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Probing of the Ligand Anatomy: Effects of the Chelating Alkoxy Ligand Modifications on the Structure and Catalytic Activity of Ruthenium Carbene Complexes

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This work is dedicated to Yves Chauvin, Richard Schrock and Robert H. Grubbs on the occasion of their being awarded the Nobel Prize for Chemistry in 2005.

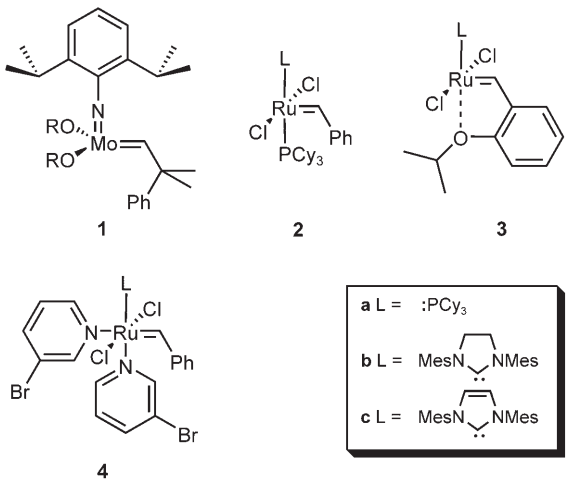
Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: Structural modifications of the Hoveyda–Grubbs ruthenium metathesis complex *via* electronic and structural withdrawing of the chelating alkoxy ligand were investigated. By decreasing the donor properties of the oxygen atom, an acceleration in catalytic activity was achieved based on facilitation of the initiation step. Conformational constraints of the chelating ether linkage led to the unexpected disturbance of the complex geometry and a vast improvement of the activity.

Keywords: carbenes; catalysis; ligand modifications; metathesis; ruthenium

Introduction

The rapid development in the area of olefin metathesis has culminated in the Nobel Prize in Chemistry being awarded to Chauvin, Schrock and Grubbs for their seminal work in the area.[1] Using this tool, chemists can now efficiently synthesise an impressive range of molecules that only a decade ago required significantly longer and tedious routes.[2,3] Especially, the discovery of efficient and selective catalysts **1**–**4** (Scheme 1) has been the key to the widespread application of olefin metathesis in organic synthesis. At the same time, new theoretical insights allow a deeper understanding of the nature of metathesis catalysts and of the mechanism of the metathesis reaction. Such understanding is crucial to the design of new metathesis catalysts which is being performed by a number of research groups.[1] Since 2002, our group has participat-



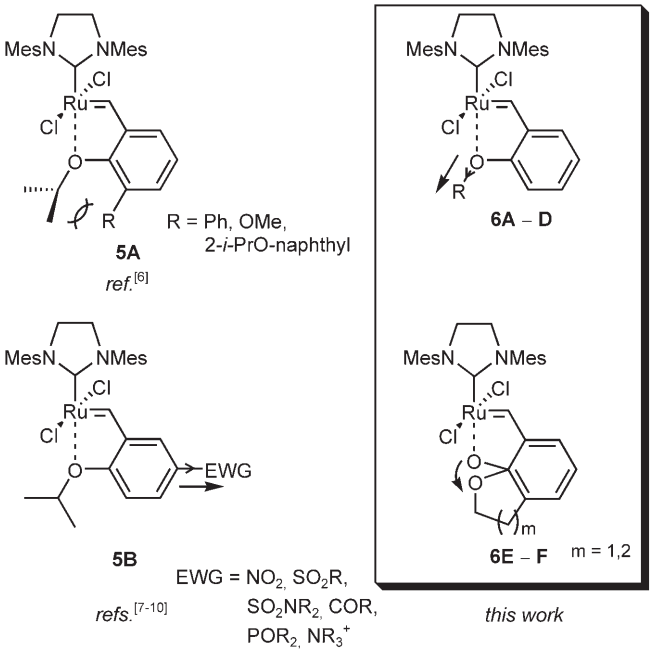
Scheme 1. Selected catalysts for olefin metathesis. *i*-Pr = isopropyl; Cy = cyclohexyl, Mes = 2,4,6-trimethylphenyl, R = chiral or achiral substituent; refs.[1–3]

ed in this research aimed at extending the scope of the reaction for substrates in which the traditional catalyst systems were not adequate.[1,4]

Results and Discussion

Blechert and Wakamatsu have shown that the substituent at the *ortho* position to the alkoxy group in the benzylidene moiety of a Hoveyda-type catalyst[5] results in a large improvement in the catalytic activity and – for example – complex **5A** is drastically more reactive not only than **3b** but also than the "second-generation" Grubbs' catalyst **2b** (Scheme 2, top left).[6] We have recently found that the 5-nitro-substituted Hoveyda-type catalyst **5B** (EWG = NO_2) possesses also a dramatically enhanced reactivity in model ring-closing (RCM), cross- (CM) and enyne-metathesis reactions (Scheme 2, bottom left).[7] Interestingly, the sensitivity of **5B** towards air and moisture was not diminished as compared with the parent Hoveyda–Grubbs complex **3b**.[8] As a result, this stable and easily accessible catalyst has found a number of successful applications in various research and industrial laboratories.[9]

We proposed that the electron-withdrawing (EWG) nitro group in the benzylidene fragment of **5B** decreases the electron density at the oxygen atom of *i*-PrO moiety and, as a result, weakens the O→Ru chelation and facilitates faster initiation of the catalytic cycle (Scheme 2, bottom left).[7,8,10] As it was shown later, also other EWG substituents (e.g., SO_2, SO_2NR_2, CF_3, F, CN, COR, NR_3^+, POR_2) exhibit similar activating effects.[11] As a continuation of our research program aimed at the study of a subtle balance between the stability of the catalyst (and its insensitivity to moisture, air and impurities), and its high activity we decided to study in detail another type of modification of **3b** – the effects of the chelating RO ligand (Scheme 2, right). This unexplored approach[12] allows one to probe the pure alkoxy ligand effect in terms of its electron density and structural constraints. Electronic activation with acceptor-type substituents on the oxygen atom retains the Ru=C carbene moiety relatively intact, as may be compared with analogue **5B**, where the nitro group influences the properties of both oxygen donor and benzylidene part across the ring. On the other hand, the possible geometrical constraints introduced to the structure of the ligand are based on a completely distinctive concept of modification of chelate stability *via* remoting of O→Ru centres (see below for details). Herein we report on the design, preparation and application properties of new, air-stable Hoveyda-type ruthenium homogeneous catalysts **6A–F** bearing a modified alkoxy chelating ligand.[12]



