Journal of Organometallic Chemistry 780 (2015) 43-48



Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Evaluation of an olefin metathesis pre-catalyst with a bulky and electron-rich *N*-heterocyclic carbene



CrossMark

Simone Manzini ^{a, 1}, César A. Urbina Blanco ^{a, 2}, David J. Nelson ^{a, 3}, Albert Poater ^b, Tomas Lebl ^a, Sébastien Meiries ^a, Alexandra M.Z. Slawin ^a, Laura Falivene ^{c, d}, Luigi Cavallo ^c, Steven P. Nolan ^{a, *}

^a EaStCHEM School of Chemistry, University of St Andrews, North Haugh, St Andrews, Fife, KY16 9ST, UK

^b Institut de Química Computacional i Catàlisi and Departament de Química, Universitat de Girona, Campus Montilivi, 17071 Girona, Catalonia, Spain

^c KAUST Catalyst Center, Physical Sciences and Engineering Division, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia

^d Department of Chemistry and Biology, University of Salerno, Via Ponte don Melillo, Fisciano I-84084, Italy

ARTICLE INFO

Article history: Received 15 December 2014 Accepted 30 December 2014 Available online 9 January 2015

Keywords: Ruthenium Olefin metathesis *N*-Heterocyclic carbene Density functional theory

ABSTRACT

The commercially-available metathesis pre-catalyst M_{23} has been evaluated alongside new complex [RuCl₂((3-phenyl)indenylidene)(PPh₃)(SIPr^{OMe})] (1), which bears a *para*-methoxy-substituted *N*-heterocyclic carbene ligand. Several model metathesis reactions could be conducted using only parts-permillion levels of ruthenium catalyst. The effects of the different NHC ligands on reactivity have been explored.

© 2015 Elsevier B.V. All rights reserved.

Introduction

N-Heterocyclic carbenes (NHCs) are one of the most important types of ligand in modern organometallic chemistry [1,2]. To allow the fine-tuning of the electronic [3] and steric [4] properties affecting the catalytic properties of the metal centres to which they are co-ordinated, numerous NHC ligands have been reported in the literature [5]. In particular, NHCs have played key roles in gold [6] and palladium [7] catalysis, and have proved to be a break-through in ruthenium-catalysed olefin metathesis [8–10]. Indeed, since the introduction of heteroleptic NHC-phosphine ruthenium olefin metathesis catalysts [11,12] (e.g. Fig. 1), they have surpassed the activity of the previous generations of bis(phosphine) complexes [13,14]. This improvement is due to factors such as the

Corresponding author.

increased affinity of the 14e⁻ species for alkene over phosphine [15], the lower energy differences between active and inactive η^2 -complexes [16], and the increased stability of the alkylidenes [17].

The required ligand sphere for a given olefin metathesis reaction can vary considerably, depending on the needs of the reaction to be catalysed [14]. In particular, by tuning the electronic and steric properties of the NHC ligand, it is possible to modulate the reactivity of the catalyst, taking into account the structure of the substrates. However, it is not always easy to predict how a structural change at the NHC can affect olefin metathesis activity. For example, when IMes is compared to its bulkier analogue IPr (which bears two *iso*propyl substituents on the *N*-aryl moiety), the latter shows higher catalytic activity. If IPr and the saturated analogue SIPr are compared, there is a considerable difference in reactivity, with the latter affording metathesis at very low catalyst loadings [18,19]. A similar trend is apparent between IMes and SIMes, but there is not yet a simple explanation for why saturated NHCs are better ligands for olefin metathesis catalysts. Further investigation of the effect of ligand properties on metathesis catalyst activity is therefore required, which can often be explored by systematic changes to the ligand sphere. The use of established metrics such as TEP [20] and percent buried volume $(%V_{bur})$ [4,21] can allow ligand properties to be quantified, while the measurement of the rates of

E-mail address: snolan@st-andrews.ac.uk (S.P. Nolan).

¹ Current address: Catalysis Research Laboratory (CaRLa), Im Neuenheimer Feld 584, 69120 Heidelberg, Germany.

² Current address: Lehrstuhl für Technische Chemie und Petrolchemie, Institut für Technische und Makromolekulare Chemie (ITMC), RWTH Aachen University, Worringerweg 1, 52074 Aachen, Germany.

³ Current address: WestCHEM Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow, G1 1XL, UK.



