Supplementary Material: Self-metathesis of Methyl oleate using Ru-NHC complexes: A kinetic study

Marc Renom Carrasco, Clémence Nikitine, Mohamed Hamou, Claude de Bellefon, Chloé Thieuleux and Valérie Meille

1. Materials and methods

Materials:

Methyl oleate and methyl elaidate (purchased from Nu-Check Prep, Inc.). Purification: 30 ml of substrate were placed in a Schlenk and degassed by freeze-pump until no more gas evolution was observed. The Schlenk was placed inside the glovebox and 6 g of Selexsorb® CD (activated at 250°C, 10^{-6} mbar, 16 h) were added and kept inside without stirring for 4 hours in the absence of light. Then, the Selexsorb® CD was removed and 7 g of alumina (activated at 250 °C, 10^{-6} mbar, 16 h) were added. The mixture was stirred for 3 days in the absence of light. Finally, the substrate was filtered to remove the alumina and stored in the glovebox freezer. Before each reaction, the amount of substrate needed was filtered through a short pad of activated alumina.
Methyl heptadecanoate (purchased from Sigma-Aldrich). Purification: Distilled under vacuum, degassed and stored in the glovebox.
Dichloromethane: distilled over CaH_2 and degassed by freeze-pump.
Ethyl vinyl ether was purchased from Sigma-Aldrich.
G-II, **HG-II** and **HG-SIPr** were purchased from Sigma-Alrdich. **HG-IMes** was prepared as described by Merino *et al.*[1]
M71-SIMes, **M71-SIPr** and **M73-SIMes** were supplied by Umicore.

General Procedure for the Kinetic Study:

All catalytic tests were carried out inside a glovebox filled with argon. ca. 1.50 g of substrate and 150 mg of methyl heptadecanoate (internal standard) were weighed inside a 5 ml vial. The vial was capped with a septum and the mixture was stirred in a sand bath at 40 °C for 20 min. Then, 20 µl of a stock solution of the catalyst in DCM (the concentration was adjusted depending on the desired substrate/catalyst ratio) was added and the reaction mixture was stirred at 40 °C and at 1000 rpm. The metathesis reaction was monitored by sampling through the septum at suitable intervals, and each aliquot was immediately quenched by an excess of ethyl vinyl ether placed in a capped GC vial. Samples were analyzed by GC on an Agilent 7890A equipped with a FID detector and DB23 column (50 m × 0.25 mm). Oven program: 80 °C (5 min), 10 °C/min, 150 °C (5 min), 10 °C/min, 250 °C (11 min). Retention times (min), see *Figure S1*: 18.2 (*E*-9-octadecene), 18.3 (*Z*-9-octadecene), 25.3 (methyl heptadecanoate), 26.4 (methyl elaidate), 26.5 (methyl oleate), 33.3 (dimethyl *E*-9-octadecene-1,18-dioate), 33.5 (dimethyl *Z*-9-octadecene-1,18-dioate).