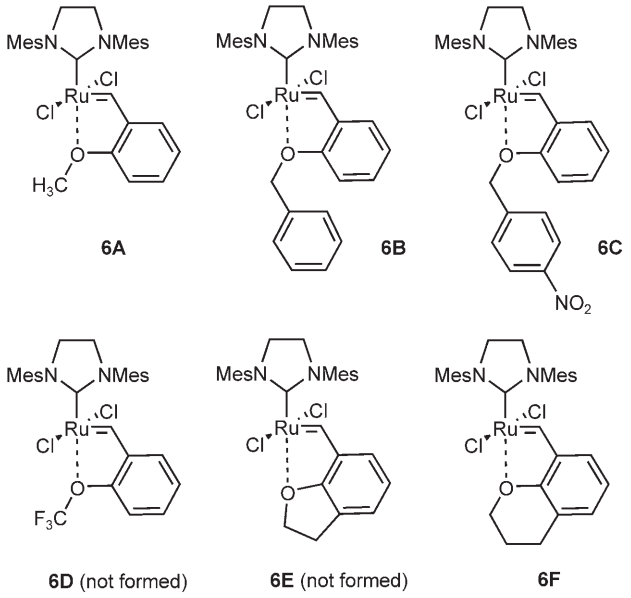
Scheme 2. Steric, electronic and structural activation strategies of the parent Hoveyda–Grubbs complex **3b**, described in the literature (**5A**,**B**) and investigated at this work (**6A–F**).

Catalyst Design

Structure-activity studies were conducted in two stages: (1) examinations of the "pure" electronic effects on the chelating OR ligand fragment of complex **3b** by the acceptor groups R (Scheme 2, top right) and (2) structural tilting of the alkoxy moiety by its incorporation into 5- and 6-membered rings (Scheme 2, bottom right).

In the design of catalysts **6A–D** (Scheme 3) based on the idea of decreasing of the OR electron density, we decided to incorporate methyl, benzyl, *p*-nitrobenzyl and trifluoromethyl substituents (R). For the initial probing of the relative effect of substituents we calculated[13,14] the isolated structures[15] of styrenes **7A–D** (Figure 1), precursors of benzylidene ligands, and compared their ESP (electrostatic potential) charges located at the oxygen atom, the approach employed by us for the examination the plethora of other ring substituted Hoveyda–Grubbs complex analogues.[16]

The resulted ESP charges (2-isopropoxystyrene, −0.381; **7A**, −0.277; **7B**, −0.248; **7C**, −0.240, **7D**, −0.333) confirmed the following order of decreasing donor properties of oxygen atom (isopropyl > methyl > benzyl > *p*-nitrobenzyl). The influence of trifluoromethyl group (**7D**) was relatively small as may be expected for its strongest electron-withdrawing character, that was manifested in substantial negative



Scheme 3. Structures of complexes **6A–F** investigated in this project.

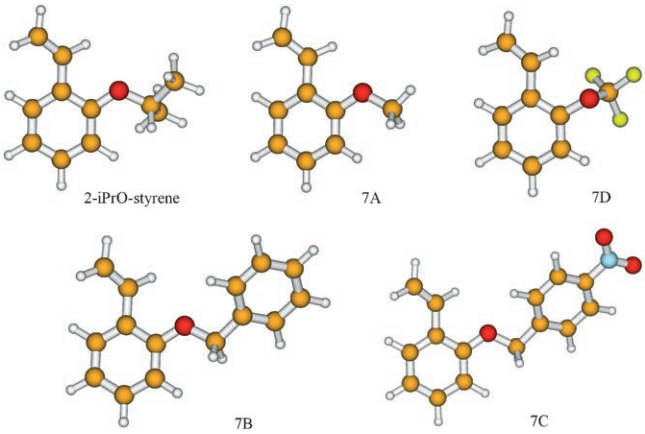


Figure 1. Structures of 2-isopropoxystyrene (ligand of **3b**) and styrenes **7A–D** (precursors of benzylidene ligands) optimised with B3LYP/6-31**.

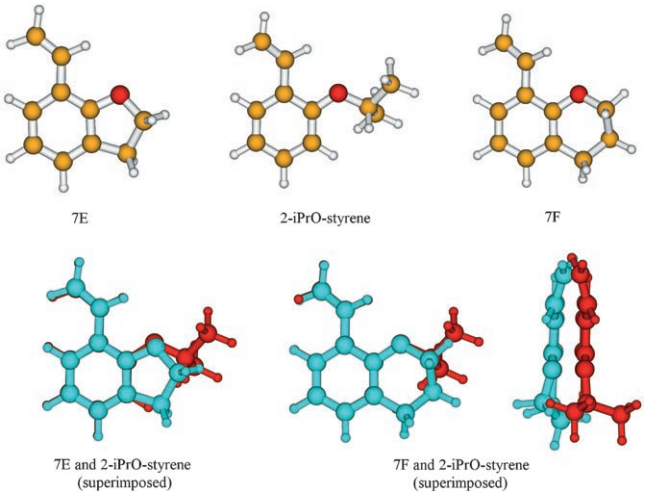


Figure 2. Structures of styrene precursor ligands (2-isopropoxystyrene, **7E** and **7F**) optimized with B3LYP/6-31** (up) and their comparative studies (bottom). Superposition of **7E** (blue) and 2-*iso*-propoxystyrene (red) accentuates the "remoteness effect" of the oxygen atom by its tilting due to the incorporation into the 5-membered ring (bottom left). Differences of key structural motifs of **7F** (blue) and 2-isopropoxystyrene (red) are much less pronounced and limited to slight out-of-plane distortion of the OR bond in **7F**, due to the conformational constraints of the 6-membered ring (bottom right).

