

Note

Metathesis of renewable unsaturated fatty acid esters catalysed by a phoban-indenylidene ruthenium catalyst

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Abstract

The phoban-indenylidene complex is a robust catalyst for self-metathesis and ethenolysis reactions of methyl oleate. The phoban-indenylidene catalyst was characterized by X-ray analysis, NMR and microanalysis and was used in various self-metathesis and ethenolysis of methyl oleate, giving rise to significantly higher end of run conversions compared to Grubbs 1st generation catalyst. These complexes are more stable and active than commercial Grubbs 1st generation catalyst, can be accessed from simple precursors and should give rise to more economical metathesis processes.

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Production of useful raw materials from natural resources is becoming more relevant as the availability of fossil fuel derived feedstocks slowly decreases [1]. In this regard, the built-in functionality, relatively low price and availability of natural seed oils render them feedstocks of the future for the chemical industry [2]. Fatty acid monoesters, such as methyl oleate, are usually derived from transesterification of seed oils with a lower alcohol, such as methanol, with concomitant production of glycerol as a by-product [3]. These feedstocks have already found application in several areas, including detergents, cosmetics and coatings, and in the bulk of these applications only the carboxy group present within oleochemicals is utilized [4].

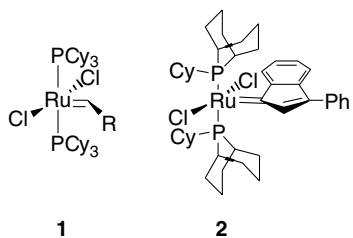
Ruthenium alkylidene complexes have attracted significant attention in recent years as efficient functional group tolerant catalysts for olefin metathesis [5]. Their relatively

high activity and ease of preparation has led to investigations of these catalysts towards metathesis of fatty acid methyl esters [6]. In particular, reactions of unsaturated fatty acid esters provide a convenient, efficient and environmentally benign route to a variety of useful commercial raw materials such as polar co-monomers [7]. Despite this, the metathesis of fatty acid methyl esters places large demands on Ru metathesis catalysts. The high carbon number (C18+) of oleochemicals can give rise to a large array of by-products if double-bond isomerisation and subsequent secondary metathesis reactions occur. In addition, the formation of equilibrium mixtures in oleochemical metathesis reactions requires a robust and temperature-stable catalyst that is capable of re-use and/or recycle [6].

We recently reported the preparation and catalytic activity of phosphabicyclononane-containing ruthenium carbene complexes [8]. These ruthenium based complexes show excellent stability to air and moisture, can be recycled by chromatography and are available from simple precursors. Herein, we report the efficiency of various metathesis

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reactions of methyl oleate catalysed by phoban-indenylidene catalyst **2** is significantly enhanced relative to Grubbs 1st generation catalyst **1**, a consequence of which is more economical processes.



We envisaged that combination of relatively inexpensive phosphorus containing ligands such as cyclohexylphoban with a Ru-indenylidene moiety could provide a non-hazardous, economic and scaleable route to Ru-alkylidene olefin metathesis catalysts [9]. The desired phoban-indenylidene complex **2** was prepared by treatment of a ca. 3:1 mixture of cyclohexylphoban with indenylidene derivative **3**, followed by precipitation from pentane (Scheme 1). Formation of **2** was monitored by ^{31}P NMR spectroscopy as the appearance of a very broad singlet at $\delta = 22.0$ ppm [10]. The signal for the single proton on C_β of the indenylidene appears as a singlet at 8.25 ppm in the ^1H NMR spectrum of **2**.

X-ray analysis [11] of **2** (Fig. 1) indicated a distorted square-pyramidal geometry about the metal center in which the carbene ligand occupies the apical position and the phosphine ligands in the basal plane occupy a *trans* position. The X-ray crystal structure of **2** confirmed that the complex bears cyclohexylphoban ligands and an indenylidene moiety.