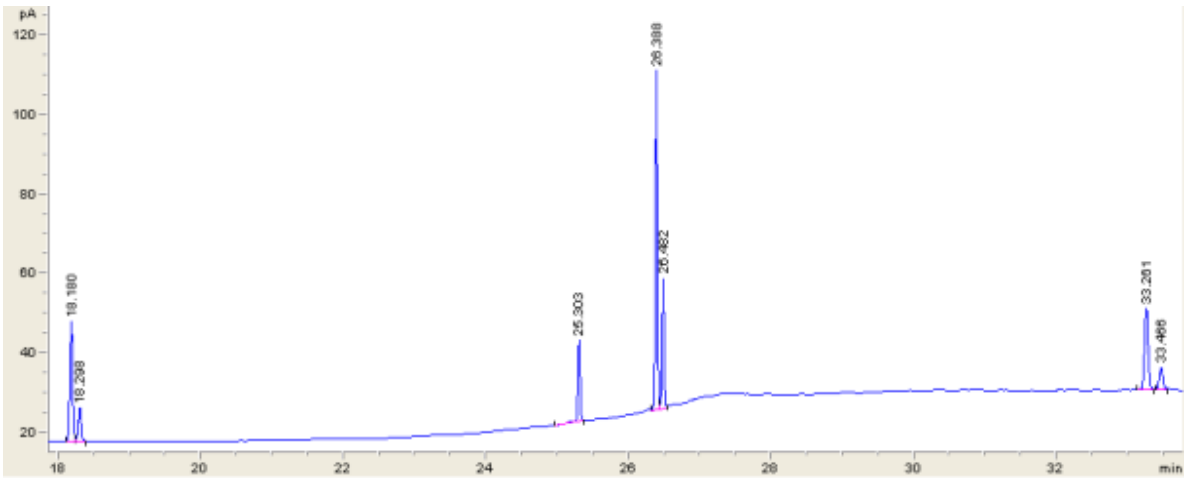

Figure S1. Representative gas chromatogram obtained during methyl oleate metathesis

2. Enumeration of All Possible Reactions

Compared to the main document, the precatalyst species $LL'Cl_2RuR'$ was named RuR' here for clarity. Moreover, as the following enumeration was performed before analyzing the possible simplifications of the kinetic model, different initiation constants have been considered:

$k_{init\ EE}$, $k_{init\ EZ}$, $k_{init\ ZE}$, $k_{init\ ZZ}$. They appear under the unique parameter k_{init} in the main text.

Here, to distinguish between initiation, propagation and regeneration constants, the term "init", "prop" or "rege" was added in the parameters. This distinction is useless in the main text since k_{init} is unique and k_{rege} has been neglected. Thus the only constants that distinguish the Z/E configuration are the propagation ones in the main document and the term "prop" was thus useless because there was no possible confusion.

Step	Equation nb	Equation	Rate
Initiation	1	RuR' + ABZ → RuA + R'BZ	$r_{init} = k_{init\ ZZ} . [RuR'].[ABZ]$
	2	RuR' + ABZ → RuA + R'BE	$r_{init} = k_{init\ ZE} . [RuR'].[ABZ]$
	3	RuR' + ABZ → RuB + R'AZ	$r_{init} = k_{init\ ZZ} . [RuR'].[ABZ]$
	4	RuR' + ABZ → RuB + R'AE	$r_{init} = k_{init\ ZE} . [RuR'].[ABZ]$
	5	RuR' + ABE → RuA + R'BZ	$r_{init} = k_{init\ EZ} . [RuR'].[ABE]$
	6	RuR' + ABE → RuA + R'BE	$r_{init} = k_{init\ EE} . [RuR'].[ABE]$
	7	RuR' + ABE → RuB + R'AZ	$r_{init} = k_{init\ EZ} . [RuR'].[ABE]$
	8	RuR' + ABE → RuB + R'AE	$r_{init} = k_{init\ EE} . [RuR'].[ABE]$
	9	RuR' + AAZ → RuA + R'AZ	$r_{init} = k_{init\ ZZ} . [RuR'].[AAZ]$
	10	RuR' + AAZ → RuA + R'AE	$r_{init} = k_{init\ ZE} . [RuR'].[AAZ]$
	11	RuR' + AAZ → RuA + R'AZ	$r_{init} = k_{init\ ZZ} . [RuR'].[AAZ]$
	12	RuR' + AAZ → RuA + R'AE	$r_{init} = k_{init\ ZE} . [RuR'].[AAZ]$

