Synthesis of a Silica-Based Heterogeneous Second Generation Grubbs Catalyst

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Abstract: The synthesis of a second generation Grubbs catalyst immobilized onto non-porous silica is described. For this purpose, a polymerizable cationic NHC precursor, 1,3-bis(1-mesityl)-4-{[(bicyclo[2.2.1]hept-5-en-2-ylcarbonyl)oxy]methyl}-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (**5**) was prepared and characterized by X-ray analysis. Oligomers were prepared therefrom using both the well-defined Schrock initiator Mo(N-2,6-*i*-$Pr_2C_6H_3$)($CHMe_2Ph$)[$OCMe(CF_3)_2$]$_2$ and the first generation Grubbs catalyst $Cl_2Ru(CHPh)(PCy_3)_2$. Ru-initiated oligomerizations were terminated with ethyl vinyl ether, Mo-initiated oligomerizations were terminated by addition of $(EtO)_3SiCH_2CH_2CH_2N{=}C{=}O$. $(EtO)_3$Si-terminated oligomers obtained by the Wittig-like reaction between the Mo-containing oligomer and the isocyanate were used for the immobilization of the NHC-precursor containing oligomers on non-porous silica. Both oligomerizations were characterized by quantitative consumption of the corresponding initiator. This allowed the controlled synthesis of oligomers *via* stoichiometry. Using both non-porous and porous silica, degrees of derivatization of 0.04 and 0.02 mmol, respectively, of cationic NHC precursor/g silica were obtained. These precursors were converted into the corresponding NHC's by standard procedures and used for the generation of a heterogeneous second-generation Grubbs catalyst. Ruthenium loadings of 5.3 and 1.3 μmol/g, corresponding to 0.5 and 0.1 weight-% of catalyst were realized. Additionally, coating techniques were applied, where C_{18}-derivatized silica-60 was loaded with oligo-**5**. Conversion into the corresponding heterogeneous catalyst revealed 4.1 μmol/g, corresponding to 0.4 weight-% of catalyst. All supported catalysts prepared by this approach were successfully used in RCM in slurry type reactions.

Keywords: heterogeneous catalysis; high throughput screening; metathesis; polymers; ruthenium

Introduction

Besides of transition metal-catalyzed C-C coupling reactions such as the Heck,[1,2] Sonogashira–Hagihara, or Suzuki coupling,[3–6] *N*- and *O*-arylations or alkylations, olefin metathesis represents one of the most powerful reactions for catalytic C-C bond formation.[7] In particular, ring-closing metathesis (RCM) has become a highly attractive tool for the synthesis of complex architectures.[8,9] So far, a broad variety of homogeneous catalytic systems is available.[10] Among the numerous binary and ternary systems, the most outstanding ones are high oxidation state Mo-based Schrock catalysts[11–14] and the ruthenium-based Grubbs initiators.[15] In spite of, or rather *because of*, their highly favorable (complementary) properties, we have started the search for analogous heterogeneous systems that combine both the properties of the parent homogeneous catalysts and the advantages of heterogenization. In case of realization, one would gain access to supported catalysts for both small-scale combinatorial chemistry and large-scale reactor technology. As others,[16] we focus on synthetic protocols that use *N*-heterocyclic carbene (NHC)-based ligands rather than the alkylidene moiety for immobilization.[17–20] In this context, we already reported on the synthesis of a second generation, NHC-based Grubbs catalyst immobilized onto a monolithic system.[21] In the following, we describe the synthetic protocol for the synthesis of a system immobilized onto non-porous and porous silica. These supported catalysts can be used for ring-closing metathesis (RCM) in batch experiments and give access to catalyst-free products.

Results and Discussion

Monomer Synthesis

2,3-Dibromo-1-propanol was converted into the dimesityl derivative **1** by reaction with 2,4,6-trimethylaniline

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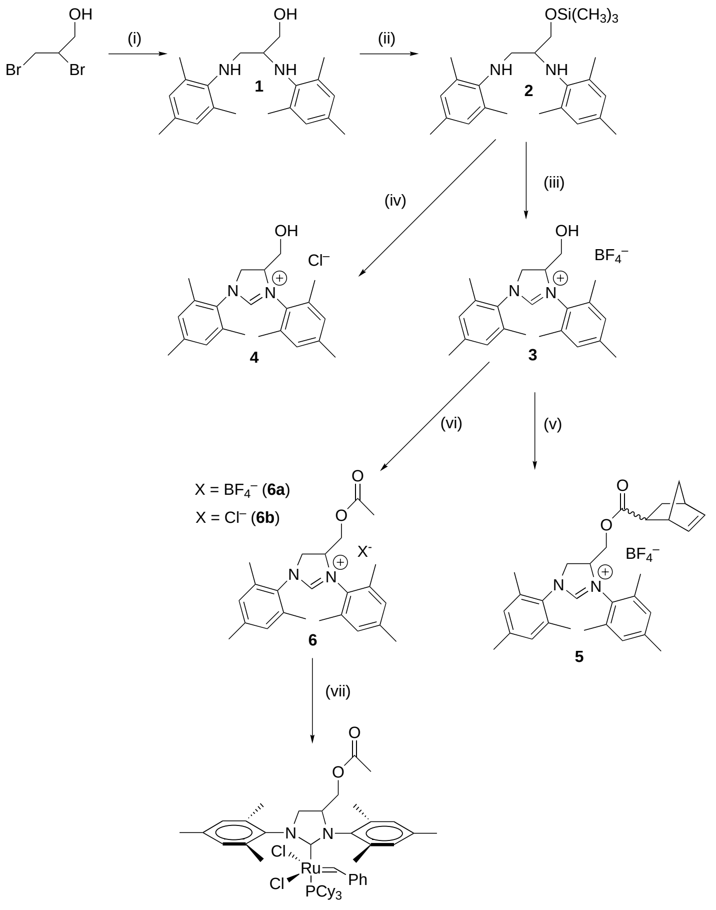


Scheme 1. Synthesis of compounds **1**–**6.** (i) a) 2,4,6-trimethylaniline, 120 °C, 19 h; b) CH_2Cl_2, 15% NaOH. (ii) CH_2Cl_2, $(CH_3)_3SiCl$, NEt_3. (iii) a) $(NH_4)BF_4$, $HC(OEt)_3$, 2 h, 110 °C; b) acetic acid. (iv) a) $(NH_4)BF_4$, $HC(OEt)_3$, 2 h, 110 °C; b) HCl. (v) CH_2Cl_2, NEt_3, norborn-5-ene-2-carboxylic chloride. (vi) CH_2Cl_2, NEt_3, acetyl chloride. (vii) a) KO-*t*-Bu, THF; b) $Cl_2Ru(CHPh)(PCy_3)_2$, toluene, 80 °C.