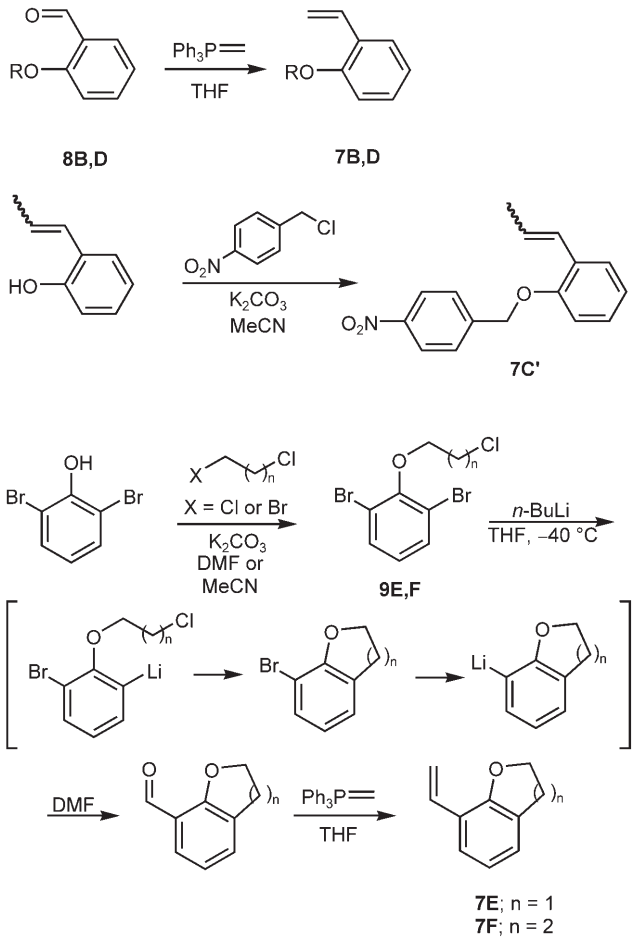
charge located at the oxygen atom within the series. This somewhat non-intuitive result was caused probably by the distinctive perpendicular conformation of the OR moiety and transfer of electron density on the way of $\pi_{arom} \rightarrow \sigma_{O\text{-}CF_3}^*$ interaction.[17,18] On the basis of the assumption that a decrease of the donor properties of oxygen activates the (pre)catalyst, we reckon that the same trend as suggested by calculations should be observed in the catalytic activity of **6A–D**.

The second strategy, less explored in the field of catalyst design and demanding a "molecular engineering" approach to the synthesis of the ligand, was based on the idea of geometrical tilting the alkoxy group away from the complexing ruthenium centre, caused by the structural constraints. As the strength of the coordination interaction can be modified by manipulation of the electronic properties and the distance between interacting centres, we recognised the second approach as promising. For simple depiction we termed this concept "remoteness effect", manifested distinctively on the coordination properties – the chelating oxygen atom is distanced away of the ruthenium centre (e.g., in structure **6E** by incorporation in 5-membered ring) without substantial modification of its electronic properties. This studies were conducted only for a small fraction of the possible structural modifications imposed by bond lengths, angles and character of the ligand skeleton. We took into consideration not only geometrical properties prompted by the imagination, but accessibility of these structures and their compliance with all catalyst structures and mechanisms of activity. The 6-membered congener **6F**, in which the O→Ru distance should not be elongated, was also studied for the purpose of comparison with the parent complex **3b** and evaluation of this concept (Figure 2).

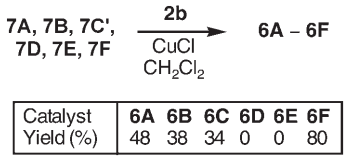
Preparation

The ligand precursor 2-vinylanisole (**7A**) was commercially available. As illustrated in Scheme 4, we used commercially available 2-alkoxybenzaldehydes **8B**, **D** as starting materials for the preparation of 2-alkoxystyrenes **7B**, **D** *via* Wittig olefination. The ligand precursor for **6C** was obtained by alkylation of 2-propenylphenol with *p*-nitrobenzyl chloride. 7-Formyl-2,3-dihydrobenzofuran **8E** was prepared from 2,6-dibromophenol in a two-step synthesis composed of alkylation with 1,3-dichloropropane and one-pot multistep Parham cyclisation[19]–DMF quenching sequence of **9E** according to the previously reported superior procedure.[20] The same conditions were used for the preparation of the 6-membered congener **8F**. (Scheme 4).[21] Wittig olefination of aldehydes **8E** and **8F** led to the formation of corresponding styrenes **7E** and **7F**.[22]

The previously optimised[7,8] exchange reaction[22] of **7A**, **7B**, **7C'** with Grubbs's carbene **2b** in the presence of CuCl used as a phosphine scavenger, followed by routine flash chromatography led to the formation of



Scheme 4. Synthesis of ligand precursors **7B**, **C′** and **D–F**.[22]



Catalyst	6A	6B	6C	6D	6E	6F
Yield (%)	48	38	34	0	0	80

Scheme 5. Preparation of the catalysts **6A–6F**.

the "RO-modified" carbenes **6A–C** as an air-stable green microcrystalline solids (34–48 % yield, Scheme 5).

The formation of the OCF_3-bearing complex **6D** and 5-membered complex **6E** was not observed under the standard reaction conditions. Unfortunately, all attempts to obtain **6D** and **6E**, either by terminating the reaction at lower conversion or by lowering the temperature, were unsuccessful. Probably, the substantial reduction of the electron density at the donor oxygen atom crosses the borderline of the stability of the complex and limits the thermodynamic force for the styrene ligand exchange process. Likewise in the case of the 5-membered styrene **6E**, chelate formation is attenuated by the excessively extended distance required for the coordination interaction.[23] To confirm this hypothesis we synthesised 6-membered analogue **6F** that, interestingly unlike other members of this series, was formed in very good isolated yield (80 %). Interesting properties of **6F** observed in further investigations showed that very subtle effects, unpredictable at the early stage, may lead to unexpected chemical behaviour.

All the synthesised compounds were stable under an air atmosphere for the time required for their preparation and purification. These complexes can be stored at room temperature in air, however, lower temperature (+4 °C) is recommended for prolonged storage (for example, **6A** and **6B** stored in refrigerator under air held their activity for over two years). Sensitivity of catalysts **6A–C** toward oxygen is generally more pronounced; for example, we observed that ~60 % of **6C** decomposed within three days when stored in a not-degassed $CDCl_3$ solution in an NMR tube at room temperature.[24] Interestingly, a solution of complex **6F** showed much higher stability, both at room temperature and 80 °C.

