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Note

Kinetic investigation of a ruthenium metathesis catalyst

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Abstract

The complex [$(IMesH_2)(PPh_2Cy)Cl_2Ru{=}CHPh$] was synthesised and shown to be an active catalyst in ring-closing metathesis of a diallylmalonate. Its phosphine exchange was investigated in C_6D_6 using magnetisation transfer ^{31}P NMR spectroscopy and it was found to operate via a dissociative mechanism with $k^{353} = 4.1 \pm 0.9\ s^{-1}$, $\Delta H^{\ddagger} = 84 \pm 10\ kJ\ mol^{-1}$ and $\Delta S^{\ddagger} = 4 \pm 28\ J\ mol^{-1}\ K^{-1}$.

Keywords: Ruthenium; Olefin metathesis; Phosphine exchange; Magnetisation transfer

1. Introduction

During the past 15 years olefin metathesis has developed into a synthetically very useful method in *e.g.* natural product and polymer synthesis [1]. The success of metathesis was also highlighted in the award of a Nobel Prize for the method in 2005 [2]. Especially the ruthenium based catalysts, developed by Grubbs and co-workers, have with their functional group tolerance, made a significant impact on organic synthesis [3]. The first ruthenium catalyst was prepared in 1992 and a few years later the catalyst [$(PCy_3)_2Cl_2Ru{=}CHPh$] was reported [4]. The second generation catalyst based on N-heterocyclic carbenes was discovered shortly thereafter and today a number of different catalysts for different purposes exist [5,6]. Both kinetic and theoretical investigations have been reported [7], but there is no detailed kinetic investigation of the actual catalytic reaction. In view of our longstanding interest in transition metal phosphine chemistry [8] we decided to investigate the effect of phosphine substituents on the second generation system and here we present the synthesis of [$(IMesH_2)(PPh_2Cy)Cl_2Ru{=}CHPh$] ($H_2IMes$ = 1,3-bis(mesityl)-4,5-dihydroimidazol-2-ylidene) and an investigation of activity in ring-closing metathesis and phosphine exchange behaviour.

2. Experimental

2.1. General procedures and materials

Air and water sensitive compounds were manipulated using standard Schlenk techniques under an atmosphere of dry argon or nitrogen or in a nitrogen-filled glove box. All chemicals used were of analytical grade or better. (H_2IMes)dichloro(phenylmethylene)(tricyclohexylphosphine)ruthenium (**1**) and diethyl diallylmalonate were purchased from Sigma Aldrich and used as received. [$(H_2IMes)(C_5H_5N)_2Cl_2Ru{=}CHPh$] (**2**) was prepared from **1** according to literature procedures [7b]. Dry solvents (distilled from Na or CaH_2) were used throughout the procedures and all glassware was oven dried. NMR measurements were performed on a Varian Unity INOVA 500 MHz spectrometer and recorded in C_6D_6 unless otherwise stated. Chemical shifts are given in parts per million downfield from TMS using residual solvent peaks (^1H) or H_3PO_4 (^{31}P δ 0) as external references. Coupling constants (J) are reported in hertz.

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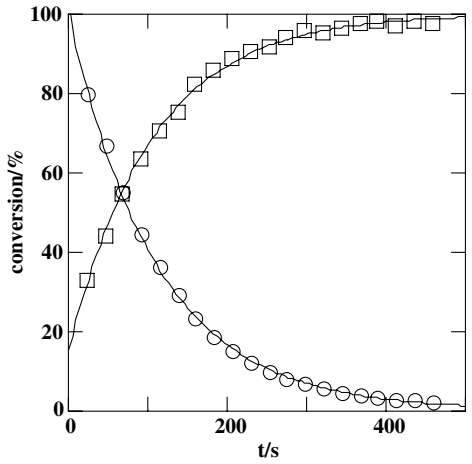


Fig. 1. Conversion of reactant and product in ring-closing metathesis (RCM) reaction (reaction (1)) as a function of time. The solid line denotes the best fit to a single exponential. Reaction monitored via ^{1}H NMR at 303 K; disappearance of the methylene protons in the starting material at δ 2.6 ppm and the concomitant growth of those in the product at δ 3.0 ppm; [diethyl diallylmalonate]$_0$ = 0.2 M; [**3**] = 0.01 M in CD_2Cl_2.

