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Studies on synthesis of quinonylidene Hoveyda-type complexes

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In a quest of redox-switchable metathesis catalysts we attempted synthesis of ruthenium quinonylidene complexes using two synthetic pathways. First, Hoveyda-type complexes bearing chelating benzylidene and naphthylidene ligands substituted with two alkoxy/hydroxy groups were synthesized and characterized. The catalysts were tested in model ring-closing metathesis reactions, and displayed interesting correlations between structure and catalytic activity. Unfortunately, numerous attempts at oxidation of the complexes to derivatives of benzo- and naphthoquinone were unsuccessful. However, the second approach, using exchange reaction of ruthenium precursor with vinylquinone ligand, gave a transient unstable product observed with ^{1}H NMR. The experimental data suggest that conjugation of electron-deficient quinones to the ruthenium centre results in intrinsically unstable species, which undergo secondary reactions under ambient conditions. Copyright © 2015 John Wiley & Sons, Ltd.

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Keywords: ruthenium; quinones; redox-switchable complexes; metathesis; catalytic activity

Introduction

Switchable catalysts[1] offer useful advantages over persistent catalytic systems, enabling control of activity and selectivity in the course of chemical transformations. In the area of olefin metathesis,[2] stimuli such as protonation,[3,4] addition of Lewis acids,[4] temperature,[5] UV irradiation[6,7] and changes of redox potential[8–11] have been demonstrated to be effective factors that may be applied to switch catalysts between the on and off states. In the latter class of complexes, for which oxidation controls the catalytic activity, structures modified with redox-active ferrocenyl group present in the *N*-heterocyclic carbene (NHC) **1a** (Fig. 1)[8] or in the chelating nitrogen ligand **1b**[9] were described. The studies were performed on the assumption that the redox process runs on the ancillary ligands,[12] and the catalytic centre of the metathesis reaction remains stable under the reaction conditions. Interestingly, oxidant additives also displayed useful effects on metathesis reactions catalysed with unmodified Grubbs and Hoveyda (**2**) complexes.[13] It was demonstrated that the presence of quinones in the reaction mixtures preserves undesired isomerizations of the olefinic products,[14] and facilitates the removal of residual ruthenium species.[10]

Following our research programme[5a,b,15] focused on the Hoveyda-type metathesis catalysts,[16] we considered chelating ligand of the complexes as a potential redox-active fragment. The benzylidene ring, incorporating two alkoxy or hydroxy substituents, can be recognized as a reduced hydroquinone form, which upon oxidation may transform into an unprecedented quinonylidene ligand (Scheme 1).[17]

In our report we present attempts at the synthesis of quinonylidene ruthenium complexes by oxidation of selected Hoveyda-type metathesis catalysts (Scheme 1, left), and ligand exchange reaction with vinylquinone (VQ; Scheme 1, right).

Results and Discussion

Synthesis of Ligands

Our studies began from the synthesis of several organic precursors derived from 1,2- and 1,4-dialkoxybenzenes, and 1,2- and 2,3-dialkoxynaphthalenes (Scheme 2, top). Compounds **3a**, **3b** and **5a–c** were synthesized from commercially available 2,5-dimethoxybenzaldehyde, *o*-vanilin and 2,3-dihydroxybenzaldehyde. Sterically demanding ligand **4** was constructed using the $AlCl_3$-catalysed Friedel–Crafts alkylation of 1,4-dimethoxybenzene with 2,5-dichloro-2,5-dimethylhexane,[18] followed by Vilsmayer formylation. Naphthalene derivatives **6** and **7** were obtained by methylation of isomeric 1,2- and 2,3-dihydroxynaphthalenes, followed by *ortho*-directed metalation and reaction with DMF.[15b] So-formed aldehydes were subjected to Wittig reagents (Me or Et) under usual conditions.[19]