	13	RuR' + AAE → RuA + R'AZ	$r_{init} = k_{init\ EZ} . [RuR'].[AAE]$
	14	RuR' + AAE → RuA + R'AE	$r_{init} = k_{init\ EE} . [RuR'].[AAE]$
	15	RuR' + AAE → RuA + R'AZ	$r_{init} = k_{init\ EZ} . [RuR'].[AAE]$
	16	RuR' + AAE → RuA + R'AE	$r_{init} = k_{init\ EE} . [RuR'].[AAE]$
	17	RuR' + BBZ → RuB + R'BZ	$r_{init} = k_{init\ ZZ} . [RuR'].[BBZ]$
	18	RuR' + BBZ → RuB + R'BE	$r_{init} = k_{init\ ZE} . [RuR'].[BBZ]$
	19	RuR' + BBZ → RuB + R'BZ	$r_{init} = k_{init\ ZZ} . [RuR'].[BBZ]$
	20	RuR' + BBZ → RuB + R'BE	$r_{init} = k_{init\ ZE} . [RuR'].[BBZ]$
	21	RuR' + BBE → RuB + R'BZ	$r_{init} = k_{init\ EZ} . [RuR'].[BBE]$
	22	RuR' + BBE → RuB + R'BE	$r_{init} = k_{init\ EE} . [RuR'].[BBE]$
	23	RuR' + BBE → RuB + R'BZ	$r_{init} = k_{init\ EZ} . [RuR'].[BBE]$
	24	RuR' + BBE → RuB + R'BE	$r_{init} = k_{init\ EE} . [RuR'].[BBE]$
	1	RuA + ABZ → RuA + ABZ	$r_{prop} = k_{prop\ ZZ} . [RuA].[ABZ]$
	2	RuA + ABZ → RuA + ABE	$r_{prop} = k_{prop\ ZE} . [RuA].[ABZ]$
	3	RuA + ABZ → RuB + AAZ	$r_{prop} = k_{prop\ ZZ} . [RuA].[ABZ]$
	4	RuA + ABZ → RuB + AAE	$r_{prop} = k_{prop\ ZE} . [RuA].[ABZ]$
	5	RuB + ABZ → RuA + BBZ	$r_{prop} = k_{prop\ ZZ} . [RuB].[ABZ]$
	6	RuB + ABZ → RuA + BBE	$r_{prop} = k_{prop\ ZE} . [RuB].[ABZ]$
	7	RuB + ABZ → RuB + ABZ	$r_{prop} = k_{prop\ ZZ} . [RuB].[ABZ]$
	8	RuB + ABZ → RuB + ABE	$r_{prop} = k_{prop\ ZE} . [RuB].[ABZ]$
Propagation	9	RuA + ABE → RuA + ABE	$r_{prop} = k_{prop\ EE} . [RuA].[ABE]$
	10	RuA + ABE → RuA + ABZ	$r_{prop} = k_{prop\ EZ} . [RuA].[ABE]$
	11	RuA + ABE → RuB + AAE	$r_{prop} = k_{prop\ EE} . [RuA].[ABE]$
	12	RuA + ABE → RuB + AAZ	$r_{prop} = k_{prop\ EZ} . [RuA].[ABE]$
	13	RuB + ABE → RuA + BBE	$r_{prop} = k_{prop\ EE} . [RuB].[ABE]$
	14	RuB + ABE → RuA + BBZ	$r_{prop} = k_{prop\ EZ} . [RuB].[ABE]$
	15	RuB + ABE → RuB + ABE	$r_{prop} = k_{prop\ EE} . [RuB].[ABE]$
	16	RuB + ABE → RuB + ABZ	$r_{prop} = k_{prop\ EZ} . [RuB].[ABE]$
	17	RuA + AAZ → RuA + AAZ	$r_{prop} = k_{prop\ ZZ} . [RuA].[AAZ]$