2.2. Preparations

2.2.1. [(IMesH$_2$)(PPh$_2$Cy)Cl$_2$Ru=CHPh] (3)

Compound **2** (0.15 g, 0.21 mmol) was stirred with diphenylcyclohexylphosphine (0.076 g, 0.28 mmol) in benzene (10 ml) for 10 min. The volume of the brown solution was then reduced to 2 ml and 5 ml of pentane was added. The solution was cooled with ice to 0 °C and stirred vigorously for 30 min to precipitate the product **3** (0.10 g; 53%) as a light brown powder. ^{1}H NMR: δ 0.6–1.22 ppm (m, 11H, PPh$_2$*Cy*), 1.5–2.2 (m, 18H, CH_3 on IMes), 5.8–6.5 (d, 4H, C_6H_2 of IMes, J = 21 Hz), 6.6–7.2 (m, 15H, P*Ph*$_2$Cy and =C*Ph*), 19.23 (d, 1H, Ru=CH, J = 27 Hz). ^{31}P NMR: δ 39.4 ppm (s).

2.3. Magnetisation transfer experiments

Phosphine exchange rates were determined by ^{31}P NMR magnetisation transfer (MT) experiments in C_6D_6. The free phosphine resonance was selectively inverted using a shaped pulse, calculated by the Pbox program of VnmrJ, and, after a variable mixing time (ranging between 5×10^{-5}–40 s), ^{31}P NMR spectra were recorded using a non-selective $\pi/2$-pulse. During the FID ^{1}H decoupling was applied. This was done for a series of free phosphine concentrations (0.037–0.137 M) and temperatures (343–373 K). The time-dependent magnetisation data were analysed using the computer program CIFIT [9].

2.4. Ring-closing metathesis kinetics

The ring-closing metathesis (RCM) reaction of 0.2 M diethyl diallylmalonate was catalysed by 0.01 M **3** in CD_2Cl_2 solvent in an NMR tube. The reaction was