The application of complex **2** towards the self-metathesis [12] and ethenolysis [13] of methyl oleate [14] (Scheme 2) was investigated and the results are depicted in Tables 1 and 2. For the self-metathesis of methyl oleate (Table 1) reactions were performed at 50 °C and were run neat. Self-metathesis reactions catalyzed by **2** gave rise to significantly higher end of run conversions compared to Grubbs 1st generation catalyst **1**. For example, with 0.0025 mol% of catalyst **2**, the self-metathesis of methyl oleate was achieved in 49% conversion after 3 h, whereas only 6.2% conversion was obtained using catalyst **1** (Entry 2, Table 1). A similar effect was observed when the substrate:cata-

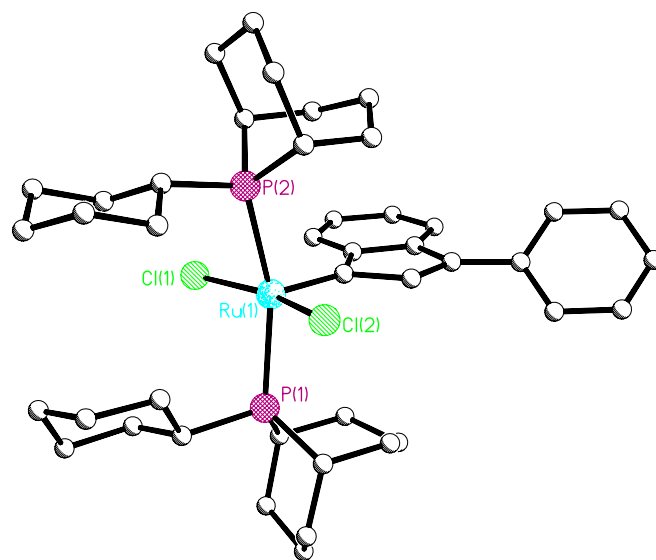
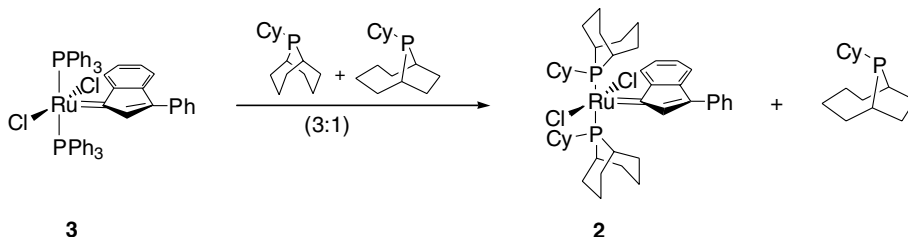


Fig. 1. Perspective drawing of $[(\text{PhobCy})_2\text{Cl}_2\text{Ru}=\text{C}_{15}\text{H}_{10}]$ (**2**).

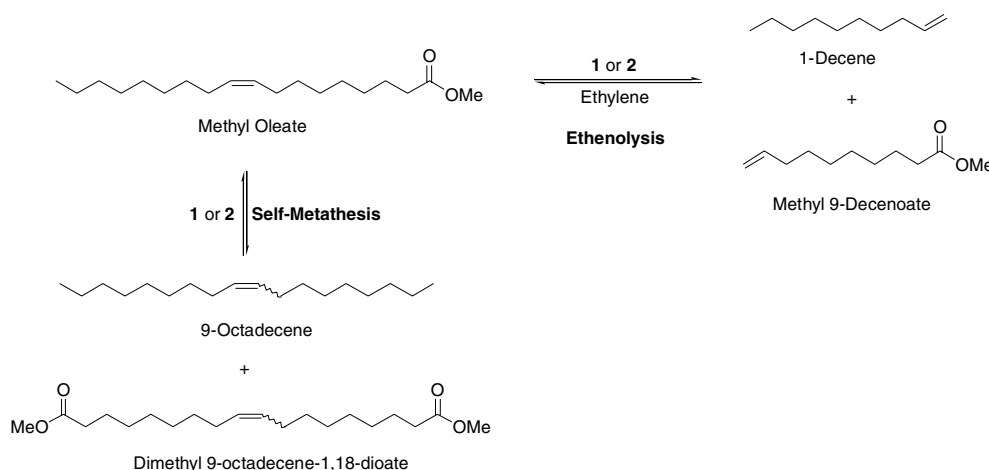
lyst ratio for the self-metathesis reaction was increased to 200 000:1 (Entry 3, Table 1), where 15 times more turnovers were achieved using catalyst **2**.