Interestingly, the synthesized ligands **3–7** seem to be also valuable substrates for the preparation of VQ ligands by direct oxidation to quinones. Unfortunately, a preliminary literature search revealed that the transformation can be a difficult task.[20] In fact, preliminary screening of oxidation of the precursors revealed only formation of complicated mixtures or dark polar degradation products.[21] Fortunately, in a further synthetic attempt we succeeded in preparation of a VQ ligand **11** (Scheme 2, bottom). Starting from a commercially available naphthoquinone (**8**), reduction with a $SnCl_2$/MeOH/HCl mixture[22] followed by alkylation with CH_3I afforded 1,4-dimethoxynaphthalene (**9**). The product was formylated with

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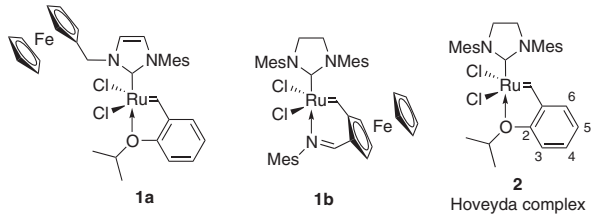
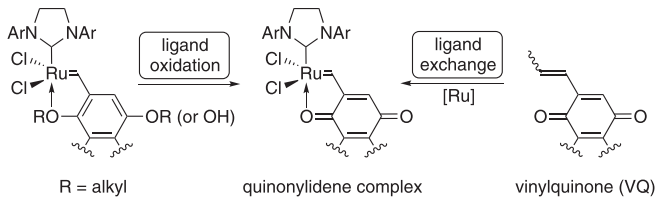
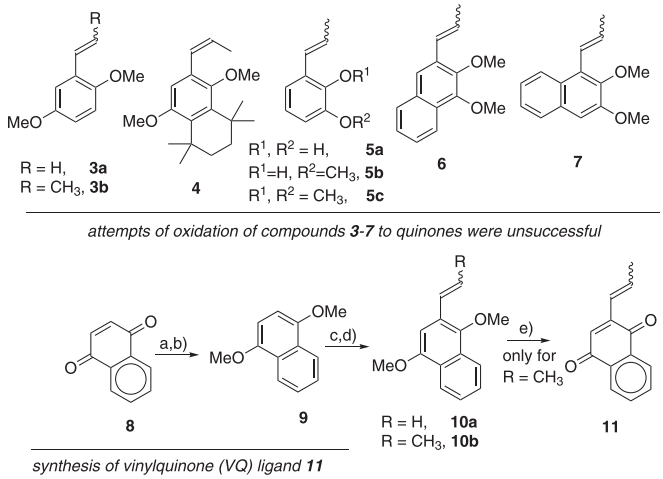


Figure 1. Selected redox-active metathesis catalysts (Mes = 2,4,6-trimethylphenyl).[8–10]



Scheme 1. Alternative syntheses of ruthenium quinonylidene complex: ligand oxidation of a substituted Hoveyda-type complex (left), and ligand exchange reaction of ruthenium precursor with vinylquinone (VQ; right). In our studies we considered derivatives of 1,2- and 1,4-dialkoxybenzene, and 1,2-, 1,4- and 2,3-dialkoxynaphthalene.



Scheme 2. Structures of alkoxyaromatic ligands **3–7** (top),[19] and synthesis of vinylquinone ligand **11** (bottom). Reagents and conditions: a) $SnCl_2 \cdot 2H_2O$, MeOH, conc. HCl_{aq}, reflux, 3 h[22]; b) CH_3I, K_2CO_3, DMF, 45 °C, 70 h, **9**, 64% over 2 steps; c) $POCl_3$, DMF, $C_2H_4Cl_2$, 80 °C, 48 h, 68%; d) $MePPh_3Br$ or $EtPPh_3Br$, *t*-PeOK, THF, 0 °C to room temperature, 30 min or 1 h, **10a**, 96%, **10b**, 95%; e) CAN, H_2O, MeCN, 0 °C to room temperature, 10 min, for R = H, product not isolated, for R = CH_3, **11**, 54%. DMF = dimethylformamide; CAN = cerium ammonium nitrate.