Fig. 1. Common commercially-available pre-catalysts.

key processes [22] such as initiation allows some insight into which aspects of the reaction mechanism are affected by these changes. Methoxy-functionalised NHCs [23] have been shown to be excellent ligands for palladium catalysts, compared to the corresponding parent NHCs [24,25]. Plenio has synthesised a range of *para*-substituted (S)IMes derivatives and explored their properties by various spectroscopic and electrochemical means, and established that *para*-substitution of the NHC ligand does indeed affect the properties of the transition metal centre [26]. We therefore wished to explore their use as ligands for metathesis pre-catalysts, comparing **1** with the recently discovered and already commercially available **M**₂₃; while only a preliminary evaluation of the catalytic activity of the latter has been disclosed, it has shown very high activity in olefin metathesis, and a full evaluation of its properties is warranted.

Results and discussion

Synthesis and characterisation of [RuCl₂((3-phenyl) indenylidene)(PPh₃)(SIPrOMe)] (**1**)

We have previously reported the synthesis, characterisation, and catalytic testing of $[RuCl_2((3-phenyl))indenylidene)(PPh_3)$ (SIPr)] (**M**₂₃) [18,27]. This complex shows promising activity in RCM and CM with less hindered substrates, reaching full conversion at 1 mol% of catalyst loading in only 0.5 h. However, the complex is not capable of promoting metathesis transformations with more hindered substrates.

New complex **1** was prepared in order to investigate how modulating the electronic nature of the aryl ring, with minimal steric changes, might affect the catalytic activity of the resulting complex. The synthesis and characterisation of SIPr^{OMe} have been previously reported by us [23,28]; it was found that it typically has a similar steric impact to SIPr, but is slightly more σ -donating and less π -accepting. Using a method analogous to the reported procedure for the synthesis of **M**₂₃ [27], complex **1** was obtained in 82% yield as an analytically-pure red solid (Scheme 1). This new complex was characterised by ¹H, ¹³C{¹H}, and ³¹P{¹H} NMR spectros-copy (see the Supporting information).

In order to evaluate the steric impact of the NHC in each complex, crystals suitable for X-ray diffraction analysis were obtained by slow diffusion of pentane into a concentrated dichloromethane solution. Representations of these crystal structures can be found in Fig. 2, while key structural properties of each complex, plus those of $[RuCl_2((3-phenyl)indenylidene)(PPh_3)(IPr)]$ (2) [19], are recorded in



Fig. 2. Molecular structures of complexes M_{23} (left) and 1 (right), determined by X-ray crystallographic analysis; thermal ellipsoids are drawn at 50% probability, and H atoms are excluded for clarity.

Table 1. Percent buried volumes (%V_{bur}) [4] were calculated using the SambVca web application [21]. The structural features of the three complexes are very similar, with only small differences in Ru–Cl. Ru–C and Ru=C bond lengths. All three complexes exhibit the same distorted square-based pyramidal geometry. The Ru-P distance in 1 is slightly shorter than in M₂₃, which may be indicative of increased *d* to π^* backbonding in the former complex. The Ru–P distance in 2 is shorter still, which might be attributed to the same effect, as unsaturated NHCs are known to be poorer π -acceptors than the corresponding saturated ligands [29–32]. In complex **1**, the torsion angle in the backbone of the NHC is larger than in M_{23} by 10°. This difference might be due to the reduced mobility of the aryl ring due to the mesomeric effect of the paramethoxy substituent which might force the imidazolium ring into a more distorted conformation. Notably, this is the only structural difference that does not concern the throw-away ligand.

Pre-catalyst initiation

The pre-catalyst initiation event determines the rate at which the active catalyst is formed during the reaction, and is therefore an

able 1	
elected bond lengths (Å) and angles ($^\circ$) in complexes $\textbf{M_{23}, 1}$ and 2.	

Complex		M ₂₃	1	2
Ru(1)-Cl(1)	(Å)	2.3690(13)	2.3660(11)	2.373(3)
Ru(1)-Cl(2)	(Å)	2.3812(14)	2.3795(11)	2.387(2)
Ru(1)-P(1)	(Å)	2.4204(17)	2.4017(11)	2.368(2)
Ru(1)-C(1)	(Å)	2.092(6)	2.101(4)	2.129(8)
Ru(1)-C(31)	(Å)	1.850(5)	1.850(4)	1.822(7)
Cl(1)-Ru(1)-Cl(2)	(°)	166.38(5)	164.85(4)	166.58(8)
C(1)-Ru(1)-P(1)	(°)	162.30(14)	162.72(11)	164.7(2)
C(1)-Ru(1)-C(31)	(°)	103.1(3)	103.14(15)	102.1(3)
N(2)-C(3)-C(4)-N(5)	(°)	9.8(5)	22.1(4)	1.8(11)
%V _{bur}		31.8%	32.0%	31.1%

