Supporting Information For

Influence of the Ease of Initiation and Stability of Ru-catalysts in Cross Metathesis E/Z Selectivity

*Cristina Luján and Steven P. Nolan**

EaStCHEM School of Chemistry, University of St Andrews, St Andrews, KY16 9ST
United Kingdom

Email: snolan@st-andrews.ac.uk

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Experimental

General considerations. All reactions were performed under N_2 atmosphere. CM reactions were performed using Radley Carousel RR98072. All reagents were purchased from Sigma Aldrich and used without further purification. Dichloromethane and toluene were dispensed from an Innovative Technology solvent purification system. ^{1}H NMR were recorded on Bruker 300, 400 or 500 MHz NMR spectrometers.

General procedure for the CM reactions:

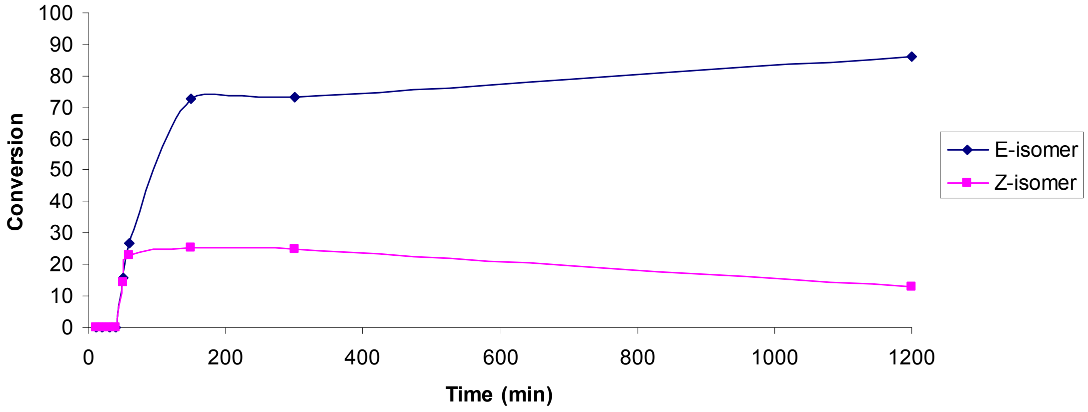
A solution of allyl benzene (0.5 mmol), *cis*-1,4-diacetoxy-2-butene (1.2 mmol) and the Ru catalyst (1 mol%) in solvent (5 mL) was stirred under N_2 atmosphere. Reaction conversion was followed by taking 0.5 mL reaction samples, quenched with ethyl vinyl ether (1 mL) and analysed by ^{1}H NMR shifts at 4.57 (*E*-isomer) and 4.77 (*Z*-isomer) ppm.[1]

CM at room temperature in CH_2Cl_2:

A solution of allyl benzene (**1**, 0.5 mmol), *cis*-1,4-diacetoxy-2-butene (**2**, 1.2 mmol) and the Ru catalyst (1 mol%) in CH_2Cl_2 (5 mL) was stirred at room temperature and under N_2 atmosphere. Reaction conversion was followed by taking 0.5 mL reaction samples, quenched with ethyl vinyl ether (1 mL) and analysed by ^{1}H NMR shifts.

Figure 1. The reactivity of **4** (SIMes/PCy_3 bearing) with time

Conversion	*E*/*Z*	*E* (%)	*Z* (%)	time (min)
0	0,0	0	100	10
0	0,0	0	100	20
0	0,0	0	100	30
0	0,0	0	100	40
30	1,1	52	48	50
50	1,2	54	46	60
98	2,9	74	26	150
98	3,0	75	25	300
99	6,7	87	13	1200