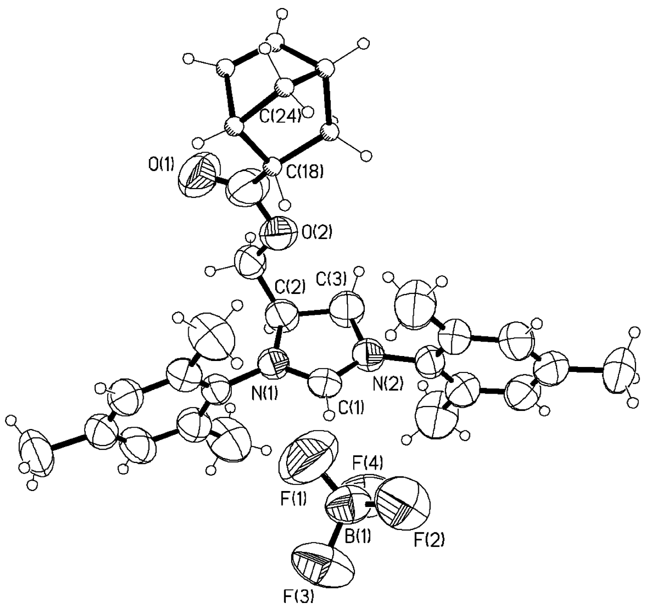
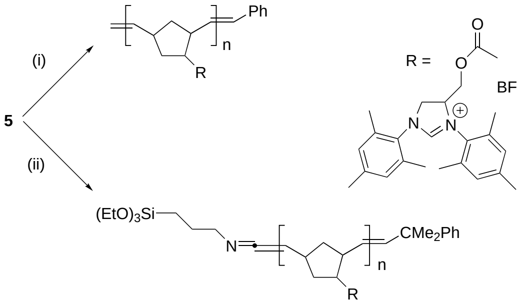


Figure 1. X-ray structure of **5** (disordered part C18A-C24A is omitted for clarity). Selected bond distances [Å] and angles [°]: N1-C1 1.311(5), N1-C2 1.491(5), N1-C4 1.445(5), N2-C1 1.305(5), N2-C3 1.481(6), N2-C10 1.439(5), C2-C3 1.525(6), N2-C1-N1 114.2(4), C1-N1-C2 109.7(3), C1-N2-C3 110.0(3), N1-C2-C3 102.8(3), N2-C3-C2 103.3(3).

(mesitylamine) and subsequent deprotonation with aqueous sodium hydroxide (Scheme 1).

In order to rule out the formation of even small amounts of a 4,5-dihydro-1*H*-oxazolium derivative instead of the desired 4,5-dihydro-1*H*-imidazolium salts **3** and **4**, the hydroxymethyl group in **1** was protected by a trimethylsilyl group *via* reaction with $(CH_3)_3SiCl$ and triethylamine in CH_2Cl_2 to form the *O*-protected species **2**. Compound **2** can be converted into the desired 4,5-dihydroimidazolium salts **3** and **4** by reaction with $HC(OEt)_3$ and ammonium tetrafluoroborate[22] and subsequent deprotection with acetic acid, respectively, hydrochloric acid. Both deprotected 4,5-dihydro-1*H*-imidazolium salts **3** and **4** can be used for the synthesis of the polymerizable NHC precursor **5** by reaction with norborn-5-ene-2-carboxylic chloride. Nevertheless, taking advantage of the high free energy that is entailed with the formation of a Si-Cl bond, the most straightforward approach to **5** is reaction of TMS-protected **3** with norborn-5-ene-2-carboxylic chloride. Since compound **5** represents a key intermediate, it was characterized by X-ray analysis. Its structure is shown in Figure 1. The compound is obtained in form of two diastereomers, with all enantiomers (*RR*, *SS*, *RS*, *SR*) present. Interestingly, only the *endo*-form is obtained. Though *endo*-isomers are generally considered to be less active in ring-opening metathesis polymerization (ROMP) compared to their *exo*-analogues, the polymerization of **5** proceeds smoothly with both Mo- and Ru-based initiators (*vide infra*).

In order to prepare a non-polymerizable analogue to **5** that can be used for the synthesis of a monomeric, soluble second-generation Grubbs initiator, compound **6** was synthesized from **3** by reaction with acetyl chloride. This NHC precursor **6** was converted to the free carbene by reaction with KO-*t*-Bu in THF at −40 °C. *In situ* NMR experiments carried out in THF-d_8 revealed that carbene formation was complete at this temperature within minutes. Without isolation, the free carbene was reacted with $Cl_2Ru(CHPh)(PCy_3)_2$ in THF[22] at 0 °C to yield $Cl_2Ru(CHPh)(Imes')(PCy_3)$, **7**, [Imes' = 1,3-di(1-mesityl)-4,5-dihydro-4-acetoxymethyl-1*H*-imidazolydene]. Similar to the systems reported by Fürstner et al.,[23] comparably low temperatures are required during synthesis in order to avoid carbene decomposition. So far we were not able to obtain **7** in pure form, yet its formation can be monitored by ^1H NMR in THF-d_8. Relevant chemical shifts are summarized in the Experimental Section.



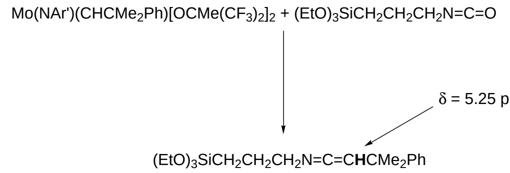
Scheme 2. Reaction of the Schrock initiator with the isocyanate. (i) a) $Cl_2Ru(CHPh)(PCy_3)_2$ in $ClCH_2CH_2Cl$; b) ethyl vinyl ether. (ii) a) Mo(N-2,6-*i*-Pr_2-C_6H_3)($CHCMe_2Ph$)($OCMe(CF_3)_2)_2$ in CH_2Cl_2; b) $(EtO)_3SiCH_2CH_2CH_2NCO$.