18	RuA + AAZ → RuA + AAE	$r_{prop} = k_{prop\ ZE} . [RuA].[AAZ]$
19	RuA + AAZ → RuA + AAZ	$r_{prop} = k_{prop\ ZZ} . [RuA].[AAZ]$
20	RuA + AAZ → RuA + AAE	$r_{prop} = k_{prop\ ZE} . [RuA].[AAZ]$
21	RuB + AAZ → RuA + ABZ	$r_{prop} = k_{prop\ ZZ} . [RuB].[AAZ]$
22	RuB + AAZ → RuA + ABE	$r_{prop} = k_{prop\ ZE} . [RuB].[AAZ]$
23	RuB + AAZ → RuA + ABZ	$r_{prop} = k_{prop\ ZZ} . [RuB].[AAZ]$
24	RuB + AAZ → RuA + ABE	$r_{prop} = k_{prop\ ZE} . [RuB].[AAZ]$
25	RuA + AAE → RuA + AAE	$r_{prop} = k_{prop\ EE} . [RuA].[AAE]$
26	RuA + AAE → RuA + AAZ	$r_{prop} = k_{prop\ EZ} . [RuA].[AAE]$
27	RuA + AAE → RuA + AAE	$r_{prop} = k_{prop\ EE} . [RuA].[AAE]$
28	RuA + AAE → RuA + AAZ	$r_{prop} = k_{prop\ EZ} . [RuA].[AAE]$
29	RuB + AAE → RuA + ABE	$r_{prop} = k_{prop\ EE} . [RuB].[AAE]$
30	RuB + AAE → RuA + ABZ	$r_{prop} = k_{prop\ EZ} . [RuB].[AAE]$
31	RuB + AAE → RuA + ABE	$r_{prop} = k_{prop\ EE} . [RuB].[AAE]$
32	RuB + AAE → RuA + ABZ	$r_{prop} = k_{prop\ EZ} . [RuB].[AAE]$
33	RuA + BBZ → RuB + ABZ	$r_{prop} = k_{prop\ ZZ} . [RuA].[BBZ]$
34	RuA + BBZ → RuB + ABE	$r_{prop} = k_{prop\ ZE} . [RuA].[BBZ]$
35	RuA + BBZ → RuB + ABZ	$r_{prop} = k_{prop\ ZZ} . [RuA].[BBZ]$
36	RuA + BBZ → RuB + ABE	$r_{prop} = k_{prop\ ZE} . [RuA].[BBZ]$
37	RuB + BBZ → RuB + BBZ	$r_{prop} = k_{prop\ ZZ} . [RuB].[BBZ]$
38	RuB + BBZ → RuB + BBE	$r_{prop} = k_{prop\ ZE} . [RuB].[BBZ]$
39	RuB + BBZ → RuB + BBZ	$r_{prop} = k_{prop\ ZZ} . [RuB].[BBZ]$
40	RuB + BBZ → RuB + BBE	$r_{prop} = k_{prop\ ZE} . [RuB].[BBZ]$
41	RuA + BBE → RuB + ABE	$r_{prop} = k_{prop\ ZZ} . [RuA].[BBE]$
42	RuA + BBE → RuB + ABZ	$r_{prop} = k_{prop\ EZ} . [RuA].[BBE]$
43	RuA + BBE → RuB + ABE	$r_{prop} = k_{prop\ EE} . [RuA].[BBE]$
44	RuA + BBE → RuB + ABZ	$r_{prop} = k_{prop\ EZ} . [RuA].[BBE]$
45	RuB + BBE → RuB + BBE	$r_{prop} = k_{prop\ EE} . [RuB].[BBE]$
46	RuB + BBE → RuB + BBZ	$r_{prop} = k_{prop\ EZ} . [RuB].[BBE]$

	47	RuB + BBE → RuB + BBE	$r_{prop} = k_{prop\ EE} . [RuB].[BBE]$
	48	RuB + BBE → RuB + BBZ	$r_{prop} = k_{prop\ EZ} . [RuB].[BBE]$
Regeneration	1	RuA + LBZ → RuL + ABZ	$r_{rege} = k_{rege\ ZZ} . [RuA].[LBZ]$
	2	RuA + LBE → RuL + ABZ	$r_{rege} = k_{rege\ EZ} . [RuA].[LBE]$
	3	RuB + LAZ → RuL + ABZ	$r_{rege} = k_{rege\ ZZ} . [RuB].[LAZ]$
	4	RuB + LAE → RuL + ABZ	$r_{rege} = k_{rege\ EZ} . [RuB].[LAE]$
	5	RuA + LBZ → RuL + ABE	$r_{rege} = k_{rege\ ZE} . [RuA].[LBZ]$
	6	RuA + LBE → RuL + ABE	$r_{rege} = k_{rege\ EE} . [RuA].[LBE]$
	7	RuB + LAZ → RuL + ABE	$r_{rege} = k_{rege\ ZE} . [RuB].[LAZ]$
	8	RuB + LAE → RuL + ABE	$r_{rege} = k_{rege\ EE} . [RuB].[LAE]$
	9	RuA + LAZ → RuL + AAZ	$r_{rege} = k_{rege\ ZZ} . [RuA].[LAZ]$
	10	RuA + LAE → RuL + AAZ	$r_{rege} = k_{rege\ EZ} . [RuA].[LAE]$
	11	RuA + LAZ → RuL + AAZ	$r_{rege} = k_{rege\ ZZ} . [RuA].[LAZ]$
	12	RuA + LAE → RuL + AAZ	$r_{rege} = k_{rege\ EZ} . [RuA].[LAE]$
	13	RuA + LAZ → RuL + AAE	$r_{rege} = k_{rege\ ZE} . [RuA].[LAZ]$
	14	RuA + LAE → RuL + AAE	$r_{rege} = k_{rege\ EE} . [RuA].[LAE]$
	15	RuA + LAZ → RuL + AAE	$r_{rege} = k_{rege\ ZE} . [RuA].[LAZ]$
	16	RuA + LAE → RuL + AAE	$r_{rege} = k_{rege\ EE} . [RuA].[LAE]$
	17	RuB + LBZ → RuL + BBZ	$r_{rege} = k_{rege\ ZZ} . [RuB].[LBZ]$
	18	RuB + LBE → RuL + BBZ	$r_{rege} = k_{rege\ EZ} . [RuB].[LBE]$
	19	RuB + LBZ → RuL + BBZ	$r_{rege} = k_{rege\ ZZ} . [RuB].[LBZ]$
	20	RuB + LBE → RuL + BBZ	$r_{rege} = k_{rege\ EZ} . [RuB].[LBE]$
	21	RuB + LBZ → RuL + BBE	$r_{rege} = k_{rege\ ZE} . [RuB].[LBZ]$
	22	RuB + LBE → RuL + BBE	$r_{rege} = k_{rege\ EE} . [RuB].[LBE]$
	23	RuB + LBZ → RuL + BBE	$r_{rege} = k_{rege\ ZE} . [RuB].[LBZ]$
	24	RuB + LBE → RuL + BBE	$r_{rege} = k_{rege\ EE} . [RuB].[LBE]$

