

(19) AUSTRALIAN PATENT OFFICE

(54) Title
Phosphorus containing ligands for metathesis catalysts

(51)⁶ International Patent Classification(s)
C07C 6/04 (2006.01) 20060101ALI2005100
B01J 31/24 (2006.01) 8BMEP **C07F**
C07F 15/00 (2006.01) 15/00
C08G 61/08 (2006.01) 20060101ALI2005100
C07C 6/04 8BMEP **C08G**
20060101AFI2005100 61/08
8BMEP B01J 20060101ALI2005100
31/24 8BMEP
PCT/ZA2003/000087

(21) Application No: 2003249331

(22) Application Date: 2003 .07 .04

(87) WIPO No: W004/005223

(30) Priority Data

(31) Number	(32) Date	(33) Country
2002/5387	2002 .07 .05	ZA

(43) Publication Date : 2004 .01 .23

(43) Publication Journal Date : 2004 .03 .11

(71) Applicant(s)
Sasol Technology (UK) Ltd

(72) Inventor(s)
McConnell, Ann Elizabeth Catherine, Dweyer, Catherine Lynn, Forman, Grant Stephen

(74) Agent/Attorney
Griffith Hack, Level 19 109 St Georges Terrace, Perth, WA, 6000

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
15 January 2004 (15.01.2004)

PCT

(10) International Publication Number
WO 2004/005223 A1

- (51) International Patent Classification⁷: C07C 6/04, C08G 61/08, B01J 31/24, C07F 15/00
- (74) Agent: LE ROUX, Mario; D M KISCH INC., P. O. BOX 781218, Sandton, 2146 (ZA).
- (21) International Application Number: PCT/ZA2003/000087
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 4 July 2003 (04.07.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 2002/5387 5 July 2002 (05.07.2002) ZA
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (for all designated States except US): SASOL TECHNOLOGY (PTY) LIMITED [ZA/ZA]; 1 Sturdee Avenue, Rosbank, Johannesburg, 2196 (ZA).

(72) Inventors; and

(75) Inventors/Applicants (for US only): DWEYER, Catherine, Lynn [ZA/ZA]; El Manor No. 6, Delius Street, SW5, Vanderbijlpark, 1911 (ZA). McCONNELL, Ann, Elizabeth, Catherine [GB/GB]; Purdie Building North Haugh, St. Andrews, Fife, Scotland, KY16 9ST (GB). FORMAN, Grant, Stephen [AU/AU]; 55 Watson Avenue, St. Andrews, Fife, Scotland, KY16 9st (GB).

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

WO 2004/005223 A1

(54) Title: PHOSPHORUS CONTAINING LIGANDS FOR METATHESIS CATALYSTS

(57) Abstract: The use of a phosphorus containing Ligand as a Ligand for a metathesis catalyst in a catalysed metathesis reaction wherein the phosphorus containing Ligand is a heterocyclic organic compound with a ligating phosphorus atom as an atom in the heterocyclic ring structure of the heterocyclic organic compound. The invention also relates to a metathesis catalyst such a phosphorus containing Ligand and to a metathesis reaction using the catalyst.

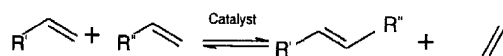
Technical Field

The invention relates to the use of a phosphorus containing ligand in the preparation of a metathesis catalyst and to the use of a phosphorus containing
 5 ligand in a catalysed metathesis reaction. The invention also relates to a metathesis catalyst including such a phosphorus containing ligand and to a metathesis reaction using the catalyst.

Background to the invention

10

There is considerable interest regarding the formation of carbon-carbon bonds via olefin metathesis. Olefin metathesis (or disproportionation) refers to the metal-catalysed redistribution of carbon-carbon double bonds. Cross metathesis (CM) can be described as a metathesis reaction between two non-cyclic olefins,
 15 which may be the same or different, for example:



Where the olefins are the same, the reaction is known as self metathesis.