Polymerization and Synthesis of Telechelic Polymers

The NHC precursor **5** can be polymerized using both ruthenium- and molybdenum-based initiators. Thus, reaction of **5** with $Cl_2Ru(CHPh)(PCy_3)_2$ in methylene chloride at 45 °C results in complete consumption of the initiator and formation of an oligomer with a theoretical degree of polymerization (DP) of 7. A reaction time of 1 hour was necessary in order to achieve complete monomer consumption. The actual DP as determined by endgroup analysis using ^{1}H NMR was 7 ± 3. Endcapping was accomplished by reaction with ethyl vinyl ether (Scheme 2).

So far, with Ru-based systems we were not able to introduce an endgroup suitable for heterogenization in a satisfactory (i.e., in a quantitative) way. We therefore performed polymerizations with the Schrock initiator Mo(N-2,6-*i*-Pr_2-C_6H_3)($CHCMe_2Ph$)($OCMe(CF_3)_2)_2$[24] in methylene chloride at ambient temperature. With this initiator, oligomerization was complete within 30 minutes. The theoretical DP of 7 was in excellent accordance with a DP of 7 ± 1 found *via* endgroup analysis using ^{1}H NMR. Again, this strongly suggests that initiation is quantitative. Since alkylsilanes react with aldehydes *via* Si-O rearrangement[25], there exist no stable silylaldehydes that could be used for endcapping. We therefore investigated the extent to which ω-(trialkoxysilyl)alkyl isocyanates might be used for this purpose. In principle, an isocyanate group should react in the same way than an aldehyde. Preliminary experiments entailed the reaction of Mo(N-2,6-*i*-Pr_2-C_6H_3)($CHCMe_2Ph$)($OCMe(CF_3)_2)_2$ with $(EtO)_3SiCH_2CH_2CH_2N{=}C{=}O$. With a ten-fold excess of isocyanate, the original alkylidene proton resonances at $\delta = 12.1$ and 12.8 ppm, respectively, disappeared and a new signal, corresponding to the new olefinic proton of the ketenimine appeared at $\delta = 5.28$ ppm. Additionally, GC-MS investigations were carried out and confirmed the formation of the proposed product $(EtO)_3SiCH_2CH_2CH_2NH^+{=}C{=}CHCMe_2Ph$ ($m/z = 364$) and the corresponding fragments $(EtO)_3Si^{\cdot +}$($m/z = 163$) and $^{\cdot}CH_2CH_2CH_2NH^+{=}C{=}CHCMe_2Ph$ ($m/z = 201$) (Scheme 3).

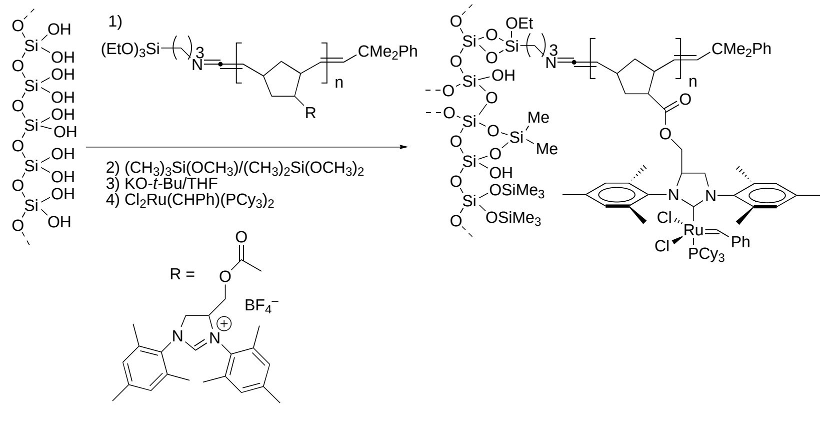
Based on these results, **5** was initiated with the Mo-based catalyst and oligomers with a DP of 7 were prepared. The living oligomer was reacted with a ten-fold excess of the isocyanate at 45 °C to yield the trialkoxysilyl-telechelic oligomer (Scheme 3).



Scheme 3. Synthesis and end-functionalization of oligomers.

Grafting of the Telechelic Oligomer onto Silica and Synthesis of the Heterogeneous Catalyst

Telechelic oligo-**5** was reacted with non-porous and porous silica (Scheme 4). Non-porous silica was chosen in order to avoid diffusion-controlled reactions within



Scheme 4. Synthesis of heterogeneous ruthenium catalyst.

medium sized pores. The potentially low catalyst loading that is usually entailed with the use of low-specific surface area supports was compensated *via* the grafting approach by the factor of 7 (i.e., the DP of the oligomer). Endcapping of the residual silanol groups was accomplished by reaction with $(CH_3)_3SiOCH_3$ and $(CH_3)_2Si(OCH_3)_2$. It should be noted that such endcapping reactions of silica are *never* quantitative, typical amounts of residual Si-OH groups are around 7–8%.[26] Nevertheless, due to the functional group tolerance of Ru-based systems and the low accessibility of these remaining Si-OH groups, this does usually not entail any problems. Recently, our group demonstrated the low accessibility of such Si-OH moieties. Thus, even highly active Mo-based Schrock initiators can be used in a *grafting from*-approach with such silica.[27]

Reaction of the grafted support with KO-*t*-Bu in THF at −30 °C yielded the free carbene which was subsequently reacted with $Cl_2Ru(CHPh)(PCy_3)_2$ to yield the immobilized second generation Grubbs catalyst. After leaching of the support with aqua regia under microwave conditions, the ruthenium content of the solution was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES). In terms of catalyst loading it is worth mentioning that only 13% of the NHC ligand were converted into the corresponding catalyst, leading to a catalyst loading of 0.5 weight-%. This value is much lower than the one found in systems based on monolithic supports, where roughly 40% of the NHC precursor could be used for immobilization, resulting in 1.4 weight-% catalyst loading.[21]. Although a non-porous support should facilitate the accessibility of any surface-bound groups, this particular silica shows a reduced accessibility of the corresponding NHC sites. We attribute this fact to the strong tendency of this support to agglomerate. Concerning the implications for catalysis, *vide infra*. In analogy, porous silica 60 was surface functionalized with 0.02 mmol of NHC precursor in the form of $(EtO)_3Si$-telechelic oligo-**5**. Conversion into the initiator was accomplished as described above, leading to a Ru-loading of 0.013%. Finally, coating techniques[28] using again $(EtO)_3Si$-telechelic oligo-**5** were applied, leading to a surface-derivatized silica 60 containing 0.09 mmol of NHC precursor. Conversion into the initiator resulted in a support containing 4.1 μmol Ru/g.