important parameter. Recently, we have determined the activation parameters of M_{23} and other ruthenium indenylidene complexes using [³¹P, ³¹P] EXSY experiments, and kinetic studies of their reactions with butyl vinyl ether [33]. While most complexes initiated *via* a dissociative mechanism (phosphine dissociation to yield a 14e⁻ species, followed by alkene co-ordination), it was found that M_{20} actually initiates *via* an interchange mechanism (concurrent phosphine dissociation and alkene co-ordination *via* a single transition state). We therefore wished to elucidate whether 1 and 2 initiated *via* the dissociative or interchange mechanism, and how the NHC ligand affects this initiation rate. Notably, interactions between the NHC *N*-aryl substituents and the ruthenium carbene fragment have been postulated to be important to the electronic structure and initiation behaviour of metathesis pre-catalysts [34–36].

Initiation rates for 1 and 2 were measured using two methods: $[^{31}P, ^{31}P]$ EXSY experiments in the presence of added PPh₃, where the exchange rate of the signals for free and bound phosphine was measured (Table 2); and reaction with butyl vinyl ether which irreversibly forms a metathesis-inactive Fischer carbene species [37] under conditions where phosphine dissociation is ratedetermining (Table 3) [15]. Unfortunately, the initiation parameters of 2 could not be measured using the former method due to competing decomposition at the temperatures necessary to effect measurable rates of phosphine exchange. These data reveal that there is very little difference in the activation parameters for the initiation of these complexes. Errors in the entropy measurements are quite large, due to the need to extrapolate to infinite temperature, but enthalpy measurements are slightly more reliable. Complex 2 initiates slightly faster than M₂₃ or 1, perhaps due to the reduced π -accepting ability of IPr versus SIPr or SIPr^{OMe}. **1** initiates only very slightly faster than M₂₃, which is consistent with the relatively small difference in TEP between the NHCs on each complex [23].

Metathesis activity

The activities of M_{23} and 1 were evaluated in a series of metathesis reactions. Complex **2** is already known to be a poor metathesis complex from our earlier study of IPr- and IPr*-bearing complexes [19], so was not evaluated further. To fully compare the activity of M₂₃, evaluate the limits of this catalyst and draw out differences in activity between M₂₃ and 1, the efficiency of these catalysts was evaluated at low catalyst loadings (100-500 ppm) (Table 4) [38,39]. As shown in the table, it is possible to achieve the RCM of less hindered substrates using only 100 ppm of the ruthenium catalyst. As the steric bulk around the reacting alkene termini is increased, the reactivity drops slightly, requiring the use of slightly higher pre-catalyst loadings. Interestingly, complex 1 performs slightly better than M₂₃ for substrates with very little steric bulk, although differences in reactivity are relatively small, but performs more poorly when steric bulk is added (e.g. entries 1 and 2, where simple methylation of one alkene leads to a four-fold drop in conversion). On balance, M₂₃ still appears to be the more useful pre-catalyst. The highest TON achieved for M_{23} is with substrate 3, reaching 32% conversion at 20 ppm of catalyst loading in only 1 h

Table 2							
Activation	parameters for	M ₂₃ and 1	determined	using [³¹ P, ³¹ P]	EXSY ex	periments.

	M ₂₃	1
$\Delta H^{\ddagger}/\text{kcal mol}^{-1}$	27 ± 1	26 ± 1
ΔS^{\ddagger} /cal K ⁻¹ mol ⁻¹	21 ± 4	19 ± 1
$\Delta G^{\ddagger}/ ext{kcal mol}^{-1}$	21 ± 2	20 ± 1

-			~	
Та	bl	e	з	

Activation parameters for M_{23} , 1 and 2 determined by reaction with butyl vinyl ether.

	M ₂₃	1	2
$\Delta H^{\ddagger}_{288.2 \text{ K}}/\text{kcal mol}^{-1}$	25 ± 2	24 ± 2	23 ± 4
$\Delta S^{\ddagger}_{288.2 \text{ K}}$ /cal K ⁻¹ mol ⁻¹	14 ± 9	11 ± 5	1 ± 11
$\Delta G^{\ddagger}_{288,2 \text{ K}}/\text{kcal mol}^{-1}$	21 ± 4	21 ± 2	22 ± 5
k _{init} (288.2 K)/s ⁻¹	5.56×10^{-5}	6.01×10^{-5}	8.49×10^{-4}

(TON 1.6 × 10⁶ and TOF 4.4 × 10³ s⁻¹). In TON terms, this makes **M₂₃** one of the best catalysts for the RCM of less hindered substrates. Notably, a low pre-catalyst loading not only has cost benefits, but simplifies purification, particularly if high-purity pharmaceuticals or materials are being prepared; the use of 100 ppm of ruthenium catalyst to prepare a molecule of mass 500 g mol⁻¹ would render the ruthenium content only 20 mg/kg (20 ppm) before work-up and any purification steps.