Structural Characterisation of the Prepared Complexes

The structures of complexes **3b**, **6A**, **6C** and **6F** have been determined[25] by the single crystal X-ray diffraction technique, in order to look for any correlations between the structural features of the complexes and their catalytic activity. In particular, we were interested in the comparison between these modified complexes and **3b** considered as a model catalyst. For the

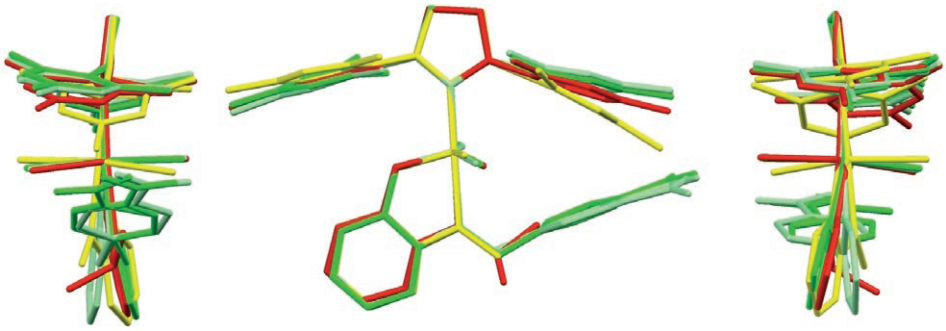


Figure 3. Superimposed X-ray structures of complexes **3b**, **6A**, **6C** using the following colour code: **3b** (red), **6A** (yellow), **6C** (green and bright-green – two molecules present in the cell).[26]

sake of better comparison of the structural parameters, the Hoveyda catalyst **3b** has also been subjected to X-ray diffraction experiment at liquid nitrogen temperature.

In the current synthetic study, compounds **6A** and **6C** represent two distinct groups of catalysts in terms of their activity and the product yields, whereas **6F** seems particularly interesting due to its very high catalytic activity and unusual chemical environment around the oxygen atom coordinating the ruthenium.

Compound **6A** crystallises in a monoclinic system, and the unit cell dimensions are very close to the parameters obtained for **3b**. The similarities in packing of these two structures follow the very close structural resemblances. Similar to the structure of **3b** and other Hoveyda–Grubbs complexes,[4,5] the ruthenium centre in **6A** is pentacoordinate, and the geometry of the ligands is very close to a square pyramid. The two chlorine atoms are *trans*-oriented in the basal plane of the square pyramid, while the other two corners of the basal square are occupied by an oxygen atom and an alkylidene carbon from the imidazolidinylidene ring, respectively. The alkylidene carbon atom resides always in the apical position.

The compounds **6C** and **6F** both crystallise in triclinic system, in the $\bar{P}1$ symmetry group. In the case of structure **6C**, which contains two independent molecules (designated **I** and **II**) in a crystallographic asymmetric unit, the main reason for the lowered symmetry is the presence of a disordered solvent molecule in the crystallographic asymmetric unit. Additionally, the *p*-nitrobenzyl moiety in the molecule **6C-I** is disordered, which may be due to the fact that there are no interactions to stabilise the moiety and there is a space for it to move in the crystal lattice. For molecule **6C-II**, the corresponding space is reduced by the presence of a solvent molecule.[26] Nevertheless, the overall geometric properties of **6C** correspond very closely to those of the other Hoveyda–Grubbs complexes characterised structurally so far, as well as to **6A** as far as the geometry of the ruthenium coordination is concerned (Figure 3).

The oxygen atom in compound **6A** shows the geometry typical for the sp^2 hybridisation type, with valence angles values close to 120 degrees similar to the values observed for the Hoveyda complex **3b**. In the case of **6C**, both independent molecules present very similar conformations, with the planarity of the oxygen atom distorted. The oxygens, as may be expected, present in both molecules a geometry closer to that of sp^3 hybridization. The *p*-nitrobenzyl moieties are oriented nearly perpendicularly to the main aromatic ring. It is worth mentioning that the aromatic rings of these moieties are in each case oriented parallel to one of the mesityl groups and the π-π interactions[27] may stabilise such a conformation.

The crystals of **6F** contain three independent molecules of the ruthenium complex (**I**, **II** and **III**) and one solvent molecule in the crystallographic asymmetric unit. The molecules **6F-I** (Figure 4) and **6F-II**

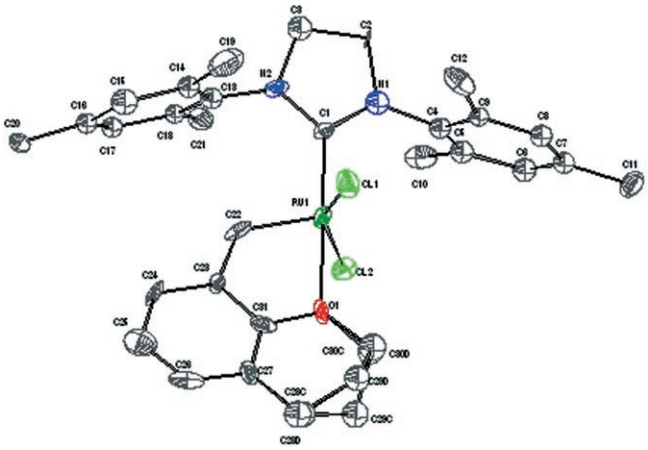


Figure 4. ORTEP representation of the complex **6F-I**. The thermal ellipsoids were drawn on the 50% probability level. Hydrogen atoms were omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Ru(1)–C(1) = 2.005(7), Ru(1)–C(22) = 1.827(7), Ru(1)–O(1) = 2.256(5), Ru(1)–Cl(1) = 2.318(2), Ru(1)–Cl(2) = 2.324(2); Cl(1)–Ru(1)–Cl(2) = 152.14(8), C(1)–Ru(1)–O(1) = 176.9(3), C(22)–Ru(1)–O(1) = 78.4(3), C(1)–Ru(1)–Cl(2) = 93.4(2), O(1)–Ru(1)–Cl(1) = 85.95(15).

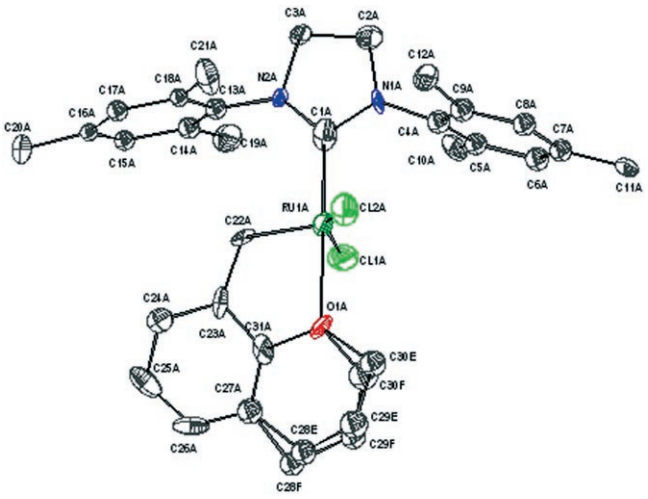


Figure 5. ORTEP representation of the complex **6F-II**. The thermal ellipsoids were drawn on the 50% probability level. Hydrogen atoms were omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Ru(1 A)–C(1 A) = 2.013(8), Ru(1 A)–C(22 A) = 1.771(7), Ru(1 A)–O(1 A) = 2.277(5), Ru(1 A)–Cl(1 A) = 2.340(3), Ru(1 A)–Cl(2 A) = 2.347(3); Cl(1 A)–Ru(1 A)–Cl(2 A) = 155.60(9), C(1 A)–Ru(1 A)–O(1 A) = 177.6(3), C(22 A)–Ru(1 A)–O(1 A) = 79.9(3), C(1 A)–Ru(1 A)–Cl(2 A) = 96.1(3), Cl(1 A)–Ru(1 A)–O(1 A) = 83.95(17).