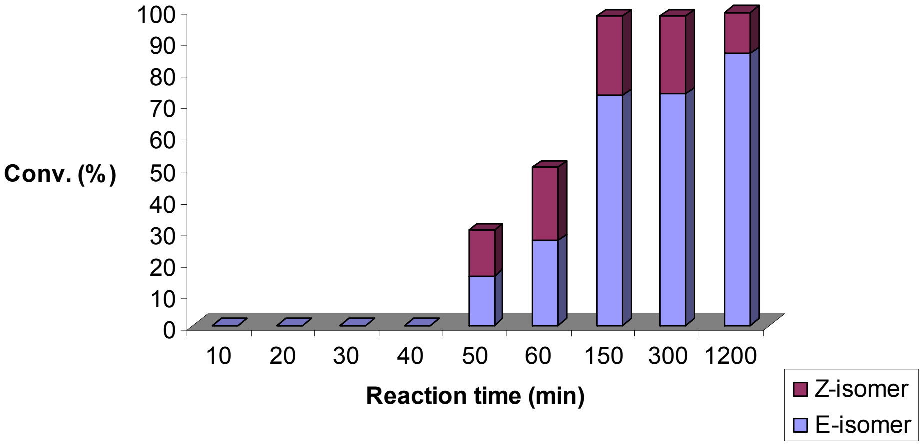
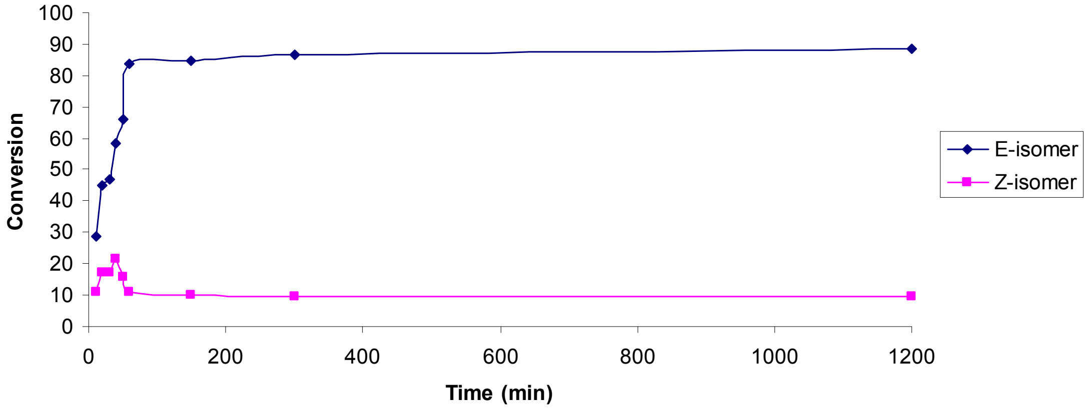


Figure 2. The reactivity of **5** (bearing SIMes/PPh_3) with time

Conversion	*E*/*Z*	*E* (%)	*Z* (%)	time (min)
40	2,6	72	28	10
62	2,6	72	28	20
64	2,7	73	27	30
80	2,7	73	27	40
82	4,2	81	19	50
95	7,5	88	12	60
95	8,4	89	11	150
96	9,2	90	10	300
98	9,5	90	10	1200