In cross-metathesis reactions at low pre-catalyst loading, the activity of the two catalysts is very similar in terms of both stereoselectivity and activity (Table 5). A greater than 20:1 E/Z ratio was

Table 4

Evaluation of 1 and M_{23} at low catalyst loadings, for model ring-closing olefin and enyne metathesis reactions. $^{\rm a}$

Entry	Substrate	Product	Cat	Loading	Conv ^b
1	EtO ₂ C CO ₂ Et	EtO ₂ C CO ₂ Et	1 M ₂₃	100 ppm 100 ppm	92% 93%
2	EtO ₂ C CO ₂ Et	4 EtO ₂ C CO ₂ Et	1 M ₂₃	100 ppm 100 ppm	25% >99%
3	Ts N 7		1 M ₂₃	100 ppm 100 ppm	>99% 96%
4	Ph N 9	Ph N	1 M ₂₃	100 ppm 100 ppm	37% 80%
5	EtO ₂ C CO ₂ Et	EtO ₂ C CO ₂ Et	1 M ₂₃	150 ppm 200 ppm	>99% 89%
7	Ph o	Ph O 14	1 M ₂₃	500 ppm 500 ppm	80% >99%
8	Ph Ph O	Ph O Ph O 16	1 M ₂₃	500 ppm 500 ppm	83% 74%
6	15 EtO ₂ C CO ₂ Et 17	EtO ₂ C CO ₂ Et	1 M ₂₃	500 ppm 500 ppm	93% 89%

^a Reaction conditions: substrate (0.25 mmol), Ru complex, 0.5 mL DCM (0.5 mol L^{-1}), under argon at room temperature (*ca*. 25 °C) in a pierced vial in the glovebox for 1 h.

^b Conversions determined by ¹H NMR spectroscopy; average of two experiments.

Table 5

Evaluation of 1 and M₂₃ at low catalyst loadings for model cross-metathesis reactions.^a



Entry	Substrate	Cat	Loading	CM product (%) ^b	Dimer (%) ^b	E/Z ratio
1	TBDMSO.	1	500 ppm	51	3	>20:1
	19	M ₂₃	500 ppm	34	2	>20:1
2	0	1	250 ppm	50	23	>20:1
	PhO	M ₂₃	250 ppm	54	13	>20:1
	20					

^a Reaction conditions: substrate (0.25 mmol), [Ru] complex, 0.5 mL DCM (0.5 mol L⁻¹), under argon at room temperature (*ca.* 25 °C) in a pierced vial in the glovebox for 5 h. ^b Conversions determined by ¹H NMR; average of two experiments.

achieved in each reaction. Interestingly, **1** appears to be slightly more selective for the formation of the dimer product in entry 2, which might be due to slightly more steric bulk, although this is quite far removed from the alkene terminus.

Due to the high activity of **M**₂₃ with different substrates at low catalyst loadings, and therefore the potential utility in industrial applications, different solvents have been evaluated at low catalyst loadings using substrate **3** as a model. Many industries, particularly the pharmaceutical industry, are reducing their usage of less acceptable solvents (such as DCM) and replacing them with more environmentally-friendly alternatives [40–42]. As can be seen in Table 6, **M**₂₃ shows excellent compatibility with green solvents, and can be used under neat conditions, accessing product **4** quantitatively and with very low catalyst loadings in solvents such as methyl *iso*-butyl ketone.

While these experiments are a good indication of the outcomes of some prototypical metathesis reactions, further information on the comparison of M_{23} and 1 was desired. Therefore, kinetic experiments were carried out, in which the RCM of 3 to form 4 (catalysed by each complex) was monitored by ¹H NMR spectroscopy (0.5 mol L⁻¹ 3 in toluene- d_8 , catalysed by 250 ppm M_{23} or 1, at 288 K). Concentration *versus* time profiles for the reactions can be found in Fig. 3(a). Only a modest difference in RCM rate was

Table 6

Evaluation of complex M_{23} a	at low catalyst	loadings in a	number of solvents.
----------------------------------	-----------------	---------------	---------------------