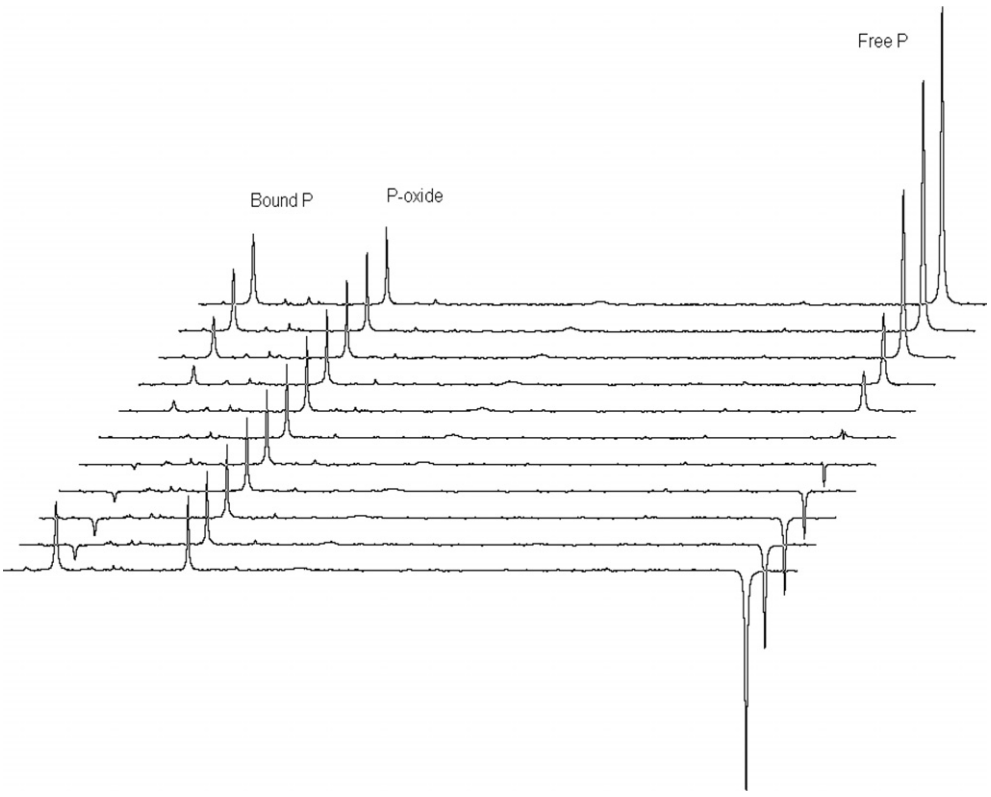


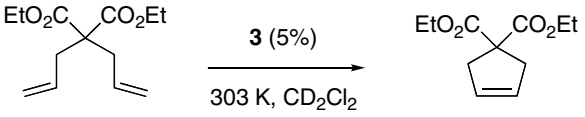
Fig. 2. Stacked ^{31}P NMR spectra in C_6D_6 showing signals of coordinated and free PPh$_2$Cy recorded after a selective inversion of the peak for free phosphine and various mixing times: 5×10^{-5}, 0.05, 0.1, 0.2, 0.5, 1, 2, 4, 8, 15 and 25 s. [**3**] = 0.023 M, [PPh$_2$Cy] = 0.067 M, T = 373 K.

monitored via NMR at 303 K by monitoring the disappearance of the methylene protons in the starting material at δ 2.6 ppm and the concomitant growth of those in the product at δ 3.0 ppm. The kinetic traces thus obtained were fitted to single exponentials.

3. Results and discussion

The new ruthenium complex, [$(H_2IMes)(PPh_2Cy)Cl_2$-Ru=CHPh] (**3**) was conveniently synthesised by a simple substitution reaction via the di-pyridine complex as previously reported for other phosphines [7b]. It was characterised by multi-nuclear NMR spectroscopy.

To investigate the potential catalytic activity of **3** it was tested in a ring-closing metathesis (RCM) reaction of commercially available diethyl diallylmalonate, illustrated in reaction (1) [10]. Diethyl diallylmalonate was chosen because RCM to diethyl cyclopentene dicarboxylate is relatively facile and the reaction is slow enough to be followed by ^{1}H NMR (in CD_2Cl_2), but also fast enough to be experimentally feasible. It has also been tested for a number of different catalysts and suggested as a benchmark reaction [11].



(1)

The kinetics of reaction (1) was examined at 303 K by following the decrease of starting material with time by ^{1}H NMR spectroscopy and the corresponding increase of product. The kinetic traces fitted well to single exponentials (cf. Fig. 1), showing that the reaction is first order in malonate.

The fit gave a value of the first-order rate constant of $(9.2 \pm 0.3) \times 10^{-3}$ s^{-1}, which, assuming a first-order dependence in ruthenium concentration [12], gives a second-order rate constant of 0.92 M^{-1} s^{-1}. This can be compared with the literature value for the corresponding PCy_3 catalyst which is 2.2 M^{-1} s^{-1} [13]. This catalyst also shows first-order behaviour with respect to the malonate as opposed to some other catalysts, which show induction periods and other more complicated behaviour [7d,11]. The rate law for the ring-closing metathesis is given in Eq. (2)

$$\text{Rate} = k[\text{malonate}][\text{Ru}] \tag{2}$$

Table 1
Exchange rate constants obtained at different phosphine concentrations in C_6D_6, [Ru] = 0.023 M, T = 353 K

[PPh_2Cy] (M)	k (s^{-1})
0.027	4.0 ± 0.1
0.067	5.0 ± 0.1
0.137	3.4 ± 0.1

To further probe the reactivity of **3** we decided to investigate the phosphine exchange. This is slow at room temperature giving rise to no visible line broadening in the ^{31}P NMR signal. A ^{31}P{^{1}H} spectrum of **3** and PPh_2Cy consists of one singlet from the free phosphine at −4 ppm and one from **3** at 37 ppm. In addition, a small peak from phosphine oxide at 29 ppm was always observed. This peak was unaffected by the experiment and it was regarded inert under the conditions chosen. In an experiment, the peak of the free phosphine was selectively inverted using a shaped 180° pulse and the peak heights of both the coordinated and the free phosphine were recorded as a function of pulse mixing time. The peak width did not change during the experiment. The reaction was treated as a simple two-site exchange according to Eq. (3)

$$P_{\text{free}} \underset{k_C}{\overset{k_F}{\rightleftharpoons}} P_{\text{coord}} \tag{3}$$