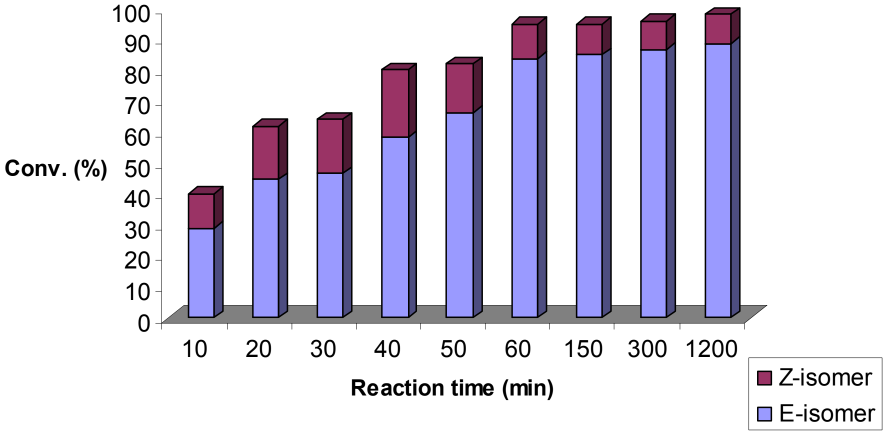
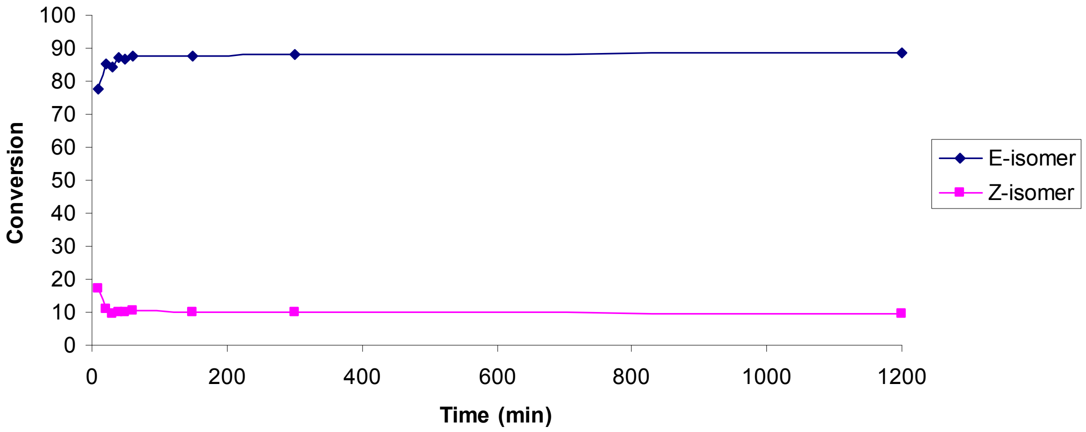


Figure 3. The reactivity of **8** (bearing SIPr/PCy_3) with time

Conversion	*E*/*Z*	*E* (%)	*Z* (%)	time (min)
95	4,5	82	18	10
96	7,9	89	11	20
94	8,7	90	10	30
97	8,9	90	10	40
97	8,5	89	11	50
98	8,3	89	11	60
98	8,6	90	10	150
98	8,7	90	10	300
98	9,2	90	10	1200