Reactivity and Use of the Heterogeneous Catalyst in RCM

Preliminary RCM experiments were carried out with diethyl diallylmalonate. The catalyst immobilized onto non-porous silica was added to a solution of this monomer in 1,2-dichlorobenzene and the mixture was heated to 50 °C for 2 hours. Irrespective of the reaction conditions used (i.e., ultrasound, microwave, changing reaction times, temperature, and solvents), the maximum turnover number (TON) that was achieved was 75. Interestingly, basically identical results (TON = 80) were obtained with catalyst immobilized onto porous silica. In principle, second generation Grubbs-type initiators immobilized on non-porous silica should behave similar to those immobilized on monolithic supports.[21] In fact, catalysts immobilized onto monolithic supports give similar maximum TON's (≅65) in the absence of any chain transfer agent (CTA). Nevertheless, the low TON's (< 5!) obtained with other, less reactive compounds such as 1,7-octadiene, *N,N*-diallyltrifluoroacetamide, diallyl ether, and diallyldiphenylsilane suggest that the stirred batch setup with this type of support is highly diffusion controlled, where reaction is too slow and decomposition of the intermediary ruthenium methylidene dominates. Apart from these sobering results, those obtained with coated supports deserve special consideration. TON's for diethyl diallylmalonate, 1,7-octadiene, and diallyl ether were 210, 55, and 16 in the *absence* of any CTA, thus exceeding data for TON of all other silica supports by far. Since coating techniques are known to reduce the specific surface area by clogging of the micropores, catalytic results can be interpreted in a way that a support containing only macropores, which facilitate diffusion, is generated. It is worth mentioning that in all cases ruthenium measurements by means of ICP-OES revealed quantitative retention of the original amount of ruthenium at the support within experimental error (±5%), thus offering access to metal-free products. In view of these data, our current research emphasizes on improved conversion of NHC precursors into the desired catalytic sites as well as on the use of cartridge systems. Results will be reported in due course.

Conclusion

Both Ru- and Mo-based initiators can polymerize cationic NHC precursors containing norborn-5-ene-2-yl groups. Mo-initiated polymerizations can be terminated with isocyanates in a Wittig-type reaction. In the case of ω-(alkoxysilyl)alkyl isocyanates, the corresponding ω-(trialkoxy)silane-containing polymers can be grafted onto silica by employing standard derivatization procedures. Subsequent conversion of the NHC precursors into the corresponding carbenes and reaction with $Cl_2Ru(CH{=}Ph)(PCy_3)_2$ yields the desired heterogenized second generation Grubbs-type initiators. The silica-based systems can be used both in slurry reactions and for the fabrication of cartridge systems for RCM.

Experimental Section

General Remarks

NMR data were obtained at 300 MHz in the indicated solvent at 25 °C on a Bruker Spectrospin 300 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in Hertz. IR spectra were recorded on a Nicolet 510 FT-IR. GC-MS investigations were carried out on a Shimadzu GCMS QP5050, using a SPB-5 fused silica column (30 m × 0.25 mm × 25 μm film thickness). Elemental analyses were carried out at the Institute of Physical Chemistry, University of Vienna. A Jobin Yvon JY 38 plus was used for ICP-OES measurements, a MLS 1200 mega for microwave experiments. Further instrumentation is described elsewhere.[29]

Syntheses of the ligands and polymerizations were performed under an argon atmosphere by standard Schlenk techniques or in an N_2-mediated dry-box (Braun, Germany) unless stated otherwise. Reagent grade diethyl ether, pentane, THF, and toluene were distilled from sodium benzophenone ketyl under argon. Reagent grade dichloromethane and 1,2-dichloroethane were distilled from calcium hydride under argon. Other solvents and reagents were used as purchased. Deionized water was used throughout. $Cl_2Ru(CHPh)(PCy_3)_2$, was purchased from Fluka. *endo*-Norborn-2-ene-5-carboxylic chloride[29] and Mo{N-2,6-(*i*-Pr_2-C_6H_3)(CHCMe$_2$Ph) [OCMe$(CF_3)_2$]$_2$},[24] were prepared according to literature procedures and checked for purity by means of NMR. Nonporous silica (Aerosil) was purchased from Degussa-Huels, Germany. Silica 60 was purchased from Merck, Germany. C_{18} derivatization was carried out according to the literature.[26]

N,N′-Dimesityl-2,3-diamino-1-propanol (1)

2,3-Dibromopropanol (20.000 g, 91.785 mmol) was treated with 2,4,6-trimethylaniline (32.267 g, 238.64 mmol). The mixture was stirred at 120 °C for 19 hours. A dark brown solid precipitated. Methylene chloride and an aqueous 15% sodium hydroxide solution (100 g, 400 mmol) were added and the mixture was stirred until all solid had completely dissolved. The organic layer was separated, washed with water and dried over sodium sulfate. The solvent was removed under vacuum and some dark red oil remained. The crude product was cleaned by column-chromatography on silica gel 60 using a 1:1 mixture of diethyl ether and pentane; yield: 14.870 g (49.6%, white solid). IR (KBr): $\tilde{\nu} = 3200$ b (νOH), 3419 s (νN_1H), 3345 m (νN_2H), 3030 m ($\nu C_{arom}H$), 2965 m ($\nu_{as}CH_3$), 2855 m (ν_sCH_3), 1615 w, 1593 w, 1483 s, 1445 s (all $\nu C{=}C_{arom}$), 1432 m ($\delta_{as}CH_3$), 1374 m (δ_sCH_3), 1248 s, 1099 s, 972 s, 872 s cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 6.80$, 6.81 (2 × s, 4H, *m*-$H_{arom.}$), 3.95 (dd, 1H, CH_2, $^2J = 10.9$ Hz, $^3J = 2.6$ Hz), 3.83 (dd, 1H, CH_2, $^2J = 10.1$ Hz, $^3J = 4.1$ Hz), 3.4 – 3.8 (sb, 2H, NH), 3.38 (m, 1H, CH), 3.22 (dd, 1H, CH_2, $^2J = 11.9$ Hz, $^3J = 5.0$ Hz), 2.98 (dd, 1H, CH_2, $^2J = 11.9$ Hz, $^3J = 4.0$ Hz), 2.1 – 2.3 (m, 19H, CH_3, OH); ^{13}C NMR ($CDCl_3$): $\delta = 142.5$, 141.8, 132.5, 130.9, 130.5, 129.8,128.5, 129.7, ($C_{arom.}$), 52.3, 56.9, 66.0 (2 × CH_2, CH), 17.8, 20.5, 20.4, 18.9 (CH_3); anal. calcd. for $C_{21}H_{30}N_2O$: C 77.26, H 9.26, N 8.58%; found: C 76.86, H 9.66, N 8.38%.