Entry	Solvent	[M ₂₃] (ppm)	Conv. (%)
1	Acetone	500	>99
2		100	97
3	CPME	500	>99
4		100	>99
5	DCM	500	>99
6		100	>99
7	1,2-DME	500	>99
8	1,4-Dioxane	500	18
9	<i>iso</i> Propanol	500	55
10	Methyl iso-butyl ketone	500	>99
11		100	99
11	2-Methyltetra-hydrofuran	500	>99
12		100	79
13	MTBE	500	>99
14	THF	500	>99
15	Toluene	500	>99
16		100	>99
17	Neat	500	>99
18		100	98

^a Reaction conditions: 3 (0.25 mmol), **M₂₃**0.5 mL DCM (0.5 mol L⁻¹), under argon at room temperature (*ca*. 25 °C) in a pierced vial in the glovebox for 1 h. Conversions determined by ¹H NMR; average of two experiments.

encountered. Treatment of the first three half-lives of kinetic data revealed excellent first order behaviour. Rate constants for the reactions could be extracted ($k_{obs} = 5.28 \times 10^{-4} \text{ s}^{-1}$ for **M**₂₃; $k_{obs} = 3.99 \times 10^{-4} \text{ s}^{-1}$ for **1**) (Fig. 3(b)).

DFT calculations

The use of DFT calculations to explore the potential energy surfaces of metathesis reactions is potentially very valuable, assisting in the rationalisation of reaction outcomes (both in terms of pre-catalyst design and substrate structure) [43–45]. Metathesis is a complex sequence of multiple steps, rendering it rather difficult to experimentally study key steps in isolation. In addition, these methods hold promise for the prediction of the efficacy of complexes that have not yet been synthesised.

The potential energy surfaces (PESs) were modelled for the reactions of three complexes with ethene: M_{23} , 1 and complex 21 which bears *para*-nitro substituents on the NHC aryl rings (which has not yet been synthesised) (Fig. 4). The latter PES was explored to identify whether the synthesis of a less electron-rich system might be advantageous, as well as to identify any key trends. Notably, energy differences between intermediates with different aryl ring substituents are rather small (0.7–3.5 kcal mol⁻¹). The SIPr^{OMe} complex 1 is predicted to initiate slightly faster than M_{23} , in agreement with experiments, with an upper barrier 0.4 kcal mol⁻¹



Fig. 3. Kinetic data for the RCM of 3 (0.5 mol L⁻¹, toluene- d_8 , 288 K with 250 ppm precatalyst), monitored by ¹H NMR spectroscopy: (a) concentration/time profiles; (b) first order treatment of kinetic data; SIPr in blue, SIPr^{OMe} in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



Fig. 4. PESs for the metathesis of ethene by 1, M₂₃ and 21.

lower in energy than for **1**. Furthermore, we conducted calculations with complex **21**, for which the upper barrier increases by 1.4 kcal mol⁻¹, demonstrating that more electron-donating groups in the *para* position of the *N*-aryl rings lead to slightly faster initiation. Bearing in mind the electronic nature of this trend, previously reported by Cavallo et al. [33], we confirmed that the sterics of the NHC ligand are not modified by the substitution of the *N*-aryl ring; all three NHCs are within a narrow window of $%V_{\text{bur}}$ that covers only 0.4%. Previous estimates of the error in $%V_{\text{bur}}$ suggest that only differences of *ca*. 2% or more are meaningful [23].

However, other key intermediates on the PES, such as η^2 -complexes and MCBs, are higher in energy (with respect to the precatalyst) for the *para*-substituted analogues, as are the barriers between these species which may explain the poorer performance of **1** in some metathesis reactions. The differences are typically very small, suggesting that *para*-substitution of the NHC aryl rings of SIPr-type NHCs is not a promising way in which to develop new and more active series of pre-catalysts.

Conclusions

In conclusion we report the synthesis of a derivative ruthenium complex bearing a para-methoxy substituted SIPr ligand and compared its reactivity with the SIPr-bearing analogue M₂₃. Both complexes are able to catalyse RCM of less hindered olefins at very low catalyst loadings and are compatible with a range of solvents, including a number of solvents that are acceptable on scale in industrial applications. In particular, M_{23} delivers the best activity across a range of substrates. Even though the difference in properties between 1 and M_{23} is minimal, the two complexes show differences in reactivity. Complex 1 proved to be more influenced by the steric environment than M23. DFT calculations showed that differences between SIPr and SIPr^{OMe}-based catalysts were typically very small, with the latter ligand favouring a slight increase in initiation rate, but rendering intermediate species generally higher in energy. NHCs such as SIPr^{OMe} are therefore unlikely to bring benefits to the field of metathesis.