Vilsmayer reagent, and olefinated to two derivatives bearing vinyl (**10a**) and propenyl (**10b**) substituents. Oxidation of the latter product with a CAN/H_2O/CH_3CN mixture[22] ran selectively and gave ligand **11**, which was isolated by chromatography in moderate yield (54%).

Synthesis of Ruthenium Complexes

The synthesized ligands were used for exchange reactions with ruthenium precursors under usual conditions (CH_2Cl_2, CuCl, 40 °C).[23] As precursors we applied commercially available indenylidene ruthenium complexes with different NHC ligands: 1,3-bis(2,4,6-trimethylphenyl)imidazoline-2-ylidene (SiMes, **12a**; Fig. 2, left) and 1,3-bis(2,6-diisopropylphenyl)imidazoline-2-ylidene (SiPr, **12b**).[24] Recently, it was demonstrated that the more sterically demanding SiPr ligand offers better stabilization of ruthenium complexes, and results in more persistent catalytic species in metathesis reactions.[25]

Reaction of precursor **12b** with a derivative of 1,4-dimethoxybenzene **3b** gave complex **13** in very good yield (91%; Fig. 2, right). A similar reaction with modified tetraline ligand **4** resulted in the formation of a green-coloured mixture, which displayed a broadened resonance in the ^{1}H NMR spectrum (*ca* 16.6 ppm).[21] However, in a preparative experiment after chromatography we collected only undefined products of secondary transformations, lacking signals in the benzylidene region (15–20 ppm). In turn naphthalene ligands **6**, **7** and **10b** displayed interesting differences in reactivity depending on the arrangement of coordinating sites on the naphthalene core.[5a,15a] Reaction of **6** with precursors **12a** and **12b** gave complexes **14** (66%) and **15** (79%), respectively. Similar attempts with ligand **7** failed to give the expected products, most probably due to steric hindrance around the C = C bond in the multiply substituted aromatic system.[15b] In turn exchange reactions with **10b** were only partially successful: precursor **12b** (SiPr) led to an unstable complex **16**[26] in moderate yield (57%), while reaction with **12a** (SiMes) monitored with ^{1}H NMR revealed formation of only traces of benzylidene product (16.56 ppm), which decomposed within hours in CD_2Cl_2 at 40 °C.[21]

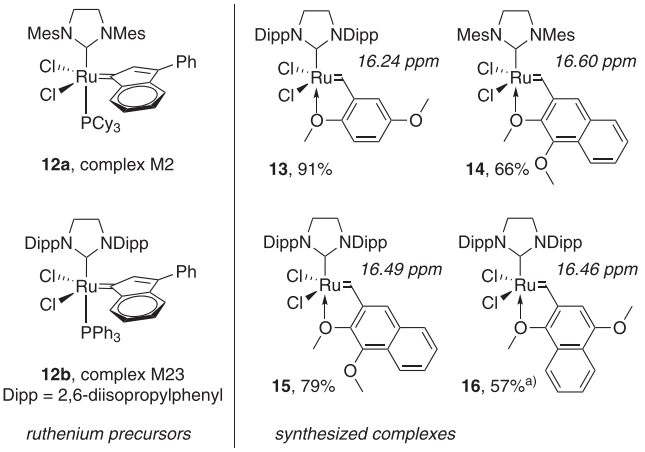
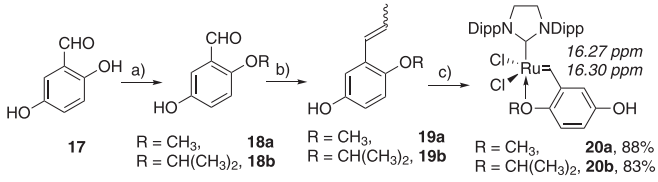


Figure 2. Indenylidene ruthenium precursors (**12a**, **12b**, left) and Hoveyda-type complexes synthesized in ligand exchange reactions (**13–16**, right). [a] Complex **16** was isolated with limited purity.