N,N′-Dimesityl-2,3-diamino-1-propoxytrimethylsilane (2)

Compound **1** (4.000 g, 12.25 mmol) was dissolved in 70 mL of methylene chloride. Triethylamine (1.8 mL, 13 mmol) and trimethylchlorosilane (1.6 mL, 13 mmol) were added sequentially and the mixture was stirred at room temperature for two hours. After this reaction time, thin layer chromatography (TLC) on silica (mobile phase diethyl ether:pentane = 1:1) showed no remaining educt. The volatiles were removed under vacuum leaving a yellow oil. Diethyl ether was added to extract the product while the triethylammonium chloride formed during the reaction precipitated. The salt was removed by filtration through celite. Removal of the solvent gave the product as yellow oil; yield: 4.88 g (100%). ^1H NMR ($CDCl_3$): $\delta = 6.83$ (d, 4H, H_{arom}), 3,67 (dd, 1H, O-CH_2, $^2J = 10.2$ Hz, $^3J = 2.1$ Hz), 3.60 (dd, 1H, O-CH_2, $^2J = 10.2$ Hz, $^3J = 3.7$ Hz), 3.49 (m, 1H, CH), 3.75 – 3.45 (b, 2H, NH), 3.29 (dd, 1H, CH_2, $^2J = 11.8$ Hz, $^3J = 5.6$ Hz), 2.98 (dd, 1H, CH_2, $^2J = 11.8$ Hz, $^3J = 6.2$ Hz), 2.82 (m, 18H CH_3), 0.1 (s, 9H, Si-CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 143.8$, 141.7, 131.1, 130.5, 129.7, 129.5, 129.4, 129.0 (C_{arom}), 62.7, 57.4, 50.6 (2 × CH_2, CH), 20.5, 18.9, 18.8, 18.4 (CH_3), 1.0 (Si-CH_3).

1,3-Bis(1-mesityl)-4,5-dihydro-4-hydroxymethyl-1*H*-imidazol-3-ium Tetrafluoroborate (3)

Compound **2** (4.880 g, 12.25 mmol) and ammonium tetrafluoroborate (1.284 g, 12.25 mmol) were dissolved in triethyl orthoformate (5 mL, 30 mmol) and the reaction mixture was heated and stirred for two hours. After this time, TLC on silica (mobile phase diethyl ether:pentane = 1:1) showed no remaining educt. The reaction mixture was cooled to 40 °C and the volatiles were removed under vacuum. A yellow oil remained. It was treated with acetic acid to remove the trimethylsilyl protecting group. Finally, all volatiles were removed under vacuum and the residue was washed with pentane, dried, and recrystallized from ethanol/pentane; yield: 1.951 g (36.5%, white solid). IR (KBr): $\tilde{\nu} = 3200$ b (νOH), 2923 m ($\nu_{as}CH_3$), 2880 m (ν_sCH_3), 1624 s ($\nu C{=}N^+$), 1481 s, 1470 sh (all $C{=}C_{arom}$), 1389 cm^{-1} m (δ_sCH_3); ^1H NMR ($CDCl_3$): $\delta = 7.80$ (s, 1H, C_2-H), 6.89 (s, 4H, *m*-H_{arom}), 4.80 (m, 1H, CH), 4.4231 (d, 2H, CH_2), 3.72 (d, 1H, CH_2, $^2J = 11.9$ Hz), 3.53 (d, 1H, CH_2, $^2J = 11.9$ Hz), 2.4 – 2.1 (m, 18 H, CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 158.1$ (C_2), 140.4, 140.2, 136.4, 135.0, 130.2, 128.4 (all C_{arom}), 65.3, 58.6, 52.1 (2 × CH_2, CH), 20.9, 20.8, 17.9, 17.5, 17.4 (all CH_3).

1,3-Bis(1-mesityl)-4,5-dihydro-4-hydroxymethyl-1*H*-imidazol-3-ium Chloride (4)

Compound **3** (4.631 g, 11.62 mmol) and ammonium tetrafluoroborate (1.218 g, 11.62 mmol) were dissolved in triethyl orthoformate (4 mL, 20 mmol) and the reaction mixture was heated and stirred for two hours. After that reaction time, TLC on silica (mobile phase = diethyl ether:pentane = 1:1) showed no remaining educt. The reaction mixture was cooled to 40 °C and the volatile compounds were removed under vacuum. A yellow solid remained. It was washed with water to remove unreacted ammonium tetrafluoroborate and dried. Afterwards the residue was washed with pentane and dried again. In order to remove the trimethylsilyl protective group the residue was stirred with 20% hydrochloric acid for several hours. With this step the anion changes from tetrafluoroborate to chloride. The solution was neutralized with 15% sodium hydroxide. Then the product was extracted with methylene chloride and dried over sodium sulfate. The product was dried under vacuum; yield: 90%. ^{1}H NMR (CDCl$_3$): $\delta = 8.20$ (s, 1H, C$_2$-H), 6.9–6.8 (m, 4H, H$_{\text{arom}}$), 4.80 (m, 2H, CH$_2$), 4.35 (t, 1H, CH), 3.78 (d, 1H, CH$_2$, $^2J = 12.81$ Hz), 3.45 (d, 1H, CH$_2$, $^2J = 12.81$ Hz), 2.4–2.2 (m, 18H, CH$_3$); ^{13}C NMR (CDCl$_3$): $\delta =$ 156.6 (C$_2$), 138.8, 138.6, 135.2, 133.1, 128.8, 128.5, 127.1 (all C$_{\text{arom}}$), 64.4, 56.6, 51.1 (2 × CH$_2$, CH), 19.4, 16.8, 16.4 (all CH$_3$).