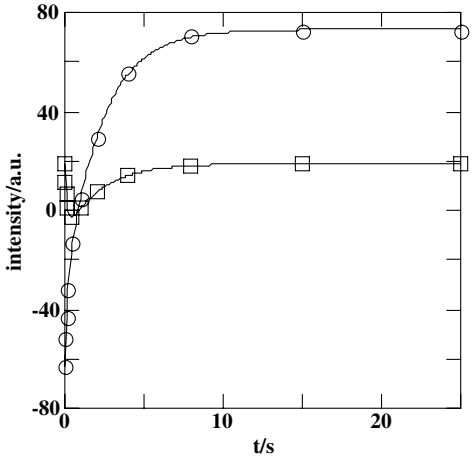


Fig. 3. Magnetisation of free and coordinated phosphine as a function of pulse mixing time. The solid lines were calculated using the parameters from the best fit and the computer program CIFIT. [**3**] = 0.023 M, [PPh_2Cy] = 0.067 M, T = 353 K, k_c = 0.935 s^{-1}, T_{1F} = 9.8 s, T_{1C} = 3.5 s.

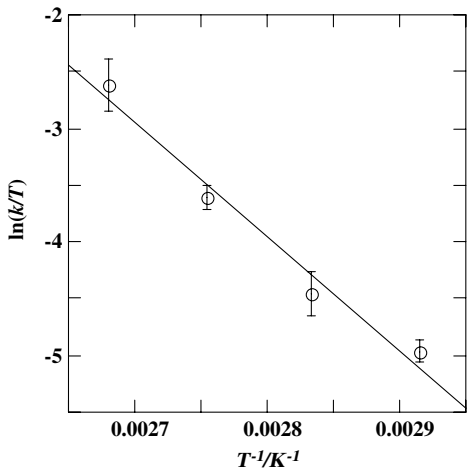


Fig. 4. Eyring plot for the phosphine exchange in **3**. Rate constants at 343, 353, 363 and 373 K are 2.4 ± 0.1, 4.1 ± 0.9, 9.8 ± 1.0 and 27.4 ± 5.6 s^{-1}, respectively.

Table 2
Comparison of phosphine exchange rate constants of **3** and values reported in literature

Catalyst	k (s^{-1})	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})	Ref.
1	0.13 ± 0.01	113 ± 8	54 ± 25	[7b]
3	4.1 ± 0.9	84 ± 10	4 ± 28	This work
[(IMesH$_2$)(PPh$_3$)Cl$_2$Ru=CHPh] (**4**)	7.5 ± 0.5	88 ± 13	21 ± 38	[7b]
[(PCy$_3$)$_2$Cl$_2$Ru=CHPh] (**5**)	9.6 ± 0.2	99 ± 2	50 ± 8	[7b]

$T = 353$ K.

The return of magnetisation to equilibrium is governed by the exchange rate constants, k_F and k_C, and the relaxation rate constants, $1/T_{1F}$ and $1/T_{1C}$ [14]. Taking into account the fact that $k_F = k_C([P_{coord}]/[P_{free}])$ (since the system is at equilibrium) this model was fitted to the time-dependent magnetisation data using the computer program CIFIT [9]. In most iterations the magnetisation at time zero and infinity were also treated as variable parameters. Fig. 2 shows a series of ^{31}P NMR spectra as a function of pulse mixing time, while Fig. 3 illustrates a typical example of data and the corresponding fit.

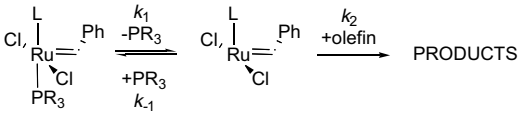
The exchange rate (R_{ex}) as predicted from Eq. (3), is given by (4), where the value of k_C thus obtained corresponds to an observed first-order rate constant for the exchange of a phosphine at the Ru metal centre:

$$R_{ex} = k_C[P_{coord}] = k[Ru] = k_F[PPh_2Cy] \quad (4)$$

Observed rate constants as a function of phosphine concentration are given in Table 1, showing that the rate is zero order in phosphine concentration, thus implying a dissociative mechanism where the rate determining step does not involve the phosphine ligand.