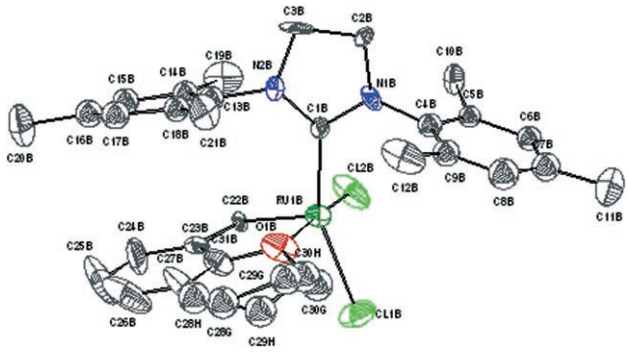


Figure 6. ORTEP representation of the complex **6F-III**. The thermal ellipsoids were drawn on the 50% probability level. Hydrogen atoms were omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Ru(1B)–C(1B) = 2.016(8), Ru(1B)–C(22B) = 1.831(7), Ru(1B)–O(1B) = 2.205(6), Ru(1B)–Cl(1B) = 2.312(3), Ru(1B)–Cl(2B) = 2.372(2); Cl(1B)–Ru(1B)–Cl(2B) = 91.01(10), C(1B)–Ru(1B)–O(1B) = 96.1(3), C(22B)–Ru(1B)–O(1B) = 80.2(3), C(1B)–Ru(1B)–Cl(1B) = 155.9(3), C(1B)–Ru(1B)–Cl(2B) = 89.6(3), Cl(1B)–Ru(1B)–O(1B) = 85.64(16).

(Figure 5) present only minor structural differences between each other and generally resemble the *trans*-dichloro coordination usual for the Hoveyda–Grubbs complexes. In the case of all the three molecules, the aliphatic fragments connected with oxygen atoms are disordered, presenting in each case two alternative conformations.

In the case of molecule **III** of compound **6F** (Figure 6), the Ru coordination scheme is changed with respect to the other molecules. The square pyramid coordination type is preserved, but the positions of the O atom and one of the chlorine atoms are switched, which results in two Cl atoms occupying the *cis* positions in the basal plane of the coordination polyhedron. As a consequence, the bicyclic moiety is oriented parallel to one of the mesityl rings and some kind of the stacking interaction may stabilise such a conformation.[27] According to the best of our knowledge this is a first example of a Hoveyda-type Ru-ether chelate possessing a *cis*-dichloro geometry.

However, the source of the unexpected behaviour of complex **6F** seems to be inconceivable for us at this stage. Related structural peculiarities of the ruthenium carbene complexes exhibiting *trans*/*cis* dichloro isomerism were precedented by Slugovc,[28] Fürstner,[29] Schrodi[30] and us[31] for oxygen and nitrogen chelates, but none of them described both isomers present in the crystal lattice. As demonstrated by recent theoretical results,[32] the equilibrium of isomers may depend on the polarity of the solvent, due to the differences of dipole moments between the forms. A brief insight into the packing of the **6F** structure suggests also that this atypical geometry may be due to the packing interactions, as the settings of the other two molecules make it impossible for **6F-III** to adopt the same conformation. Undoubtedly the inward conformational constraints governed by some chair-like character of 6-membered ring impinges planarisation of the oxygen centre and partially disturbs the π-type conjugation with the ruthenium centre. This may facilitate the breaking of O→Ru coordination and by subtle structural harmonisation also favour the *cis*-dichloro geometry of complex.[33]

The ^{1}H NMR spectrum of this compound recorded in $CDCl_3$ exhibits high symmetry usually attributed to the *trans*-dichloro geometry,[30] however, in the same spectrum a second trace benzylidene signal was present that may be assigned to the appearance of the second isomer.[34] In all activity studies we used the solid catalyst that, after dissolution in deuterated chloroform, exhibited a highly symmetrical spectrum (typical *trans*-dichloro geometry). The dynamic equilibrium that exists during the crystallisation (from DCM/EtOH mixture) may suggest, that isomerisation comprising the dissociation-isomerisation-association steps[32] is relatively fast, as may be supported by the higher activity (faster initiation, as compared with **3b**).

Some selected geometrical parameters concerning the ruthenium coordination and the neighbourhood of the coordinating oxygen atom are worth discussing in more detail.[26] It is immediately visible that the Cl–Ru and C22–Ru distances are nearly identical in the cases of all the structures. There is a considerable

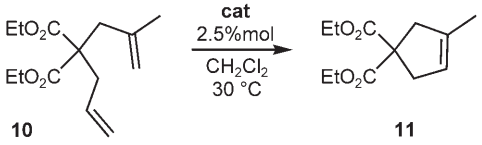
variation of the C1–Ru distance, with a maximum value for **6A** and **6F** and the minimum for **6C-I**. However, a more pronounced difference is seen between the O–Ru distance for **6F-III** (2.21 Å, considerably shorter) and all the other molecules (2.26–2.27 Å). It is therefore justified to say that the O–Ru interaction has somehow a different character for the *cis*-dichloro conformer, that can be attributed to the lack of the strongly σ-donating NHC ligand in the relative *trans* position.

The C1–Ru–O and Cl–Ru–Cl angles, which may be considered as descriptors of the accessibility of the ruthenium atom, seem to be the same for all but the **6F-III** molecule. The former angle is always close to 177°, while the latter oscillates between 156° and 158°, although for both **6F-I** and **6F-II** we observe a decrease in its value (152° and 155° accordingly). The decrease may be attributed to the disorder in the aliphatic chain next to the O atom. In the case of the structure of **6F-III**, the corresponding angles are C1–Ru–Cl1 (156°) and O–Ru–Cl2 (173°). These values are close to those observed before, but the angles with specific values appear in different planes with respect to the NHC ring. It is worth mentioning, therefore, that the access to the catalytic ruthenium centre seems to be easier in the case of the *cis*-dichloro conformation of the catalyst, even without the breaking of the crucial O–Ru bond.