1,3-Bis(1-mesityl)-4-{[(bicyclo[2.2.1]hept-5-en-2-ylcarbonyl)oxy]methyl}-4,5-dihydro-1*H*-imidazol-3-ium Tetrafluoroborate (5)

Compound **4** (1.952 g, 4.524 mmol) was dissolved in methylene chloride, then triethylamine (1 mL, 7 mmol) was added. The mixture was chilled to −50 °C and treated with norborn-2-ene-5-carboxylic acid chloride (0.85 mL, 5.4 mmol, *endo*:*exo* = 8:1). The reaction mixture was stirred for 2 hours, the cooling bath was removed and the mixture was stirred for another 5 hours. The volatiles were removed under vacuum and a pinkish solid remained. This residue was washed with water and dried. Afterwards the residue was washed with pentane and dried again. The crude product was recrystallized from ethanol/pentane; yield: 1.296 g (52.3%, white crystals). IR (KBr): $\tilde{\nu} = 3060$ w (νC$_{\text{NBE}}$=C-H), 2973 s (ν_{as}CH$_3$), 2869 m (ν_{s} CH$_3$), 1736 s (νC=O), 1628 s (C=N$^+$), 1481 m, 1460 m (all νC=C$_{\text{arom}}$), 1383 m (δ_{s}CH$_3$), 713 cm^{-1} m (δ_{a}=C$_{\text{NBE}}$-H); ^{1}H NMR (CDCl$_3$): $\delta = 8.13, 8.11$ (2 × s, 1H, C$_2$-H *endo/exo*), 6.92 (m, 4H, H$_{\text{arom}}$), 6.14, 6.04, 5.80 [all m, 2H, H$_{\text{NBE}}$(db)], 5.17 (m, 1H, CH), 4.68 (m, 1H, CH$_2$), 4.30–3.92 (m, 3H, CH$_2$), 3.04, 2.89, 2.82 (all m, 3H, all H$_{\text{NBE}}$), 2.4–2.2 (m, 18H, CH$_3$), 1.85, 1.63, 1.41, 1.25 (all m, 4H, all H$_{\text{NBE}}$); ^{13}C NMR (CDCl$_3$): $\delta = 175.6, 174.1$ (C=O *exo/endo*), 159.7 (C$_2$), 141.0, 140.8, 138.4, 135.8, 135.7, 136.6, 135.5 132.1, 132.0, 130.8, 130.4, 130.2, 128.7, 128.5, (all C$_{\text{arom}}$ + C$_{\text{NBE}}$), 62.7, 62.6, (CH, CH$_2$), 53.0, 52.9, 50.1, 49.9, 46.7, 46.1, 46.0, 43.3, 42.8, 41.8 (all C$_{\text{NBE}}$ + CH$_2$), 29.9, 29.6 (C$_{\text{NBE}}$), 21.3, 21.2, 18.3, 18.0, 17.9, 17.8, 17.7 (all CH$_3$); anal. calcd. for C$_{30}$H$_{37}$BF$_4$N$_2$O$_2$: C 66.18, H 6.85, N 5.15%; found: C 65.87, H 6.90, N 5.03%. Crystals suitable for X-ray analysis were obtained from ethanol:pentane.

1,3-Bis(1-mesityl)-4-acetoxymethyl-4,5-dihydro-1*H*-imidazol-3-ium Tetrafluoroborate (6)

Compound **4** (0.500 g, 1.16 mmol) was dissolved in methylene chloride and then triethylamine (0.2 mL, 1.4 mmol) was added. The mixture was chilled to −50 °C and treated with acetyl chloride (55 μL, 0.77 mmol) and acetic anhydride (71 μL, 0.75 mmol). The reaction mixture was stirred for 2 hours, the cooling bath was removed, and the mixture was stirred for another 6 hours. The volatile compounds were removed under vacuum. The residue was washed with pentane and dried. Then the residue was washed with water and dried again. Recrystallization from ethanol/pentane gave the product as white crystals; yield: 0.103 g (19.2%). IR (KBr): $\tilde{\nu} = 2956$ m (ν_{as}CH$_3$), 2859 w ((ν_{s}CH$_3$), 1750 (νC=O), 1628 (νC=N$^+$), 1481 m, 1462 m (all νC=C$_{\text{arom}}$), 1383 cm^{-1} (δ_{s}CH$_3$); ^{1}H NMR (CDCl$_3$): $\delta = 8.09$ (s, 1H, C$_2$-H), 6.93 (s, 4H, H$_{\text{arom}}$), 5.22 (m, 1H, CH), 4.71 (t, 1H, CH$_2$), 4.21 (m, 2H, CH$_2$), 3.96 (d, 1H, CH$_2$), 2.35–2.20 (m, 18 H, C$_{\text{arom}}$-CH$_3$), 2.03 (s, 3H, C=OCH$_3$); ^{13}C NMR (CDCl$_3$): $\delta =$ 169.8 (C=O), 159.1 (C$_2$), 140.7, 140.5, 135.3, 135.2, 130.5, 130.2, 129.8, 128.0 (all C$_{\text{arom}}$), 62.0, 61.3, 52.5 (2 × CH$_2$, CH), 21.0, 20.9, 20.6, 18.0, 17.4, 17.2 (all CH$_3$); anal. calcd. for C$_{24}$H$_{31}$BF$_4$N$_2$O$_2$: C 61.77, H 6.7, N 6.01%; found: C 61.23, H 6.86, N 5.81%.