The temperature dependence of k was determined giving the Eyring plot in Fig. 4. Activation parameters are $\Delta H^{\ddagger} = 84 \pm 10$ kJ mol^{-1} and $\Delta S^{\ddagger} = 4 \pm 28$ J mol^{-1} K^{-1}. This is consistent with a dissociative mechanism which is also the accepted mechanism for olefin metathesis [7,10b,15,16]. Table 2 gives a comparison of the determined rate constant and activation parameters with some literature values. Although the entropy of the current exchange is close to zero the value of the enthalpy excludes an associative mechanism; as shown for complexes **1** and **4** an enthalpy in this range approximately corresponds to a Ru–P bond enthalpy and hence this bond must be broken in the transition state also in the exchange at **3** [7e,7f].

Sanford et al. [7] found that the rate constant for phosphine exchange for catalysts with the general structure [L(PR$_3$)Ru=CHR′] ranged over six orders of magnitude with variation in ligands (X, L, R, R′). As expected the rate of phosphine exchange for **3** is intermediate to that of **1** and **4**. In a dissociative process steric bulk is usually assumed to increase the reaction rate but for compounds **1**, **3** and **4** the opposite trend is observed, *i.e.* the most bulky phosphine, PCy_3, dissociates with the lowest rate. Of course, electronic factors must also be considered. Indeed, the most electron donating phosphine (as seen by *e.g.* the highest pK_a-value and the lowest Tolman electronic parameter [17]) also has the lowest rate of exchange. This also correlates fairly well with the enthalpy of activation which is around 25 kJ/mol higher for **1** compared to **3** and **4**, where the difference is small in comparison to the error, especially given that different solvents where used (C_6D_6 for **3** and toluene-d_8 for **1**, **4** and **5**).



Scheme 1.

In terms of catalytic activity the behaviour of **3** is very similar to that of **1** with a rate constant for RCM around two times lower. As expected the activity is much higher than that of the first generation catalysts. As noted before by Grubbs and co-workers the correlation between phosphine dissociation rate and catalytic activity is inverse [7]. By considering a general reaction as illustrated in Scheme 1 this was explained in terms of the k_{-1}/k_2 values, which are much lower for the second generation catalysts.

Compounds **1**, **3** and **4** give rise to the same intermediate (having the same L ligand in Scheme 1) and they therefore have the same the k_2-value for any given olefin and the k_{-1}/k_2 ratio will reflect the k_{-1} rate. For **1** and **4** it was reported that **1** had a slightly lower k_{-1}/k_2 ratio, indicating that k_{-1} is lower for the PCy_3 re-entry [18]. One could also argue that the lower activity of **3** is indicative of a higher k_{-1} rate for the PPh_2Cy entry. This would mean that phosphine dissociation is determined by electronic factors making it slowest for the most strongly binding phosphine, PCy_3, whereas the phosphine re-entry, which is an associative process, is mainly governed by steric factors thus being less favoured for more bulky phosphines. Clearly, this latter conclusion relies on several assumptions and further measurements would be needed to verify it.

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References

[1] R.H. Grubbs (Ed.), Handbook of Metathesis, vol. 3, Wiley-VCH, Weinheim, 2003.