Molecules **I** and **II** of compound **6F** present a geometry of the oxygen atom resembling that observed in **6C**. The hybridisation of oxygen atoms may be assumed as distorted sp^2, and the aliphatic fragment next to the oxygen atom is rather labile, as was the case in **6C** molecule **II**.

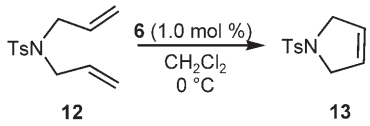
Relative Reactivity Studies

Having a panel of NHC-containing ruthenium complexes in hand, we decided to study in detail their catalytic activity. For such comparative investigations of the relative activity, we chose a model RCM reaction of diethyl 2-allyl-2-methallylmalonate **10**, leading to the formation of cyclic product **11** bearing a trisubstituted double bond (Scheme 6).[7,8] The results show that the initial rate of metathesis was markedly enhanced in the case of the benzyl- and 4-nitrobenzyl-substituted **6B** and **6C**. After 15 min the yields of **11** were 84% and 87% respectively (99% after 60 min), as opposed to 4% and 9% obtained for O-*i*-Pr- and OCH_3-substituted **3b** and **6A** (33% and 43% after 1 h). An analogous experiment was conducted with complex **6F**. Interestingly, this formed in a high yield a complex that showed similarly high activity as the more unstable **6B** and **6C** (90% after 15 min and 99% after 60 min).



Time [min]	Yield [%]				
	3b	**6A**	**6B**	**6C**	**6F**
15	9	4	82	87	90
30	22	12	93	93	95
45	34	23	95	98	99
60	43	33	97	99	99

Scheme 6. Model RCM reaction of **10**.



Scheme 7. Model RCM reaction of **12**.

To allow a more accurate comparison of the activity of potent **6B**, **6C** and **6F**, we chose a challenging RCM reaction of diene **12** at 0 °C (Scheme 7).[7,8] According to Blechert and Wakamatsu, **2b** gave only *ca.* 30% of cyclised **13** under these conditions.[6a] The results, illustrated in Figure 7, reveal that both benzylidene-type catalysts **6B**, **6C** and **6F** are significantly more reactive than **3b** (Scheme 1), confirming the hypothesis of the influence of electronic and structural stimulation on the catalytic activity.

An additional illustration of the good activity of **6C** and **6F** is given in Scheme 8 for the cyclisation of eneyne **14**,[8a] which proceeds in the presence of 1 mol% of catalyst. It should be noted, however, that the nitro-substituted Hoveyda catalyst **5B** is even more potent at 0 °C (Scheme 7 and Scheme 8).

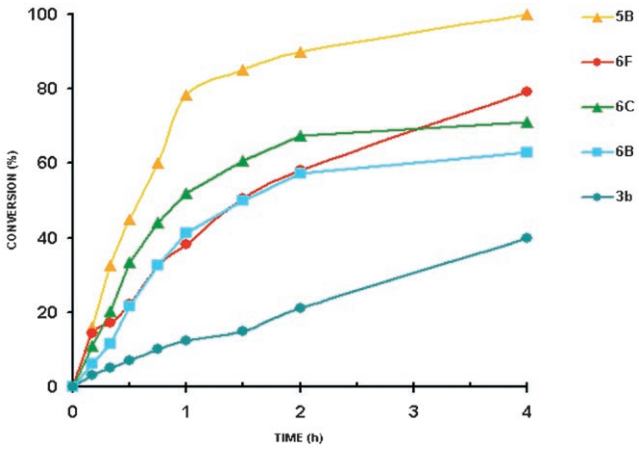
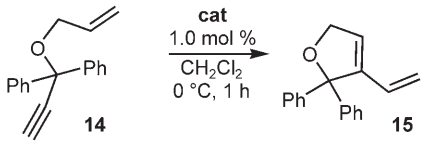
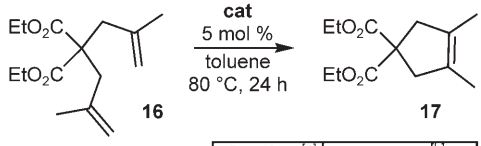


Figure 7. Plot of the reaction conversion in function of time for RCM of *N*-tosyldiallylamine (**12**), as presented at Scheme 7.



Catalyst	6B	6C	6F	5B[a]
Yield [%]	58	71	79	98

Scheme 8. Ene-yne cycloisomerization of **14**. [a] EWG = NO_2; ref.[8a]



Catalyst[a]	2b	3b	5B[b]	6F
Yield [%]	10	0	0	15

Scheme 9. Formation of tetrasubstituted double bond promoted by **2b**, **3b**, **5B** (EWG = NO_2) and **6F**. [a] Yields determined by GC. [b] 5 mol% catalyst, 40 °C, CH_2Cl_2, 24 h.

Having established the application profile of the altered Hoveyda catalysts in the formation of di- and trisubstituted C/C double bonds (Schemes 6–8), we focused our efforts on the most demanding case – the formation of tetrasubstituted C/C double bonds.[8a] As can be seen from Scheme 9, both **2b** and **6F** effected the cyclisation of malonate **16**, albeit in low yield (10–15%). Interestingly, slightly higher yields of the cyclisation of **16** have been reported by Grubbs for **2b** (31% yield, 5 mol%; 24 h in refluxing DCM; yield based on NMR)[35] and by Fürstner for **2c** (47% yield, 5 mol%; toluene, 80 °C, 24 h; GC yield).[27a]

Conclusions

Newly designed and prepared complexes **6A, 6C** and **6F** were characterised by X-ray measurements. Precatalyst **6A** possessed one and **6C** two molecules in the unit cells of slightly different structural parameters. Their geometrical properties correspond strictly to those of other structurally characterised Hoveyda–Grubbs-type complexes. Complex **6F** exhibited unprecedented structural fluxing – in the crystallographic unit cell we observed three structurally distinct molecules, two of the typical *trans*-dichloro geometry and one substantially distorted *cis*-dichloro isomer.

The results of the model reactions (Scheme 6-8) reveal that both *electronically activated* 2-benzyloxy-substituted complexes **6B** and **C** are significantly more reactive than the parent Hoveyda catalyst **3b.** Interestingly, the *structurally altered* complex **6F** shows similarly high activity as the more sensitive **6B** and **6C** while maintaining high thermal and air stability. Although the modifications outlined herewith lead to catalysts that are visibly more active than **3b**, the enhancement of reactivity is somewhat lower than that observed for sterically (**5A**) and electronically (**5B**) activated complexes. This observation has strong implications for the future catalyst design, which will be studied in more detail during our research program.