Acknowledgements

SPN thanks the European Research Council (227817) (Advanced Investigator Award 'FUNCAT'), the EU (CP-FP 211468) (Seventh Framework Programme Project 'EUMET'), and the Engineering and Physical Sciences Research Council for funding. SPN is a Royal Society Wolfson Merit Award holder. AP thanks the Spanish MINECO for a Ramón y Cajal contract (RYC-2009-05226) and European Commission for a Career Integration Grant (CIG09-GA-2011-293900).

Experimental

General information:

All reagents were used as received. Dichloromethane and toluene were dispensed from a solvent purification system from MBraun. Catalyst syntheses were performed in a MBraun glovebox containing dry Ar and less than 1 ppm oxygen. ¹H, ³¹P{¹H}, and ¹³C {¹H} Nuclear Magnetic Resonance (NMR) spectra were recorded on Bruker Avance 300 or Bruker Avance II 400 Ultrashield NMR spectrometers. The EXSY experiments were recording using the previous procedure. **M**₂₃ was purchased from Umicore and used as received. Compound **19** was synthesised in accordance with the reported procedure. Elemental analyses were performed at the London Metropolitan University. Solvents were dried and degassed according to the literature. SIPr^{OMe} was synthesised according to the previously reported procedure. Substrates **1**, **3**, **4**, **5**, **7**, **9**, **11**, **13**, **15**, **17**, **20**, **21** and products **2**, **4**, **6**, **8**, **10**, **12**, **14** and **18** have previously been described in the literature [46–48].

Synthesis of [RuCl₂(SIPr^{OMe})(PPh₃)(3-phenylindenylidene)](1):

In the glovebox, M_{10} (1.00 g, 1.13 mmol) and SIPr^{OMe} (914 mg, 1.2 mmol)) were charged to a Schlenk flask and dissolved in toluene (3 mL). The reaction was taken out of the glovebox and stirred at 40 °C for 5 h under Ar. After this time, the mixture was allowed to

cool to RT and the solvent was removed under vacuum. The remaining solid was recrystallised from a mixture of dichloromethane/pentane. The mixture was filtered, washed with cold methanol (2 \times 5 mL) and cold hexane (8 \times 25 mL), affording $[RuCl_2(SIPr^{OMe})(PPh_3)(3-phenylindenylidene)] \quad (1) \quad (750 mg,$ 0.49 mmol, 44%) as a microcrystalline solid. ¹H NMR (C₆D₆, 400 MHz): $\delta = 8.04$ (d, I = 7.2 Hz, 1H), 7.74 (d, I = 7.9 Hz, 2H), 7.38 (m, 8H), 7.21 (m, 2H), 6.92 (m, 16H), 6.83 (d, J = 3.2 Hz, 1H), 6.63 (m, 1H), 6.45 (d, *J* = 2.9 Hz, 1H), 6.26 (d, *J* = 2.9 Hz, 1H), 3.53 (s, 3H) 3.10 (s, 3H) 1.77 (d, *I* = 6.5 Hz, 3H), 1.57 (d, *I* = 6.5 Hz, 3H), 1.77 (d, I = 6.5 Hz, 3H) 1.20 (m, 13H) 0.85 (m, 9H) ppm. ¹³C{¹H} NMR $(CD_2Cl_2, 75 \text{ MHz})$: $\delta = 299.9, 160.9, 159.9, 152.2, 151.5, 149.9, 149.2, 149.2, 151.5, 149.9, 149.2$ 143.0, 141.3, 140.8, 139,3, 137.2, 135.1, 132.1, 131.7, 130.9, 130.7, 129.3, 129.3, 129.1, 127.0, 116.1, 110.6, 110.4, 108.7, 116.7, 55.2, 54.7, 54.2, 34.2 30.4, 29.4, 29.0 27.8, 27.2, 27.0, 26.9, 25.8, 24.2, 24.0, 23.9, 22.7, 22.3 ppm. ${}^{31}P{}^{1}H$ NMR (162 MHz, C₆D₆) δ = 29.89 ppm. Anal. Calcd for C₆₂H₆₇Cl₂N₂O₂PRu C, 69.26; H, 6.28; N 2.61; Found: C, 69.10; H, 6.37; N, 2.70.

General procedure for RCM and enyne reactions:

Inside the glovebox stock solutions were prepared of substrate (2.5 mmol/1 mL) and catalyst (0.025 mmol/4 mL) in the appropriate solvent. An aliquot of substrate was then measured into a 4 mL vial, then a volume of the same solvent required to reach a concentration of 0.5 M was added, followed by a corresponding aliquot of the catalyst to reach the desired catalyst loading. The reaction was stirred for 1 h and ¹H NMR of the reaction mixture was recorded to determine conversion.