1,3-Bis(1-mesityl)-4-acetoxymethyl-4,5-dihydro-1*H*-imidazol-3-ium Chloride (6b)

1,3-Bis(1-mesityl)-4,5-dihydro-4-hydroxymethyl-1*H*-imidazol-3-ium chloride (0.500 g, 1.32 mmol) was dissolved in methylene chloride and then triethylamine (0.2 mL, 1.4 mmol) was added. The mixture was chilled to −50 °C and treated with acetyl chloride (55 μL, 0.77 mmol) and acetic anhydride (71 μL, 0.75 mmol). The reaction mixture was stirred. After removal of the cooling bath after two hours, the mixture was stirred for another 6 hours. The volatile compounds were removed under vacuum and a brownish solid remained. It was dissolved in methylene chloride and extracted with water. The water phase was concentrated to a few milliliters and sodium chloride was added. The product was reextracted with methylene chloride (5 × 60 mL) and dried over sodium sulfate. After removal of the solvent the product was recrystallized from ethanol/pentane; yield: 0.090 g (17%, white solid). ^{1}H NMR (CDCl$_3$): $\delta = 9.44$ (s, 1H, C$_2$-H), 6.82 (s, 4H, H$_{\text{arom}}$), 5.39 (m, 1H, CH), 4.86, 4.30, 4.08, 3.92 (all m, all 1H, 2 × CH$_2$), 2.35–2.10 (m, 18H, C$_{\text{arom}}$-CH$_3$), 1.97 (s, 3H, C=OCH$_3$).

Tricyclohexylphosphine[1,3-bis(1-mesityl)-4-acetoxymethyl-4,5-dihydroimidazol-2-ylidene][benzylidene]ruthenium(IV) Dichloride (7)

A suspension of **7** (10.5 mg, 22.8 μmol) in THF-d_8 (0.5 mL) was chilled to −40 °C and a solution of potassium *t*-butoxide (2.6 mg, 22.8 μmol) in THF (0.5 mL) was added. The reaction mixture was stirred for 10 minutes at −40 °C. A solution of Cl$_2$ Ru(CHPh)(PCy$_3$)$_3$ (13.1 mg, 15.9 μmol) in THF-d_8 (0.5 mL) was added, the solution was stirred for another 2 hours at 0 °C and then warmed to room temperature. All attempts to isolate this compound in a pure form have failed so far. Nevertheless, the formation of **8** in approximately 35% yield can be monitored by ^{1}H NMR: ^{1}H NMR (THF-d_8): $\delta = 19.2$ (Ru=C$\underline{\text{H}}$Ph), 7.3–7.0 (H$_{\text{arom}}$).

Oligo-5

Method A: Compound **5** (80 mg, 0.15 mmol) was dissolved in methylene chloride and treated with a solution of Mo(N-2,6-*i*-Pr$_2$-C$_6$H$_3$)[CHC(CH$_3$)$_2$Ph][OC(CH$_3$)(CF$_3$)$_2$]$_2$ (17 mg; 22 μmol) in methylene chloride. The yellow reaction mixture was stirred for half an hour at room temperature. The mixture was endcapped with a solution of ferrocene aldehyde (40 mg, 184 mmol) in methylene chloride and stirred for 5 hours at room temperature. The oligomer was precipitated by addition of pentane, filtered off, thoroughly washed with pentane and dried; yield: 69 mg (86%). ^{1}H NMR (CD$_2$Cl$_2$): $\delta = 8.3$–7.9 (sb, n × 1H, NC-HN), 7.2 – 6.9 (m, n × $4H_{arom}$ + $5H_{endgroup}$), 5.4 – 5.0 (b, n × $2H_{db}$ + n × $1H_{CH}$), 4.8 – 3.7 (b, n × $4H_{CH2}$ + $9H_{endgroup}$), 3.0 × 2.6 (b, n × $3H_{NBE}$), 2.5 – 1.0 (b, n × $18H_{CH3}$ + n × $4H_{NBE}$ + $6H_{endgroup}$).

Method B: Compound **5** (80 mg, 0.15 mmol) was dissolved in dichloroethane and treated with a solution of $Cl_2Ru(PCy_3)_2(CHPh)$ (18 mg, 22 μmol) in dichloroethane. The reaction mixture was heated to 45 °C and stirred for two hours. The reaction mixture was endcapped by adding ethyl vinyl ether. Then the oligomers were precipitated by addition of pentane, filtered, washed with pentane and dried; yield: 70.1 mg (87%). ^1H NMR (CD_2Cl_2): δ = 8.2 – 7.9 (sb, n × 1H, NC-HN), 7.4 – 6.9 (m, n × $4H_{arom}$ + $5H_{endgroup}$), 5.5 – 5.0 (b, n × $2H_{db}$ + n × $1H_{CH}$), 4.7 – 4.4 (b, n × $1H_{CH2}$), 4.3 – 3.9 (b, n × $3H_{CH2}$), 3.0 – 2.6 (b, n × $3H_{NBE}$), 2.5 – 2.1 (b, n × $18H_{CH3}$), 1.93, 1.72, 1.57, 1.26 (n × $4H_{NBE}$).

Reaction of Schrock Initiator with Isocyanate

$Mo(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)[CHC(CH_3)_2Ph][OC(CH_3)(CF_3)_2]_2$ (5 mg, 7 μmol) and 3-isocyanatopropyltriethoxysilane (9 mg, 40 mmol) were combined in $CDCl_3$. The mixture was stirred for eight hours at 45 °C. The color of the solution changed from yellow to dark brown. The alkylidene signal at δ = 12.1/12.8 ppm disappeared, a new signal at δ = 5.28 ppm appeared.