Experimental Section

General Remarks

Unless otherwise noted, all reactions were carried out under argon in pre-dried glassware using Schlenk techniques. The solvents were dried by distillation over the following drying agents and were transferred under argon: THF (K/benzophenone), toluene (Na), *n*-pentane, *n*-hexane, CH_2Cl_2 (CaH_2), Et_2O ($LiAlH_4$). Flash column chromatography: Merck silica gel 60 (230–400 mesh). NMR (^1H, ^{13}C): spectra were recorded on Bruker AVANCE 500, Varian Gemini 200 and 400 spectrometers in $CDCl_3$; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. IR: Perkin–Elmer Spectrum 2000 and 1170 FT-IR, wavenumbers in cm^{-1}. MS and HR-MS (EI, LSI-MS): AMD 604 Intectra GmbH (70 eV). MS (ESI): Mariner Perseptive Biosystems, Inc. GC analyses were conducted on an HP 6890 chromatograph with HP 5 column. Microanalyses were provided by Institute of Organic Chemistry, PAS, Warsaw. See the Supporting Information for the preparation and characterisation data for catalysts' precursors **7A**, **7B**, **7C'** and **7D–F**.

General Procedure for Preparation of Complexes 6

Styrene precursor **7** (0.120 mmol), CuCl (13 mg; 0.132 mmol) and CH_2Cl_2 (8 mL) were placed in a Schlenk flask. Afterwards carbene complex **2b** (102 mg; 0.132 mmol) was added and the resultant solution was stirred under argon at 40 °C for 20 min. From this point forth, all manipulations were carried out under air with reagent-grade solvents. The reaction mixture was concentrated under vacuum, the resultant material was dissolved in AcOEt (6 mL), the precipitate was filtered off and the solution evaporated to dryness. Finally the residue was purified by column chromatography on silica. Elution with *c*-hexane:AcOEt (9:1) removes **6** as a green band. The solvent was evaporated and product dissolved in a small amount AcOEt, then *n*-pentane was added and slowly evaporated until green crystals precipitated. The precipitate was filtered off, washed with *n*-pentane and dried under vacuum to afford complex **6** as green crystals.

Complex 6A: Isolated as a dark green microcrystalline solid; yield: 48%. ^1H NMR (500 MHz, $CDCl_3$): $\delta = 2.45$ (s, 6H), 2.50 (s, 12H), 3.90 (s, 3H), 4.18 (s, 4H), 6.86–7.00 (m, 3H), 7.11 (s, 4H), 7.50–7.58 (m, 1H), 16.57 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 292.0$, 210.7, 153.9, 144.3, 138.8, 138.7, 136.2, 129.7, 129.5, 123.3, 122.0, 111.6, 58.5, 51.7, 21.2, 19.3; IR (KBr): $\nu = 3446$, 2946, 2918, 2855, 1594, 1575, 1480, 1419, 1293, 1262, 1155, 1109, 1034, 1015, 851, 790, 746 cm^{-1}; MS (EI): m/z (rel. intensity) = 598 (36, M^+), 511 (13), 406 (19), 392 (43), 304 (100), 287 (31), 259 (8), 240

(5), 158 (30), 144 (22), 130 (17), 122 (27), 107 (24), 91 (98), 65 (26), 50 (97), 41 (22), 36 (40); HR-MS (ESI): m/z = 598.1094, calcd. for $M^{+\cdot}$ ($C_{29}H_{34}N_2O^{35}Cl_2{}^{102}Ru$): 598.1092; anal. calcd. for $C_{29}H_{34}Cl_2N_2ORu$: C 58.19, H 5.73, N 4.68, Cl 11.85, Ru 16.88; found: C 58.34, H 5.95, N 4.80, Cl 12.02, Ru 16.93. Crystals suitable for X-ray analysis were obtained by layering *n*-hexane over a solution of the catalyst in dichloromethane and allowing it to stand for a few days at room temperature.

Complex 6B: Isolated as a light green microcrystalline solid; yield: 38%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.45 (s, 6H), 2.50 (s, 12H), 4.16 (s, 4H), 5.31 (s, 2H), 6.72 (d, J = 8.3 Hz, 1H), 6.87–6.97 (m, 2H), 7.09 (s, 4H), 7.28–7.30 (m, 3H), 7.35–7.41 (m, 1H), 7.44–7.51 (m, 2H), 16.64 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 292.0, 210.3, 153.7, 144.5, 138.6, 138.5, 136.3, 135.0, 129.6, 129.5, 128.4, 128.0, 127.8, 123.3, 122.1, 113.7, 75.0, 51.8, 21.1, 19.2; IR (KBr) ν = 3005, 2949, 2916, 1591, 1574, 1477, 1451, 1416, 1398, 1293, 1262, 1208, 1156, 1107, 1035, 981, 854, 794, 747 cm^{-1}; MS (EI): m/z (rel. intensity) = 674 (2, $M^{+\cdot}$), 548 (4), 512 (4), 442 (3), 406 (9), 372 (5), 304 (22), 286 (7), 195 (20), 167 (24), 149 (43), 126 (8), 91 (100), 71 (10), 65 (10), 57 (12), 41 (7); HR-MS (ESI): m/z = 674.1375, calcd. for $M^{+\cdot}$ ($C_{35}H_{38}N_2O^{35}Cl_2{}^{102}Ru$): 674.1405; anal. calcd. for $C_{35}H_{38}Cl_2N_2ORu$: C 62.31, H 5.68, N 4.15, Cl 10.51, Ru 14.98; found: C 62.53, H 5.75, N 4.30, Cl 10.71, Ru 15.12.

Complex 6C: Isolated as a light green microcrystalline solid; yield: 34%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.40 (s, 6H), 2.42 (s, 12H), 4.09 (s, 4H), 5.33 (s, 2H), 6.71 (d, J = 8.3 Hz, 1H), 6.89–6.95 (m, 2H), 7.03 (s, 4H), 7.38–7.43 (m, 1H), 7.57–7.62 (m, 2H), 8.09 (d, J = 8.6 Hz, 2H), 16.64 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 291.9, 209.1, 153.0, 147.7, 144.3, 141.7, 138.8, 138.5, 136.3, 129.5, 129.1, 124.0, 123.6, 122.5, 113.3, 72.6, 51.8, 21.1, 21.0, 19.1; IR (KBr) ν = 3685, 3601, 2982, 2958, 2925, 2857, 1733, 1607, 1593, 1576, 1525, 1479, 1453, 1420, 1401, 1375, 1348, 1316, 1293, 1209, 1193, 1158, 1109, 1037, 1013, 937, 919, 901, 856, 793, 644, 591, 579, 558 cm^{-1}; anal. calcd. for $C_{35}H_{37}Cl_2N_3O_3Ru$: C 58.41, H 5.18, N 5.84, Cl 9.85; found: C 58.36, H 5.20, N 5.62, Cl 9.73. Crystals suitable for X-ray analysis were obtained by layering *n*-pentane over a solution of the catalyst in ethyl acetate and allowing it to stand for one day at room temperature.