Propagation rates

$$R_{ABZ} = -(r_1^{pro} + r_2^{pro} + r_3^{pro} + r_4^{pro} + r_5^{pro} + r_6^{pro} + r_7^{pro} + r_8^{pro}) + (r_1^{pro} + r_7^{pro} + r_{10}^{pro} + r_{16}^{pro} + r_{21}^{pro} + r_{23}^{pro} + r_{30}^{pro} + r_{32}^{pro} + r_{33}^{pro} + r_{35}^{pro} + r_{42}^{pro} + r_{44}^{pro})$$

$$R_{ABE} = -(r_9^{pro} + r_{10}^{pro} + r_{11}^{pro} + r_{12}^{pro} + r_{13}^{pro} + r_{14}^{pro} + r_{15}^{pro} + r_{16}^{pro}) + (r_2^{pro} + r_8^{pro} + r_9^{pro} + r_{15}^{pro} + r_{22}^{pro} + r_{24}^{pro} + r_{29}^{pro} + r_{31}^{pro} + r_{34}^{pro} + r_{36}^{pro} + r_{41}^{pro} + r_{43}^{pro})$$

$$R_{AAZ} = -(r_{17}^{pro} + r_{18}^{pro} + r_{19}^{pro} + r_{20}^{pro} + r_{21}^{pro} + r_{22}^{pro} + r_{23}^{pro} + r_{24}^{pro}) + (r_3^{pro} + r_{12}^{pro} + r_{17}^{pro} + r_{19}^{pro} + r_{26}^{pro} + r_{28}^{pro})$$

$$R_{AAE} = -(r_{25}^{pro} + r_{26}^{pro} + r_{27}^{pro} + r_{28}^{pro} + r_{29}^{pro} + r_{30}^{pro} + r_{31}^{pro} + r_{32}^{pro}) + (r_4^{pro} + r_{11}^{pro} + r_{18}^{pro} + r_{20}^{pro} + r_{25}^{pro} + r_{27}^{pro})$$

$$R_{BBZ} = -(r_{33}^{pro} + r_{34}^{pro} + r_{35}^{pro} + r_{36}^{pro} + r_{37}^{pro} + r_{38}^{pro} + r_{39}^{pro} + r_{40}^{pro}) + (r_5^{pro} + r_{14}^{pro} + r_{37}^{pro} + r_{39}^{pro} + r_{46}^{pro} + r_{48}^{pro})$$

$$R_{BBE} = -(r_{41}^{pro} + r_{42}^{pro} + r_{43}^{pro} + r_{44}^{pro} + r_{45}^{pro} + r_{46}^{pro} + r_{47}^{pro} + r_{48}^{pro}) + (r_6^{pro} + r_{13}^{pro} + r_{38}^{pro} + r_{40}^{pro} + r_{45}^{pro} + r_{47}^{pro})$$

$$R_{ABZ}/[RuR] = -(4.k_{zz}^{pro} + 4.k_{ze}^{pro}).[ABZ] + 2.k_{zz}^{pro}.[ABZ] + 2.k_{ez}^{pro}.[ABE] + 2.k_{zz}^{pro}.[AAZ] + 2.k_{ez}^{pro}.[AAE] + 2.k_{zz}^{pro}.[BBZ] + 2.k_{ez}^{pro}.[BBE]$$