Oligo-5 Containing an R-$Si(OCH_2CH_3)_3$ Endgroup

For immobilization purposes, **5** (150 mg, 0.274 mmol) was dissolved in methylene chloride and treated with a solution of $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2\text{-}C_6H_3)(CHCMe_2Ph)[OC(CH_3)(CF_3)_2]_2$ (14 mg; 18 μmol) in methylene chloride. The yellow reaction mixture was stirred for half an hour at room temperature. A solution of 3-isocyanatopropyltriethoxysilane (39 mg, 160 μmol) in methylene chloride was added to terminate the reaction. The mixture was stirred and heated to 45 °C for four hours. The color of the solution changes from yellow to dark brown. To precipitate the oligomer, pentane was added to the solution. The oligomers were filtered off, thoroughly washed with pentane and dried; yield: 0.145 g (97%, slightly salmon-colored solid). ^1H NMR (CD_2Cl_2): δ = 8.3 – 7.9 (sb, n × 1H, NC-HN), 7.2 – 6.8 (b, n × $4H_{arom}$ + $5H_{endgroup}$), 5.5 – 5.0 (b, n × 2Hdb + n × 1H, CH), 4.7 – 4.4 (b, n × 1H, CH_2), 4.3 – 3.9 (b, n × 3H, CH_2), 3.8 (m, $6H_{endgroup}$), 3.3 –2.6 (b, n × $3H_{NBE}$ + $2H_{endgroup}$), 2.5 – 2.1 (b, n × $18H_{CH3}$), 2.0 – 1.0 (n × $4H_{NBE}$ + $9H_{endgroup}$ + $4H_{endgroup}$); triethoxysilyl endgroup: δ = 3.68 (OCH_2) and 1.14 (CH_3); ^{13}C NMR (CD_2Cl_2): δ = 175 (C=O), 160 (N-C-N), 140, 135, 130 (all C_{arom} + C_{NBE}), 62, 61, 59 (CH + CH_2), 48, 41, 37 (C_{NBE}), 21, 18, 17 (CH_3).

Oligo-5 Loaded Non-Porous Silica

Non-porous silica was dried under vacuum at 200 °C for two days. Poly-**5** containing $Si(OCH_2CH_3)$ endgroups (120 mg) was dissolved in methylene chloride. Non-porous silica (4 g) was added and the reaction mixture was refluxed at 45 °C for 4 hours. In order to cap the excess of silanol groups a mixture of methoxytrimethylsilane (120 mg, 1.15 mmol) and dimethoxydimethylsilane (90 mg, 0.75 mmol) in methylene chloride was added. The mixture was refluxed at 45 °C for 72 hours. Afterwards the derivatized silica was filtered off, washed with methylene chloride and dried. Analysis found: C 2.68, H 0.51, N 0.12%, corresponding to a loading of 40 μmol **5**/g silica.

Generation of the Immobilized Ru-Catalyst

Poly-**5** grafted silica (1.50 g, corresponding to 60 μmol NHC precursor) was suspended in THF (10 mL), chilled to −35 °C and KO-*t*-Bu (8.1 g, 72 μmol) was added. While warming to −20 °C, the suspension was stirred for 10 minutes. A solution of $Cl_2Ru(CHPh)(PCy_3)_2$ (49 mg, 72 μmol) in THF (5 mL) was added and the reaction mixture was sonicated for 2 hours at ambient temperature. The silica was filtered off, washed with THF, methylene chloride and pentane and dried under vacuum. Analysis found: Ru 0.054% (5.3 μmol/g).

Oligo-5 Loaded Porous Silica 60

Silica 60 was dried under vacuum at 200 °C for two days. $Si(OCH_2CH_3)$-telechelic oligo-**5** (169 mg) was dissolved in methylene chloride. Silica 60 (4.0 g) was added and the reaction mixture was refluxed at 50 °C for 6 hours. In order to cap the excess of silanol groups, a mixture of methoxytrimethylsilane (420 mg, 4.03 mmol) and dimethoxydimethylsilane (350 mg, 2.91 mmol) in methylene chloride was added. The mixture was refluxed at 50 °C for 14 hours. Finally, the silica was filtered off, washed with methylene chloride and dried under vacuum. Loading with NHC precursors: 0.06 wt-% N, corresponding to 20 μmol NHC precursor/g silica. The preparation of the heterogeneous catalyst was carried out as described for non-porous silica. Analysis found: Ru 0.013% (1.3 μmol/g).

Oligo-5 Coated Porous Silica 60

The $Si(OCH_2CH_3)$-telechelic oligo-**5** (200 mg) was dissolved in methylene chloride and the solution was added to C_{18} derivatized silica 60 (4.0 g, particle size 43 – 60 μm). The solvent was slowly removed under vacuum (700 torr) and the residue was dried under high vacuum. 5 weight-% coating correspond to a loading of 90 μmol NHC-precursor/g silica. The preparation of the heterogeneous catalyst was carried out as described for non-porous silica. Analysis found: Ru 0.041% (4.10 μmol/g).

RCM Experiments (Slurry Reactions)

Diethyl diallylmalonate (20 mg, 0.08 mmol) was dissolved in 1,2-dichlorobenzene (2 mL) and the supported catalyst (40 mg) was added. The reaction mixture was heated to 50 °C for 2 hours. After removal of the catalyst by filtration, the yield was determined by ^1H NMR in $CDCl_3$.

Leaching of the Support

Aqua regia (3.0 mL) was added to the heterogeneous catalyst (30 mg). The mixture was placed inside high-pressure Teflon tubes and leaching was carried out under microwave conditions (50, 600, and 450 W pulses, respectively, $t = 32$ minutes). After cooling to room temperature, the mixture was filtered and measured by ICP-OES ($\lambda = 240.272$ nm, ion line). The background was measured at $\lambda = 240.287$ and 240.257 nm, respectively.

X-Ray Crystallographic Study of 5

Monoclinic, space group $P2_{(1)}/c$ (No.14), $a = 21.031(2)$ Å, $b = 9.6800(4)$ Å, $c = 14.660(1)$ Å, $\beta = 101.907(3)^{\circ}$, $V = 2920.3(4)$ Å^3, $Z = 4$, $\rho_{calc} = 1.238$ g cm^{-3}, $T = 223$ K, $\mu = 0.094$ mm^{-1}, $Mo\text{-}K_{\alpha}$-radiation ($\lambda = 0.71073$ Å), colorless plate $0.4 \times 0.4 \times 0.06$ mm^3. 10430 reflections were collected on a Nonius KappaCCD diffractometer with 2193 reflections $> 2\sigma(I)$. The structure was solved and refined using SHELXS83 and SHELXL97 to $R1 = 0.0695$ and $wR2 = 0.1778$ for 2193 unique reflections. Non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms were placed at calculated positions and refined isotropically using a riding model. A 1:1 disorder of the norbornenyl group C18-C24:C18A-C24A occurs with split and overlying positions. The chiral centers C18 and C18A are enantiomeric. This disorder itself is induced by the diastereomeric compound with two chiral centers at C2 and C18, all 4 chiral combinations (*RR*, *RS*, *SR* and *SS*) are equally represented in the centrosymmetric unit cell. Further crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 177467. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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