Scheme 3. Syntheses of ruthenium complexes **20a** and **20b** bearing phenolic substituents. Reagents and conditions: a) CH_3I, K_2CO_3, DMF, room temperature, 23 h, then chromatography, **18a**, 33%, or iPrBr, K_2CO_3, DMF, room temperature, 20 h, then 50 °C, 16 h, then chromatography, **18b**, 22%; b) $EtPPh_3Br$, *t*-PeOK, THF, 0 °C to room temperature, 30 min, **19a**, 83%, **19b**, 93%; c) **12b** (1.0 equiv.), **19a** or **19b** (1.2 equiv.), CuCl (1.5 equiv.), CH_2Cl_2, 40 °C, 30 min, **20a**, 88%, **20b**, 83%.

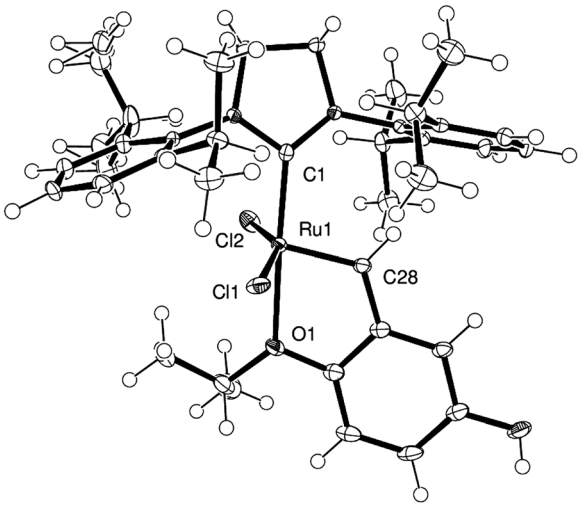


Figure 3. ORTEP[28] representation of complex **20b**, shown as displacement ellipsoids drawn at the 50% probability level. Selected bond distances (Å) and angles (°): Ru1–C1 = 1.9782(18), Ru1–C28 = 1.8273(18), Ru1–O1 = 2.2885(13), Ru1–Cl1 = 2.3411(5), Ru1–Cl2 = 2.3141(5), C1–Ru1–C28 = 99.43(8), C1–Ru1–O1 = 172.68(6), Cl1–Ru1–Cl2 = 152.37(2).

Finally, for studies of oxidation of the ruthenium complexes we prepared two more metathesis catalysts bearing one alkoxy and one hydroxy substituent in the benzylidene ring. The corresponding ligands were prepared in parallel syntheses starting from monoalkylation of 2,5-dihydroxybenzaldehyde with MeI and iPrBr, followed by the Wittig reaction. Then exchange reactions of ligands **19a** and **19b** with SiPr precursor **12b** gave complexes **20a** (OMe) and **20b** (iPrO) isolated in 88 and 83% of yield, respectively (Scheme 3).

The synthesized complexes **13–16** and **20a**,**b** were characterized with ^{1}H NMR and ^{13}C NMR, IR and HRMS.[27] In addition the detailed structure of SiPr complex **20b** was obtained from X-ray studies. Key parameters of the structure were consistent with data of similar complexes described in the literature (Fig. 3).

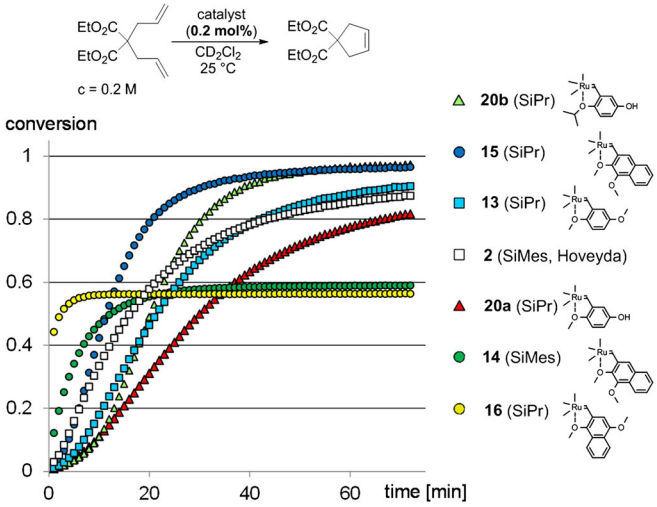


Figure 4. Reaction profiles of RCM of DEDAM determined using ^{1}H NMR spectroscopy (0.2 M concentration of substrate, 25 °C, CD_2Cl_2) with 0.2 mol % of the catalyst.[32]