$$R_{ABE}/[RuR] = -(4.k_{ee}^{pro} + 4.k_{ez}^{pro}).[ABE] + 2.k_{ze}^{pro}.[ABZ] + 2.k_{ee}^{pro}.[ABE] + 2.k_{ze}^{pro}.[AAZ] + 2.k_{ee}^{pro}.[AAE] + 2.k_{ze}^{pro}.[BBZ] + 2.k_{ee}^{pro}.[BBE]$$

$$R_{AAZ}/[RuR] = -(4.k_{zz}^{pro} + 4.k_{ze}^{pro}).[AAZ] + k_{zz}^{pro}.[ABZ] + k_{ez}^{pro}.[ABE] + 2.k_{zz}^{pro}.[AAZ] + 2.k_{ez}^{pro}.[AAE]$$

$$R_{AAE}/[RuR] = -(4.k_{ee}^{pro} + 4.k_{ez}^{pro}).[AAE] + k_{ze}^{pro}.[ABZ] + k_{ee}^{pro}.[ABE] + 2.k_{ze}^{pro}.[AAZ] + 2.k_{ee}^{pro}.[AAE]$$

$$R_{BBZ}/[RuR] = -(4.k_{zz}^{pro} + 4.k_{ze}^{pro}).[BBZ] + k_{zz}^{pro}.[ABZ] + k_{ez}^{pro}.[ABE] + 2.k_{zz}^{pro}.[BBZ] + 2.k_{ez}^{pro}.[BBE]$$

$$R_{BBE}/[RuR] = -(4.k_{ee}^{pro} + 4.k_{ez}^{pro}).[BBE] + k_{ze}^{pro}.[ABZ] + k_{ee}^{pro}.[ABE] + 2.k_{ze}^{pro}.[BBZ] + 2.k_{ee}^{pro}.[BBE]$$

3. Correlation matrixes

Correlation matrix for pre-catalysts: G-II, HG-II, M71-SiMes and M73-SiMes

	k_{zz}	k_{ze}	k_{ez}	k_{ee}	k_{ini} (G II)	k_{ini} (HG II)	k_{ini} (M71-SiMes)	k_{ini} (M73-SiMes)
k_{zz}	1	0.322	0.261	0.150	−0.241	−0.274	−0.117	−0.113
k_{ze}	0.322	1	0.431	0.171	−0.285	−0.297	−0.184	−0.180
k_{ez}	0.261	0.431	1	0.215	−0.303	−0.314	−0.244	−0.245
k_{ee}	0.150	0.171	0.215	1	−0.278	−0.213	−0.191	−0.184
k_{ini} (G II)	−0.241	−0.285	−0.303	−0.278	1	0.239	0.174	0.171
k_{ini} (HG II)	−0.274	−0.297	−0.314	−0.213	0.239	1	0.164	0162
k_{ini} (M71-SiMes)	−0.117	−0.184	−0.244	−0.191	0.174	0.164	1	0.141
k_{ini} (M73-SiMes)	−0.113	−0.180	−0.245	−0.184	0.171	0.162	0.141	1

Correlation matrix for pre-catalysts: HG-SiPr and M71-SiPr

	k_{zz}	k_{ze}	k_{ez}	k_{ee}	k_{ini} (HG-SiPr)	k_{ini} (M71-SiPr)
k_{zz}	1	0.587	0.482	0.666	−0.153	−0.194
k_{ze}	0.587	1	0.73	0.648	−0.106	−0.127
k_{ez}	0.482	0.73	1	0.561	−0.219	−0.24
k_{ee}	0.666	0.648	0.561	1	−0.201	−0.106
k_{ini} (HG-SiPr)	−0.153	−0.106	−0.219	−0.201	1	0.012
k_{ini} (M71-SiPr)	−0.194	−0.127	−0.24	−0.106	0.012	1

References

1. E.Merino, E.Poli, U.Díaz, D.Brunel. Synthesis and characterization of new ruthenium N-heterocyclic carbene Hoveyda II-type complexes. Study of reactivity in ring closing metathesis reactions *Dalton Trans.* **2012**, *41*, 10913–10918.