General procedure for CM reactions:

Inside the glovebox stock solutions were prepared of substrate (2.5 mmol/1 mL) and catalyst (0.025 mmol/4 mL) in the appropriate solvent. An aliquot of substrate was then measured into a 4 mL vial, then a volume of the same solvent required to reach a concentration of 0.5 M was added, followed with a corresponding aliquot of the catalyst to reach the desired catalyst loading. After this, 2 equivalents of the electron poor olefin (0.5 mmol) were added. The progress of the reaction was monitored by ¹H NMR. At reaction completion solvent was removed under vacuum and the crude residue was checked by ¹H NMR. Conversion was determined by ¹H NMR spectroscopy by integrating the characteristic signals for allylic proton resonances.

NMR initiation kinetics with butyl vinyl ether:

Inside a glovebox, 400 µL of a stock solution of complex in toluene- d_8 (0.0106 mmol/400 µL; 0.1325 mmol/5 mL) and an amount of toluene- d_8 so that the total volume of the solution after addition of butyl vinyl ether was 600 µL were introduced into a screw-cap NMR tube. The solution was left to equilibrate at the desired temperature, and then the butyl vinyl ether (in equivalents relative to [Ru]) was injected into the solution; the progress of the reaction was followed by ³¹P{¹H} and ¹H NMR every 10 min.

Appendix A. Supplementary material

CCDC 999049 (1) and 999050 (M_{23}) contain 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.

Appendix B. Supporting information

Supplementary data related to this article can be found at http:// dx.doi.org/10.1016/j.jorganchem.2014.12.040.