Activity Studies

In the next step we tested the synthesized catalysts in model ring-closing metathesis (RCM) reactions of diethyldiallylmalonate (DEDAM) using standard conditions (0.2 M of substrate with 0.2 mol% of catalyst in CD_2Cl_2 at 25 °C), and monitored their conversions with ^{1}H NMR spectroscopy.[15b] The results are presented in Figure 4.

The obtained data revealed interesting correlations:

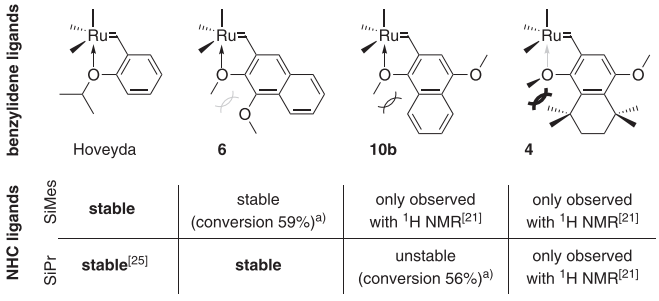
(1) Complex **20a**, bearing an OMe coordination site and free hydroxyl group attached to position 5 of the benzylidene ring (cf. Fig. 1), was less active than **13**, an analogue with two methoxy substituents. In general the difference agrees with the electronic control of activity of the Hoveyda-type complexes,[29] and the effect of substituents expressed with the Hammett parameters (σ_p),[30] where the OH group is a more powerful electron donor than OMe (−0.37 versus −0.27).[31]

(2) Faster product accumulation for catalyst **20b** with OiPr coordinating site as compared with **20a** (OMe) seems to be puzzling in the light of experimental results of Plenio and co-workers, where the opposite trend was observed for SiMes complexes.[31a] One can speculate that more bulky SiPr ligand causes a severe barrier to substrate approach in the initiation step[33] and thus a dissociative mechanism of initiation predominates. As a consequence complex **20b** with bulkier OiPr group initiates faster, due to destabilization of the chelate ring.

(3) In turn, the behaviour of naphthalene complexes **14–16** can be attributed to the spectrum of steric activation, caused by the repulsion of etheral coordinating site with adjacent substituents of the benzylidene ring. The effect, first demonstrated by Blechert and co-workers[34] and quantified by Percy and co-workers,[25] arises from out-of-plane distortion of the alkoxy substituent that weakens the O → Ru bond and accelerates the initiation process. As steric hindrance increases for a series of ligands, the destabilization reaches the limit required for complex isolation, as displayed by **4** (Scheme 4). At the same time the presence of sterically demanding NHC ligand (SiPr) acts in the opposite direction, stabilizing the complexes, and interplay of both factors controls activity profiles of the metathesis catalysts.[25,35]

Attempts at Synthesis of Quinonylidene Complexes

In the following we focused on the synthesis of ruthenium quinonylidenes, starting from attempts at oxidation of the synthesized Hoveyda-type complexes **13–16** and **20a**,**b**. In the



Scheme 4. Properties of Hoveyda-type complexes as a function of structure of benzylidene and NHC ligands.[25] a) Numbers in parentheses describe maximum conversions of DEDAM substrate (Fig. 4), when the catalysts are deactivated.

reactions we tested the following oxidants: CAN, Fremy's salt (potassium nitrosodisulfonate), DDQ (2,3-dichloro-5,6-dicyanoquinone), chloranil (1,4-tetrachloroquinone), and for hydroxy-substituted complexes **20a**,**b** also PCC (pyridinium chlorochromate), and Dess–Martin periodinane.[21,36] Unfortunately, all of the reactions ran non-selectively, and partial or complete decomposition of substrates occurred, detected as a disappearance of resonance in the benzylidene region of ^{1}H NMR spectrum (15–20 ppm). Although in some cases we observed trace amounts of unidentified species, their transitory character discouraged us from attempts of isolation on a preparative scale.