Interestingly, the self-metathesis of methyl oleate is only one of the few examples of metathesis reactions where the key propagating species is *not* a Ru methylidene species. Because the double-bond present within methyl oleate is internal, the propagating species becomes an alkylidene, a consequence of which should be a longer lived catalyst [15]. In addition, the absence of significant amounts of ethylene being produced or consumed in the reaction should reduce the amount of degenerate reactions of the active metathesis catalyst that can lead to unproductive metathesis [6]. Despite this, self-metathesis of methyl oleate catalysed by Grubbs 1st generation catalyst **1** affords poor conversions (Table 1). On the basis of the foregoing, it seems reasonable to suggest that decomposition of catalyst **1** does not necessarily require methylidene intermediates [16]. In addition, the results obtained above are consistent with our previous observations that phoban-based metathesis catalysts are less temperature sensitive than Grubbs 1st generation catalyst **1** [8].

Ethenolysis reactions of methyl oleate catalysed by phoban-indenylidene catalyst **2** gave rise to higher end of run conversions to 1-decene and methyl 9-decenoate compared



Scheme 1.



Scheme 2.

Table 1
Self-metathesis reactions of methyl oleate to 9-octadecene and dimethyl 9-octadecene-1,18-dioate via Ru-alkylidene catalysts

Entry ^a	Substrate: catalyst ratio ^b	Catalyst ^c	Conv. (%) ^{d,e}	Selectivity to products (%) ^d	Productive TON ^f
1	20000:1	1	10.5	94.5	1985
		2	49.6	97.8	9702
2	40000:1	1	6.2	92.1	2284
		2	49.0	97.3	19071
3	200000:1	1	2.5	93.7	4685
		2	37.1	96.5	71603

^a Reactions were reproducible within 95% accuracy.

^b Purified by passing through alumina before use.

^c 50 °C, neat, 3 h.

^d Determined by GC.

^e Reaction reaches equilibrium at 50% conversion.

^f Productive TON = TON × selectivity to required product.

Table 2
Ethenolysis reactions of methyl oleate to 1-decene and methyl 9-decenoate via Ru-alkylidene catalysts

Entry ^a	Substrate: catalyst ratio ^b	Catalyst ^c	Conv. (%) ^d	Selectivity to products (%) ^d	Productive TON ^e
1	5000:1	1	53.0	98.9	2621
		2	60.0	99.2	3229
2	10000:1	1	49.6	99.0	4918
		2	69.8	99.1	6917
3	20000:1	1	43.0	98.5	8542
		2	63.9	97.4	12450

^a Reactions were reproducible within 95% accuracy.

^b Purified by passing through alumina before use.

^c 10 bar ethylene, 50 °C, neat, 2 h.

^d Determined by GC.

^e Productive TON = TON × selectivity to required product.

to Grubbs 1st generation catalyst **1** (Table 2). For example, ethenolysis of neat methyl oleate at 50 °C using 10 bar of ethylene employing a substrate:catalyst ratio of 20000:1 afforded the desired products in 64% conversion using

catalyst **2** (Entry 3, Table 2). Under the same conditions, only 43% conversion was obtained using catalyst **1**. It should be noted that methyl oleate ethenolysis reactions catalysed by the phoban-indenylidene catalyst **2** can also be run at higher reaction temperatures. For example, ethenolysis of neat methyl oleate at 65 °C using 10 bar of ethylene employing a substrate:catalyst ratio of 30000:1 afforded the desired products in 41% conversion using catalyst **2**. Under the same conditions, only 13% conversion was obtained using catalyst **1**.

In summary, the phoban-indenylidene complex **2** is a robust catalyst for self-metathesis and ethenolysis reactions of methyl oleate. These Ru-indenylidene complexes are more stable and active than Grubbs 1st generation catalyst **1**, can be accessed from simple precursors and should give rise to more economical metathesis processes. Studies aimed at further increasing the efficiency and applicability of phoban metathesis catalysts are ongoing.