References

- [1] W.A. Herrmann, Angew. Chem. Int. Ed. 41 (2002) 1290–1309.
- [2] S. Diez-Gonzalez, N. Marion, S.P. Nolan, Chem. Rev. 109 (2009) 3612-3676.
- [3] D.J. Nelson, S.P. Nolan, Chem. Soc. Rev. 42 (2013) 6723-6753.
- H. Clavier, S.P. Nolan, Chem. Commun. 46 (2010) 841-861. [4]
- T. Dröge, F. Glorius, Angew. Chem. Int. Ed. 49 (2010) 6940-6952. [6] S.P. Nolan, Acc. Chem. Res. 44 (2011) 91-100.
- [7] G.C. Fortman, S.P. Nolan, Chem. Soc. Rev. 40 (2011) 5151-5169. [8]
- G.C. Vougioukalakis, R.H. Grubbs, Chem. Rev. 110 (2009) 1746-1787.
- [9] C. Samojlowicz, M. Bieniek, K. Grela, Chem. Rev. 109 (2009) 3708-3742.
- [10] F. Boeda, H. Clavier, S.P. Nolan, Chem. Commun. (2008) 2726-2740. [11] J. Huang, E.D. Stevens, S.P. Nolan, J.L. Petersen, J. Am. Chem. Soc. 121 (1999)
- 2674-2678. [12] M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, Org. Lett. 1 (1999) 953-956.
- [13] T. Ritter, A. Hejl, A.G. Wenzel, T.W. Funk, R.H. Grubbs, Organometallics 25 (2006) 5740-5745.
- [14] M. Bieniek, A. Michrowska, D.L. Usanov, K. Grela, Chem. Eur. J. 14 (2008) 806-818.
- [15] M.S. Sanford, J.A. Love, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 6543-6554.
- [16] B.F. Straub, Angew. Chem. Int. Ed. 44 (2005) 5974-5978.
- [17] S.H. Hong, A.G. Wenzel, T.T. Salguero, M.W. Day, R.H. Grubbs, J. Am. Chem. Soc. 129 (2007) 7961-7968.
- [18] C.A. Urbina-Blanco, A. Leitgeb, C. Slugovc, X. Bantreil, H. Clavier, A.M.Z. Slawin, S.P. Nolan, Chem. Eur. J. 17 (2011) 5045–5053.
- [19] S. Manzini, C.A. Urbina Blanco, A.M.Z. Slawin, S.P. Nolan, Organometallics 31 (2012) 6514-6517.
- [20] C.A. Tolman, Chem. Rev. 77 (1977) 313-348.
- [21] A. Poater, B. Cosenza, A. Correa, S. Giudice, F. Ragone, V. Scarano, L. Cavallo, Eur. J. Inorg. Chem. 2009 (2009) 1759-1766.
- [22] D.J. Nelson, S. Manzini, C.A. Urbina-Blanco, S.P. Nolan, Chem. Commun. 50 2014) 10355-10375.
- [23] D. Nelson, A. Collado, S. Manzini, S. Meiries, D.B. Cordes, A.M.Z. Slawin, S.P. Nolan, Organometallics 33 (2014) 2048-2058.
- [24] S. Meiries, K. Speck, D.B. Cordes, A.M.Z. Slawin, S.P. Nolan, Organometallics 32 (2012) 330-339.
- [25] G. Le Duc, S. Meiries, S.P. Nolan, Organometallics 32 (2013) 7547-7551.
- [26] S. Leuthäußer, D. Schwarz, H. Plenio, Chem. Eur. J. 13 (2007) 7195–7203.
- [27] C.A. Urbina-Blanco, S. Manzini, J.P. Gomes, A. Doppiu, S.P. Nolan, Chem. Commun. 47 (2011) 5022-5024.
- [28] S. Meiries, S.P. Nolan, Synlett 25 (2014) 393-398.
- [29] S. Fantasia, J.L. Petersen, H. Jacobsen, L. Cavallo, S.P. Nolan, Organometallics 26 (2007) 5880-5889.
- [30] O. Back, M. Henry-Ellinger, C.D. Martin, D. Martin, G. Bertrand, Angew. Chem. Int. Ed. 52 (2013) 2939–2943.
- [31] A. Liske, K. Verlinden, H. Buhl, K. Schaper, C. Ganter, Organometallics 32 (2013) 5269-5272.
- [32] R. Dorta, E.D. Stevens, N.M. Scott, C. Costabile, L. Cavallo, C.D. Hoff, S.P. Nolan, J. Am. Chem. Soc. 127 (2005) 2485-2495.
- [33] C.A. Urbina-Blanco, A. Poater, T. Lebl, S. Manzini, A.M.Z. Slawin, L. Cavallo, S.P. Nolan, J. Am. Chem. Soc. 135 (2013) 7073-7079.
- [34] S. Leuthäußer, V. Schmidts, C.M. Thiele, H. Plenio, Chem. Eur. J. 14 (2008) 5465-5481.
- [35] R. Credendino, L. Falivene, L. Cavallo, J. Am. Chem. Soc. 134 (2012) 8127-8135. [36] H.-C. Yang, Y.-C. Huang, Y.-K. Lan, T.-Y. Luh, Y. Zhao, D.G. Truhlar, Organo-
- metallics 30 (2011) 4196-4200.
- [37] J. Louie, R.H. Grubbs, Organometallics 21 (2002) 2153-2164.
- [38] L.H. Peeck, R.D. Savka, H. Plenio, Chem. Eur. J. 18 (2012) 12845–12853.
- [39] R. Kadyrov, Chem. Eur. J. 19 (2013) 1002–1012.
- [40] R.K. Henderson, C. Jimenez-Gonzalez, D.J.C. Constable, S.R. Alston, G.G.A. Inglis, G. Fisher, J. Sherwood, S.P. Binks, A.D. Curzons, Green Chem. 13 (2011) 854-862.
- [41] K. Alfonsi, J. Colberg, P.J. Dunn, T. Fevig, S. Jennings, T.A. Johnson, H.P. Kleine, C. Knight, M.A. Nagy, D.A. Perry, M. Stefaniak, Green Chem. 10 (2008) 31–36.
- [42] D. Prat, O. Pardigon, H.-W. Flemming, S. Letestu, V. Ducandas, P. Isnard, E. Guntrum, T. Senac, S. Ruisseau, P. Cruciani, P. Hosek, Org. Proc. Res. Dev. (2013).
- [43] R. Credendino, A. Poater, F. Ragone, L. Cavallo, Cat. Sci. Technol. 1 (2011) 1287-1297.
- [44] I.H. Hillier, S. Pandian, J.M. Percy, M.A. Vincent, Dalton Trans. 40 (2011) 1061 - 1072.
- [45] A. Poater, N. Bahri-Laleh, L. Cavallo, Chem. Commun. 47 (2011) 6674-6676.
- [46] H. Clavier, S.P. Nolan, Chem. Eur. J. 13 (2007) 8029-8036.
- [47] D. Rix, F. Caijo, I. Laurent, F. Boeda, H. Clavier, S.P. Nolan, M. Mauduit, J. Org. Chem. 73 (2008) 4225-4228.
- [48] F. Boeda, X. Bantriel, H. Clavier, S.P. Nolan, Adv. Synth. Catal. 350 (2008) 2959-2966.