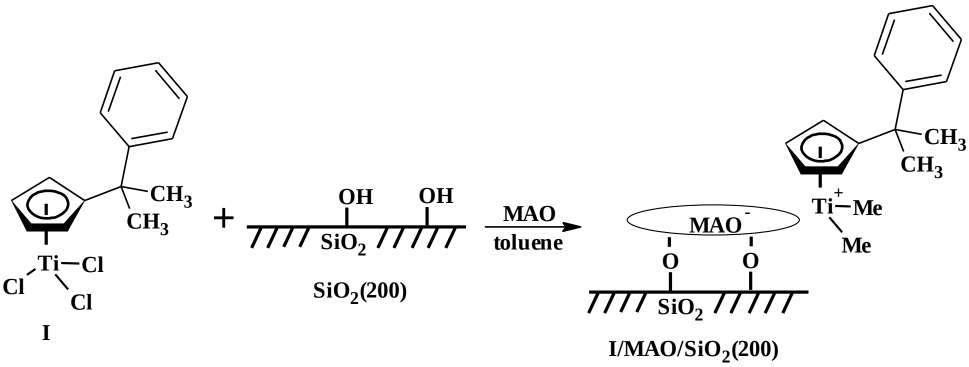
The final goal of this thesis was the study of ethylene trimerization activity and the selectivity to 1-hexene of all prepared derivatives. It was observed, that the activity is influenced by σ-ligand bonded to Ti (*e.g.* activity of Cl >> O*i*-Pr), probably as a result of different rate of alkylation of complex during initial stage of catalyst activation. On the other side, only negligible effect was observed in the case of cyclopentadienyl substitution at C6 carbon (replacing Me group with but-3-enyl group). All prepared heterogeneous systems showed lower activity in comparison with their homogeneous precursor, but their easier manipulation still support their widespread application.

The immobilization strategy through the rigid aromatic tether was not finished for the sake of time due to the encountered problems during the synthetic part and it is the challenge for further research.

7. FUTURE OUTLOOK

This thesis successfully worked up two possible methods to the heterogenization of complexes on the surface of supports and the key part was already published in Journal of Organometallic Chemistry.[71] We assume that further strategies could be proposed as well. Based on the experiences of Rytter and co-workers with design of heterogeneous catalytic system[72], we are suggesting the synthesis of heterogeneous catalytic system **cat/MAO/support** and the preliminary results were already obtained.

This heterogeneous system was designed as an ionic compound of MAO-modified siliceous support with titanium complex **I** (**Scheme 31**). The reaction of silica SiO_2(200) with 1000 equivalents of MAO gave the MAO-modified silica that was mixed with Hessen's complex **I**. The proposed ionic compound **I/MAO/SiO_2(200)** was then used as heterogeneous trimerization catalyst.



Scheme 31: Ionic heterogeneous catalytic system

The preliminary results showed that even this approach is viable and the trimerization experiments showed the catalytic behaviour comparable with other heterogeneous systems, concretely the activity A (for $n_{Ti} \approx 5$ μmol) = 23 $kg_{1\text{-hexene}}/mol_{Ti}\cdot bar\cdot h$ and only negligible amount of C_{10} fraction (1$\%_{wt}$) was observed. Unfortunatelly, the selectivity to 1-hexene was only moderate (61$\%_{wt}$), where an increased PE amount (38$\%_{wt}$) was obtained. Therefore, the catalyst composition/preparation should be further optimized.

8. LIST OF ABBREVIATIONS

A	activity in production of 1-hexene
BET	Brunauer-Emmett-Teller
Cp	cyclopentadienyl
Cp*	permethylcyclopentadienyl
COD	1,5-cyclooctadiene
δ	chemical shift
DFT	density functional theory
dppf	1,1′-bis(diphenylphosphino)ferrocene
EI	electron ionization
EPR	electron paramagnetic resonance
ESI	electrospray ionization
Et	ethyl
EWG	electron-withdrawing group
FT	Fourier transform
FID	flame ionization detector
GC	gas chromatography
η	hapticity
HDPE	high-density polyethylene
HMPA	hexamethylphosphoramide
ICP	inductively coupled plasma
IR	infrared
i-Bu	isobutyl
i-Pr	isopropyl
J	spin-spin coupling
λ	wavelength
L	ligand
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
$M^{+\cdot}$	molecular ion peak
MAO	methylaluminoxane

MDPE	medium-density polyethylene
Me	methyl
m.p.	melting point
MS	mass spectrometry
NBD	norbornadiene
n-BuLi	butyllithium
NMR	nuclear magnetic resonance
OES	optical emission spectrometry
OR	alkoxide
O*i*-Pr	isopropoxide
O*t*-Bu	*tert*-butoxide
PE	polyethylene
Ph	phenyl
PhLi	phenyllithium
PMHS	polymethylhydrosiloxane
POSS	polyhedral oligomeric silsesquioxane
R	alkyl
rpm	revolutions per minute
RT	room temperature
S	selectivity to 1-hexene
SHOP	Shell higher olefin process
t-BuLi	*t*-butyllithium
TEOS	tetraethyl orthosilicate
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMEDA	tetramethylethylenediamine
TMS	trimethylsilyl
TLC	thin-layer chromatography
TOF	turnover frequency
VLDPE	very-low-density polyethylene
UHMWPE	ultra-high-molecular-weight polyethylene

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