Finally, we attempted alternative syntheses of quinonylidene complexes in exchange reactions of SiPr precursor **12b** with VQ ligand **11**. The experiments were performed under protective atmosphere, and a variety of conditions were tested. In most cases the mixtures turned dark red violet within minutes after combining the reagents, and TLC analyses revealed the presence of less polar orange substances (mainly substrates, *c*-hexane:ethyl acetate 6:1, $R_f \geq 0.5$), accompanied by a very polar red violet spot (*c*-hexane: ethyl acetate 6:1, $R_f = 0$; ethyl acetate, $R_f \approx 0.3$). The latter product was isolated by column chromatography giving a dark red violet coloration of the collected fractions, and a dark glassy solid after evaporation. To our surprise ^{1}H NMR analyses of the substance revealed no signals in the benzylidene region, and only few broadened resonances corresponding to aromatic and aliphatic fragments.[21] In the same way a long-accumulated ^{13}C NMR spectrum was poor, suggesting a structure of oligomers, or paramagnetic species. To shed more light on the process we repeated the ligand exchange reaction in an NMR tube and monitored it using ^{1}H NMR spectroscopy (Fig. 5; Scheme 5, top).

Interestingly, in the spectrum we observed a large signal at 16.71 ppm (s, 1H), which slowly decayed with the formation of a minor resonance at 16.55 ppm. At the same time in the aliphatic region (corresponding to structure of the NHC ligand) other resonances observed at 4.20 (s, 4H), 3.54 (sept, $J = 6.8$ Hz, 4H) and 1.27 ppm (d, $J = 6.8$ Hz, 24H) decreased in a parallel manner, with the formation of only minor amounts of secondary by-products.[21] Although the exact structure of the major kinetic product was not determined, it is reasonable to assign it as the quinonylidene complex **21**. Fast accumulation of the intermediate under the reaction conditions (observed at first acquisition after combining of the

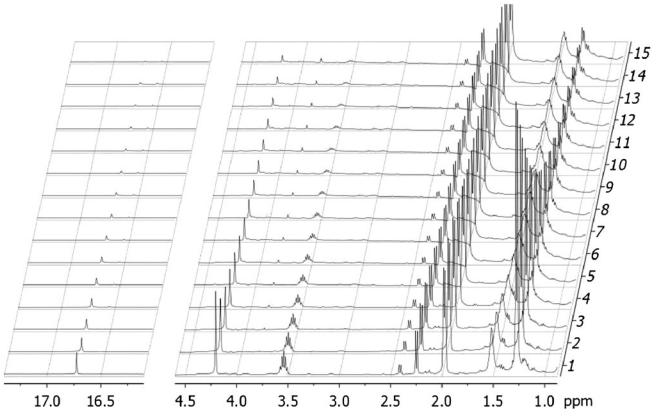
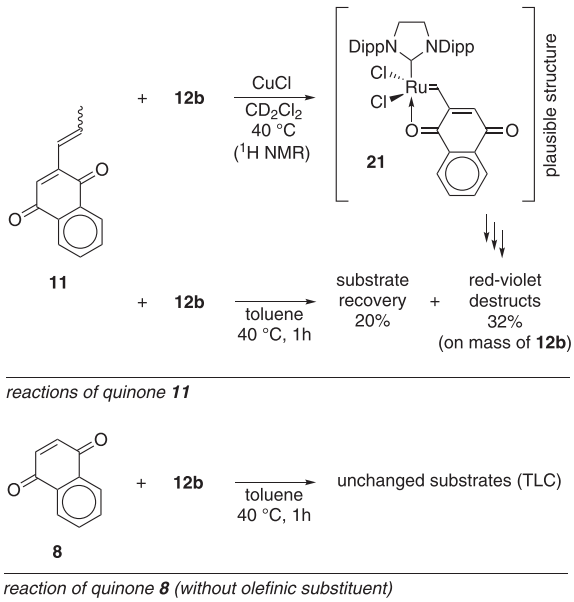