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- [10] Preparation of complex **2**: A solution of cyclohexylphoban (ca. 3:1, 672 mg, 3 mmol) in CH_2Cl_2 (10 ml) was added to a solution of complex **3** (1.0 g, 1.04 mmol) in CH_2Cl_2 (10 ml) under a nitrogen atmosphere and stirred at room temperature for 24 h. After such time the solvent was removed under vacuum and pentane (40 ml) was added. The resulting brown solid was filtered and washed with petroleum ether (40/60 fraction, 3×20 ml) to afford complex **2** as a brown powder (598 g, 72% yield). ^{31}P (^1H) NMR (121 MHz, C_6D_6): $\delta = 22.0$ (bs); ^1H NMR (300 MHz, C_6D_6): $\delta = 8.25$ (s, 1H, C-1), 7.80–6.75 (m, 9H), 2.80 (s, 4H, PCH of Phoban), 2.26–0.40 (m, 46H, Phoban H); ^{13}C (^1H) NMR (75 MHz, CD_2Cl_2): $\delta = 294.5$ (m, Ru = CH–), Anal. Calc., for $\text{C}_{43}\text{H}_{60}\text{Cl}_2\text{P}_2\text{Ru}$: C, 63.69; H, 7.46. Found: C, 63.68; H, 7.55%.
- [11] Red single crystals suitable for X-ray diffraction were obtained by evaporation of an ether solution. Several different crystals were examined and four different complete datasets were obtained. The best data were obtained using a small crystal and copper radiation. $\text{C}_{43}\text{H}_{60}\text{Cl}_2\text{P}_2\text{Ru}$, $M_r = 810.82$, monoclinic, space group $\text{P}2(1)/c$, $a = 22.336(9)$ Å, $b = 17.602(7)$ Å, $c = 9.796(4)$ Å, $\beta = 95.514(11)^\circ$, $V = 3834(3)$ Å³, $T = 173(2)$ K, $Z = 4$, $\rho_{\text{calcd}} = 1.357$ g cm⁻³, $\mu_{\text{Cu K}\alpha} 5.597$ mm⁻¹, Rigaku MM007 generator/Saturn92 detector, Cu K α radiation, 51939 reflections collected, 6839 unique [$R_{\text{int}} = 0.1491$], $R_1 = 0.1137$ (5916 observed reflections), $wR_2 = 0.2231$. Supplementary data are available from the Cambridge Crystallographic Data Centre, CCDC 606535. Although the relatively high R factor precludes detailed analysis of the bondlengths and angles, but this does not preclude overall establishment of the configuration and general formula.
- [12] Representative procedure: A 50 mL three-necked round bottom flask was fitted with a dry-ice reflux condenser, thermometer and septum. A needle was inserted through the septum and connected to a gas supply via a needle valve to ensure a slow and steady stream of argon through the reaction solution. Methyl oleate (15.0 g, 51 mmol) was added to the reaction vessel and the reaction was heated to 50 °C. Catalyst **2** (4.1 mg, 0.0051 mmol, substrate:catalyst ratio = 10 000:1) was weighed into an aluminum weighing tray and added to the reaction mixture. Samples were taken at regular intervals via syringe through the septum. Conversion and selectivity were measured by GC with an MDN column. Calibrations of products and methyl oleate were performed by preparing a range of known concentrations of standard solutions to obtain a calibration curve and by using an internal standard as reference. Reactions were reproducible within 95% accuracy.
- [13] Representative procedure: A 50 mL stainless-steel autoclave fitted with dip-tube for sampling was charged with methyl oleate (12 g, 40.0 mmol), tetradecane (2.5 g, internal standard), and saturated with ethylene. Catalyst **2** (8.1 mg, 0.010 mmol) was weighed and transferred into a Schlenk flask under argon, and dissolved in toluene (5 mL, degassed). An aliquot (1 mL) of this stock solution was transferred to the autoclave. The autoclave was pressurized (10 bar of ethylene) and heated via computerized temperature controller to the desired temperature. Samples were taken at regular intervals using a dip-tube. Samples were taken at regular intervals using a dip-tube apparatus, and conversion and selectivity were measured by GC with an MDN column using an internal standard as reference. Reactions were reproducible within 95% accuracy.
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