Complex 6F: Isolated as a green microcrystalline solid; yield: 80%. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.97–2.07 (m, 2H), 2.41 (s, 6H), 2.46 (s, 12H), 2.81 (t, J = 6.3 Hz, 2H), 4.12 (s, 4H), 4.22 (t, J = 5.3 Hz, 2H), 6.69–6.80 (m, 2H). 7.07 (s, 4H), 7.18–7.22 (m, 1H), 16.50 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 292.4, 211.4, 149.7, 143.6, 138.8, 138.7, 136.4, 129.5, 129.4, 123.8, 122.7, 119.5, 69.6, 51.7, 23.5, 22.6, 21.2, 19.3; IR (KBr) ν = 3437, 2951, 2918, 1607, 1574, 1480, 1440, 1415, 1398, 1264, 1220, 1188, 1153, 1068, 1024, 983, 917, 852, 818, 802, 754 cm^{-1}; MS (EI): m/z (rel. intensity) = 628 (3, $M^{+\cdot}$), 627 (2), 626 (6), 625 (4), 624 (6), 623 (4), 622 (3), 552 (2), 524 (2), 405 (2), 392 (6), 307 (10), 305 (26), 304 (100), 303 (89), 301 (9), 290 (33), 289 (42), 288 (11), 275 (11), 274 (11), 260 (7), 246 (5), 245 (6), 185 (4), 160 (42), 159 (17), 158 (26), 148 (48), 145 (30), 133 (35), 132 (25), 131 (29), 120 (16), 117 (17), 115 (22), 105 (21), 104 (13), 103 (14), 92 (15), 91 (38), 78 (12), 77 (22), 65 (14), 63 (9), 53 (6), 51 (15); HR-MS (ESI): m/z = 624.1245, calcd. for $M^{+\cdot}$ ($C_{31}H_{36}N_2O^{35}Cl_2{}^{102}Ru$): 624.1248; anal. calcd. for $C_{31}H_{36}Cl_2N_2ORu$: C 59.61, H 5.81, N 4.48, Cl 11.35, Ru 16.18; found: C 59.77, H 5.96, N 4.69, Cl 11.54, Ru 16.38. Crystals suitable for X-ray analysis were obtained by slow evaporation of a dichloromethane/anhydrous ethanol solution of the catalyst for few hours at room temperature.

General Procedure for RCM

To a mixture of an alkene (1.0 mmol) in CH_2Cl_2 (50 mL, *c* 0.02 M) was added a solution of precatalyst **6** (0.01–0.05 mmol, 1–5 mol%) in CH_2Cl_2 (1 mL). The resulting mixture was stirred at 0–35 °C for 0.1–16 h. The crude product was analysed by GC. During the progress of the reaction aliquots (0.25 mL) were taken in regular intervals and quenched immediately with an ice-cold solution of ethyl vinyl ether (0.25 mL, 2 M in CH_2Cl_2) and analysed by GC. The responses of the FID detector were calibrated using *n*-nonane as an internal standard.

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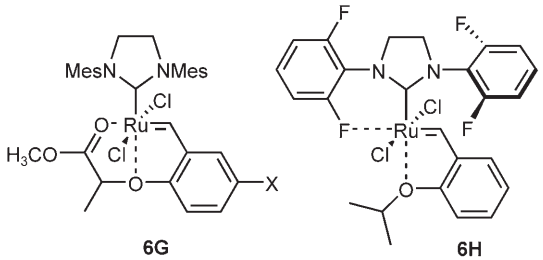

6G 6H

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[15] Taking into considerations simplified character of these calculations we decided to permanently twist the vinyl group out of the alkoxy substituent to avoid sterical congestion between them, leading to random fluctuations (twisting, distortions, etc.) within the series.

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[23] On the base of optimised rigid structures of 2-*i*-PrO-styrene and **7E** the estimated elongation of the O→Ru bond in ruthenium complex **6E** should amount to around 0.17 Å, as compared with **3b** and **6F**.
[24] For comparison of the stability and structures of methyl and isopropoxyl Hoveyda first generation catalysts, see refs.[5a,b] The similar trends in terms of the stability and catalytic activity of its NHC-substituted nitro congeners were described in ref.[8a]
[25] Crystalographic data (excluding structural factors) for the structures reported in this paper has been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition numbers: CCDC 620588 (**3b**), CCDC 620589 (**6A**), CCDC 620590 (**6C**), and CCDC 620591 (**6F**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EW, UK (Fax: (+44)-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.
[26] For independent ORTEP drawings of **3b**, **6A**, **6C**, see the Supporting Information.
[27] For similar interpretation of π-face interactions in Ru carbene complexes containing NHC ligands, see: a) A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, Ch. W. Lehmann, R. Mynott, F. Stelzer, O. R. Thiel, *Chem. Eur. J.* **2001**, *7*, 3236; b) M. Süssner, H. Plenio, *Chem. Commun.* **2005**, 5417; c) N. Ledoux, B. Allaert, S. Pattyn, H. V. Mierde, C. Vercaemst, F. Verpoort, *Chem. Eur. J.* **2006**, *12*, 4654.
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[33] Theoretical and structural studies on such O-Ru π-type conjugation are undergoing and will be published by us in the due course.
[34] The ^{1}H NMR signal of the benzylidene proton of **6F** in $CDCl_3$ appeared at $\delta = 16.50$ ppm, while a trace signal was observed at $\delta = 17.40$ ppm. In another experiment after dissolution of the sample in CD_2Cl_2 we observed a fast equilibration process, that was completed within few minutes at room temperature, giving a final composition of isomers of ~90:10 (assigned as "*trans* dichloro" to "*cis* dichloro" on the base of trend of chemical shifts for nitrogen chelate-type complexes observed for *trans*- and *cis*-dichloro isomers, respectively, see ref.[31]). Investigations of this isomerisation process will be published in due course.
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