Figure 5. ^{1}H NMR studies of an exchange reaction between quinone ligand **11** and ruthenium precursor **12b** (SiPr). The array experiment was conducted in CD_2Cl_2 with CuCl catalyst at 40 °C, and the acquisitions 1–15 were repeated in 10 min intervals. Horizontal scale on both insets is given in ppm.



Scheme 5. Results of reactions between ruthenium precursor **12b** (SiPr) and VQ ligand **11** (top) and 1,4-naphthoquinone (**8**; bottom).

substrates), simplified pattern in the aliphatic region of the spectrum, consistent with symmetric *trans*-Cl_2 geometry of the product (considering a *cis*-Cl_2 geometry of the starting **12b**), and the chemical shift of resonance attributed to the Ru=C*H* group (deshielded *ca* +0.4 ppm as compared with other SiPr Hoveyda-type complexes) support the hypothesis. However, at the same time the structure seemed to be intrinsically unstable, and vanished within hours giving only minor amounts of isomerized or rearranged products observed with ^{1}H NMR.

Additional support for the idea was obtained from studies of reaction between ruthenium precursor **12b** and unsubstituted naphthoquinone **8** (Scheme 5, bottom). In contrast to the reactivity of VQ ligand **11**, naphthoquinone **8** failed to react with **12b** in a toluene solution (40 °C, 1 h).[37] From the result we suppose that reaction with **11** most likely begins from metathesis of the olefinic fragment, following a common mechanism of synthesis of the Hoveyda-type complexes. Unfortunately, direct conjugation of quinone to the ruthenium centre manifests in destabilization of the resulting structure[38] plausibly by weakening of the Ru···O interaction,[29,39] or an intramolecular redox process giving paramagnetic Ru(III) species.[40]

Conclusions

We synthesized a set of chelating Hoveyda-type ligands derived from 1,2- and 1,4-dialkoxybenzene, and 1,2-, 1,4- and 2,3-dialkoxynaphthalene (**3–7** and **10**). First, the organic precursors were subjected to different oxidants to transform into VQs. The attempts succeeded in CAN oxidation of **10b** to afford **11**. In the next step dialkoxyligands **3–7** and **10** were used for exchange reactions with indenylidene ruthenium precursors **12a**,**b** (SiMes and SiPr, respectively). We observed that ligands that display pronounced steric hindrance around the olefinic group (**4**) or etheral coordinating site (**7**) fail to react, or destabilize the resulting chelates. However, less sterically demanding substrates resulted in the formation of ruthenium Hoveyda-type complexes **13–16**. Analogously we

synthesized two other ruthenium benzylidenes bearing phenolic substituent in position 5 of the benzylidene ring (**20a**,**b**). All of the catalysts were tested in model RCM reactions, and revealed correlations of activities with electronic and steric effects of the substituents. Attempts at oxidative transformations of the complexes to ruthenium quinonylidenes failed, leading mainly to decompositions. However, ^{1}H NMR studies of exchange reaction between VQ ligand **11** and SiPr complex **12b** revealed formation of transient complex assigned to the ruthenium quinonylidene **21**. Under ambient conditions the product underwent secondary reactions, giving polar red violet destructs. We suspect that the intrinsic instability of ruthenium quinonylidene derives from destabilization of the chelate ring, or intramolecular redox processes, which leads to paramagnetic Ru(III) species.

Experimental Section

Text and figures giving NMR spectra and experimental procedures for the syntheses of **3–7**, **9–11**, **13–16** and **18–20** are available in the supporting information. CCDC-1026979 (complex **20b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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