[2] (a) Y. Chauvin, Angew. Chem., Int. Ed. 45 (2006) 3740;
(b) R.R. Schrock, Angew. Chem., Int. Ed. 45 (2006) 3748;
(c) R.H. Grubbs, Angew. Chem., Int. Ed. 45 (2006) 3760.
[3] (a) D.L. Wright, Curr. Org. Chem. 3 (1999) 211;
(b) D. Astruc, New J. Chem. 29 (2005) 42;
(c) M. Mori, Adv. Synth. Catal. 349 (2007) 121.
[4] (a) S.T. Nguyen, L.K. Johnson, R.H. Grubbs, J. Am. Chem. Soc. 114 (1992) 3974;
(b) S. T Nguyen, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 115 (1993) 9858;
(c) P. Schwab, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 118 (1996) 100.
[5] (a) M. Scholl, T.M. Trnka, J.P. Morgan, R.H. Grubbs, Tetrahedron Lett. 40 (1999) 2247;
(b) T. Weskamp, F.J. Kohl, W.A. Herrmann, J. Organomet. Chem. 582 (1999) 362;
(c) M. Scholl, S. Ding, C.W. Lee, R.H. Grubbs, Org. Lett. 1 (1999) 953;
(d) J. Huang, E.D. Stevens, S.P. Nolan, J.L. Petersen, J. Am. Chem. Soc. 121 (1999) 2674.
[6] (a) J.S. Kingsbury, J.P.A. Harrity, P.J. Bonitatebus, A.H. Hoveyda, J. Am. Chem. Soc. 121 (1999) 791;
(b) K. Grela, S. Harutyunyan, A. Michrowska, Angew. Chem., Int. Ed. 41 (2002) 4038;
(c) H. Wakamatsu, S. Blechert, Angew. Chem., Int. Ed. 41 (2002) 2403.
[7] (a) M.S. Sanford, M. Ulman, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 749;
(b) M.S. Sanford, J.A. Love, R.H. Grubbs, J. Am. Chem. Soc. 123 (2001) 6543;
(c) J.A. Love, M.S. Sanford, M.W. Day, R.H. Grubbs, J. Am. Chem. Soc. 125 (2003) 10103;
(d) E.L. Dias, S.T. Nguyen, R.H. Grubbs, J. Am. Chem. Soc. 119 (1997) 3887;
(e) F. Bernardi, A. Bottoni, G.P. Miscione, Organometallics 22 (2003) 940;
(f) C. Adlhart, P. Chen, J. Am. Chem. Soc. 126 (2004) 3496.
[8] See for example: (a) A.C. Ferreira, R. Crous, L. Bennie, A.M.M. Meij, K. Blann, B.C.B. Bezuidenhoudt, D.A. Young, M.J. Green, A. Roodt, Angew. Chem., Int. Ed. 46 (2007) 2273;
(b) M. Makunya, R. Meijboom, A.J. Muller, A. Roodt, J. Organomet. Chem. 690 (2005) 4159;
(c) R. Crous, M. Datt, D. Foster, L. Bennie, C. Steenkamp, J. Huyser, L. Kirsten, G. Steyl, A. Roodt, Dalton Trans. (2005) 1108;
(d) O.F. Wendt, R.J. Deeth, L.I. Elding, Inorg. Chem. 39 (2000) 5271;
(e) A. Fischer, O.F. Wendt, J. Chem. Soc., Dalton Trans. (2001) 1266.
[9] A.D. Bain, J.A. Cramer, J. Magn. Res. 118A (1996) 21.
[10] (a) S.T. Nguyen, R.H. Grubbs, J.W. Ziller, J. Am. Chem. Soc. 115 (1993) 9858;
(b) E. L Dias, S.T. Nguyen, R.H. Grubbs, J. Am. Chem. Soc. 119 (1997) 3887.
[11] T. Ritter, A. Hejl, A.G. Wenzel, T.W. Funk, R.H. Grubbs, Organometallics 25 (2006) 5740.
[12] A first-order dependence has been found for other catalysts, see Ref. [10b].
[13] This was studied under similar conditions but using a starting concentration of 0.1 M, see Ref. [11].
[14] J.J. Led, H.J. Gesmar, Magn. Res. 49 (1982) 444.
[15] S.F. Vyboishchikov, M. Bühl, W. Thiel, Chem. Eur. J. 8 (2002) 3962.
[16] S. Fomine, S.M. Vargas, M.A. Tlenkopatchev, Organometallics 22 (2003) 93.
[17] For values for PCy_3 and PPh_3 see: (a) R.C. Bush, R.J. Angelici, Inorg. Chem. 27 (1988) 681;
(b) A. Roodt, S. Otto, G. Steyl, Coord. Chem. Revs. 245 (2003) 125.
[18] The comparison has to be treated with some caution since the ratios were measured at different temperatures.