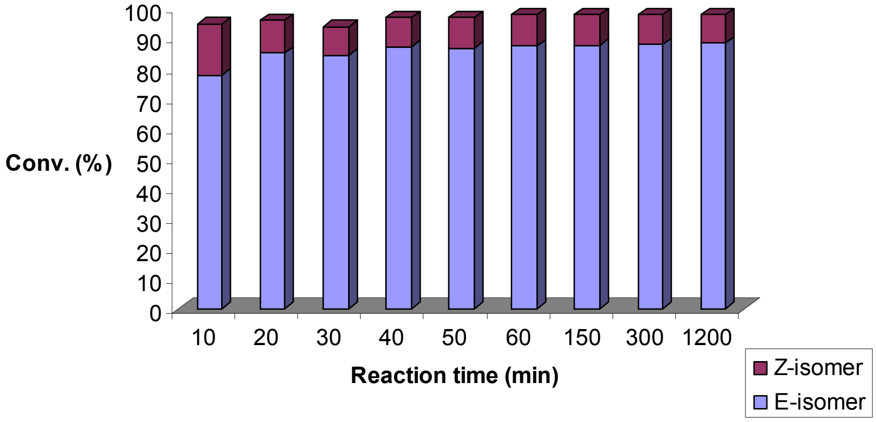
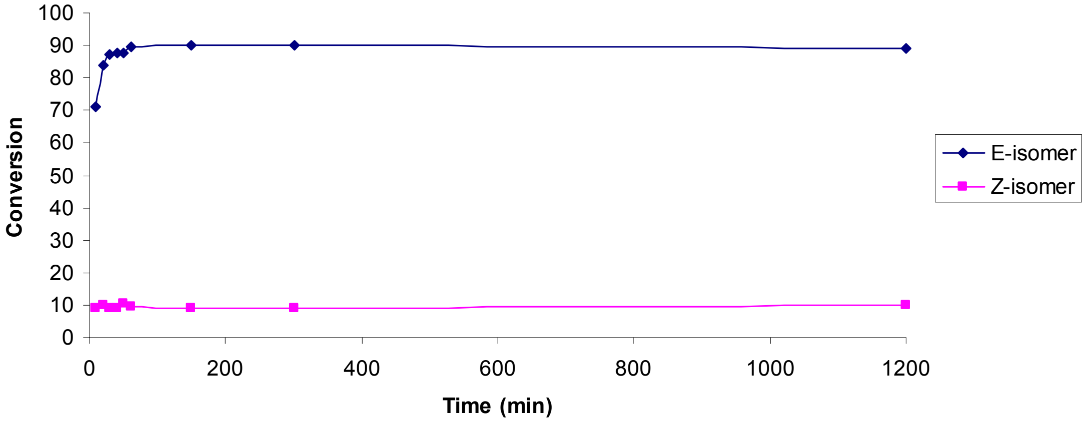
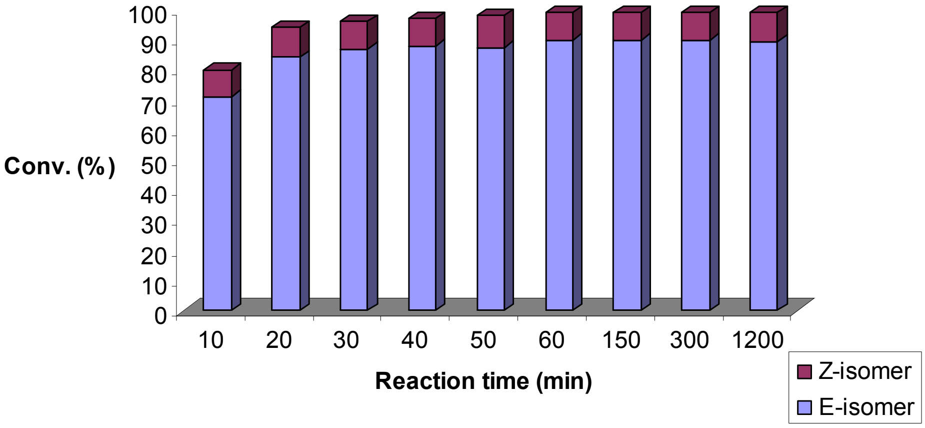


Figure 4. The reactivity of **9** (bearing SIPr/PPh_3) with time

Conversion	*E*/*Z*	*E* (%)	*Z* (%)	time (min)
80	8,0	89	11	10
94	8,5	89	11	20
96	9,7	91	9	30
97	9,6	91	9	40
98	8,3	89	11	50
99	9,7	91	9	60
99	9,8	91	9	150
99	9,9	91	9	300
99	9,1	90	10	1200





CM at 80 ºC in toluene:

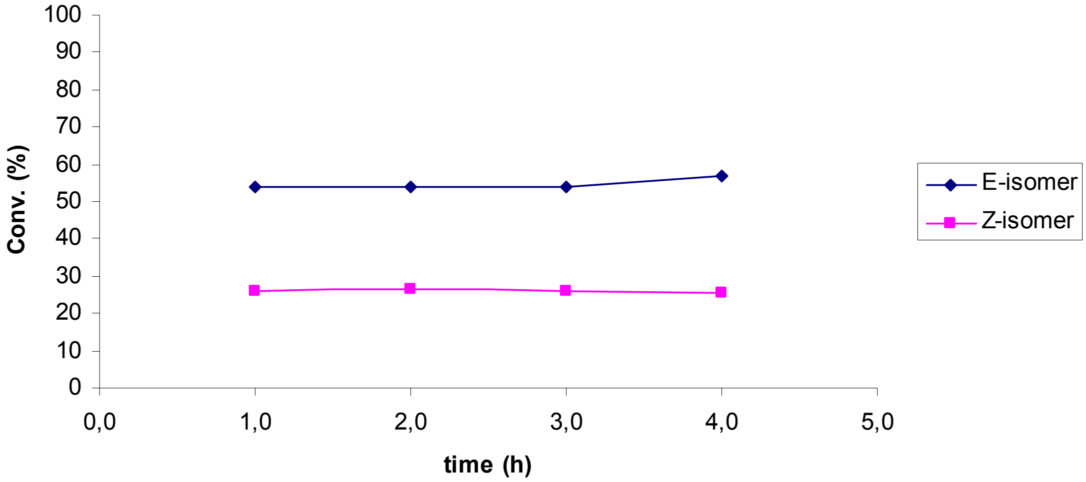
A solution of allyl benzene (**1**, 0.5 mmol), *cis*-1,4-diacetoxy-2-butene (**2**, 1.2 mmol) and the ancillary ligand (8 mol%) and the Ru catalyst (1 mol%) in toluene (5 mL) was stirred at 80 ºC and under N_2 atmosphere. Reaction conversion was followed by taking 0.5 mL reaction samples, quenched with ethyl vinyl ether (1 mL) and analysed by ^{1}H NMR shifts.

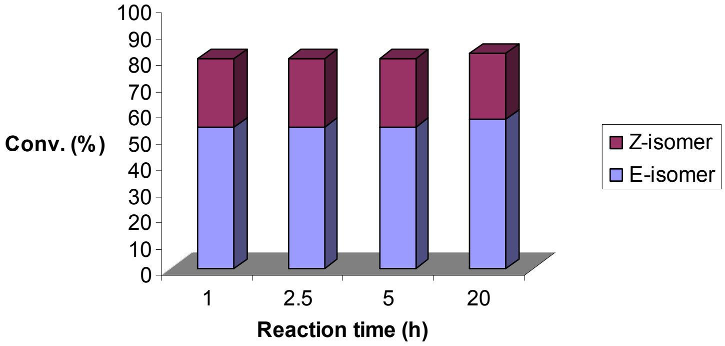
CM in the presence of ancillary ligand excess:

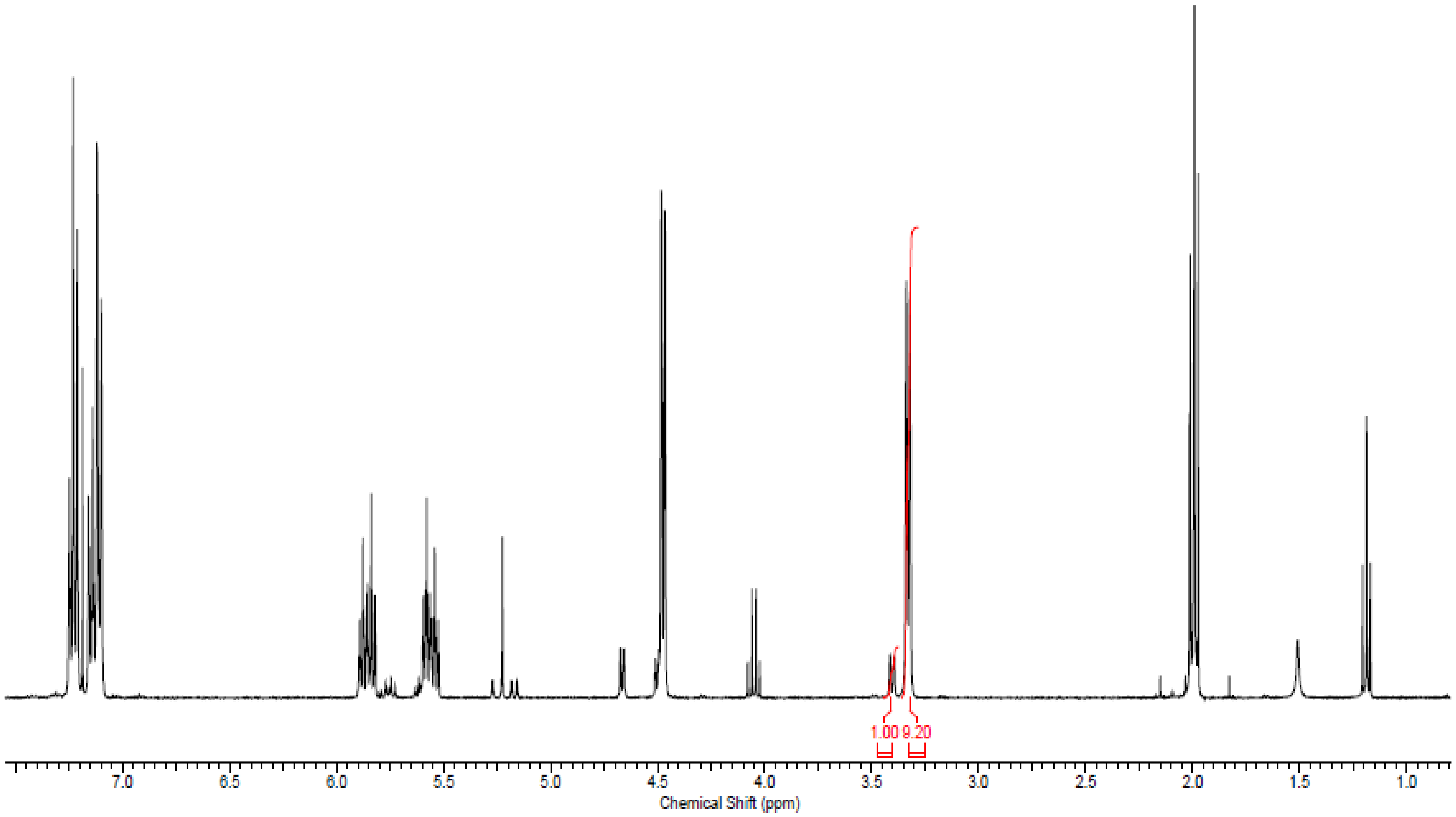
A solution of allyl benzene (**1**, 0.5 mmol), *cis*-1,4-diacetoxy-2-butene (**2**, 1.2 mmol) and the ancillary ligand (8 mol%) and the Ru catalyst (1 mol%) in CH_2Cl_2 (5 mL) was stirred at room temperature and under N_2 atmosphere. Reaction conversion was followed by taking 0.5 mL reaction samples, quenched with ethyl vinyl ether (1 mL) and analysed by ^{1}H NMR shifts.

Figure 5. CM reaction in the presence of SIMes/PCy_3 **4** and an excess of PCy_3

Conversion	***E*/*Z***	***E* (%)**	***Z* (%)**	**time (h)**
80,0	5,30	67	33	1,0
80,0	5,20	67	33	2.5
80,0	5,30	67	33	5,0
82,0	5,40	69	31	20,0


Conv. (%)
100
90
80
70
60
50
40
30
20
10
0
0,0
1,0
2,0
3,0
4,0
5,0
time (h)
E-isomer
Z-isomer


Conv. (%)
100
90
80
70
60
50
40
30
20
10
0
1
2.5
5
20
Reaction time (h)
Z-isomer
E-isomer



E/*Z*-4-Phenylbut-2-en-1-yl acetate (3) ^{1}H NMR

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(1) W.H. Henderson, C.T. Check, N. Proust, J.P. Stambuli, *Org. Lett.* **2010**, *12*, 824-827.