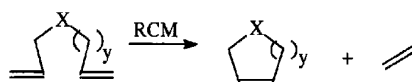
20 Ring-opening metathesis polymerization (ROMP) is a variant of olefin metathesis reactions wherein cyclic olefins (for example) produce polymers and co-polymers, for example:

2



Ring-closing metathesis (RCM) represents a process in which an acyclic diene (for example) is cyclised to produce a cycloalkene, for example;

5



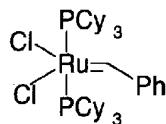
As indicated above metathesis reactions take place in the presence of a catalyst.

A great deal of research has been done in an attempt to synthesise and isolate catalysts which are able to catalyse homogeneous olefin metathesis reactions.

- 10 More particularly the synthesis of Group VIII transition metal metathesis catalysts has lead to catalysts with increased functional group tolerance and stability with respect to conditions such as air, water and acids.

During the 1990's the so-called "1st generation Grubbs catalyst" of formula **1a**

- 15 was developed:



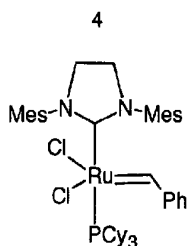
.....(1a)

- 20 where Cy is cyclohexyl.

This well defined ruthenium (Ru) alkylidene catalyst afforded high selectivities, high reaction rates and good tolerance for oxygenates in feed during homogeneous olefin metathesis reactions, including cross metathesis, ring closing metathesis and ring opening metathesis polymerisation. These processes
5 have many potential commercial applications for the commodities, pharmaceutical and fine chemicals industries as well as in the field of speciality polymers. Several reviews describe the development and applications of Grubbs-type catalysts (for example *Acc. Chem. Res.* 2001, 34, 18-24; *Angew. Chem., Int. Ed.*, 2000, 39, 3012-3043).

10

Much research has been carried out to investigate the effect of changing the nature of the ligands, (for example *J. Am. Chem. Soc.* 1997, 119, 3887 – 3897; *Tetrahedron Lett.* 1999, 40, 2247-2250; *Angew. Chem., Int. Ed.* 1998, 37, 2490-2493) resulting in the development of second generation Grubbs catalysts. The
15 main thrust of second generation Grubbs catalyst research has related to a move away from the use of phosphine ligands to the use of highly nucleophilic N-heterocyclic carbenes for homogeneous metathesis reactions. Formula **1b** shows the structure of the standard second generation Grubbs catalyst. While this catalyst shows greater reactivity compared to catalyst **1a**, it is more expensive
20 than the first generation catalyst.

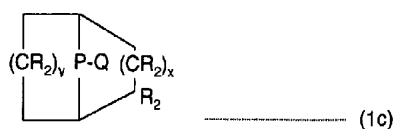


where Cy = cyclohexyl and Mes = mesityl

.....(1b)

5

In the case of hydroformylation reactions, research has continued into the use of phosphine ligands. It will be appreciated that in a hydroformylation process an olefinic feedstock is reacted with carbon monoxide and hydrogen at elevated temperatures and pressures in the presence of a hydroformylation catalyst to produce oxygenated products. The hydroformylation catalyst is selected according to the particular oxygenated products which are required from a particular olefinic feedstock and may typically be phosphine and/or phosphite ligand modified rhodium (Rh) or cobalt (Co) catalyst. Many different phosphine and phosphite ligands have been suggested in the past. For example US 3,400,163 discloses bicyclic heterocyclic sec-and tert-phosphines of the general formula **1c** and it is stated that these phosphines are useful in the hydroformylation of olefins.



US 3,420,898 discloses olefin hydroformylation reactions in the presence of a cobalt catalysts with phosphine ligand of formula **1c**.

5 Research has indicated that those phosphine ligands which appeared to lead to catalysts with higher selectivities and reaction rates in homogeneous metathesis reactions were often not suitable for the types of catalysts used in hydroformylation reactions, for example $\text{HCo}(\text{CO})_3\text{P}$ where P represents a phosphine ligand, for example tricyclohexyl phosphine (PCy_3).

10

However, it has now surprisingly been found that certain relatively inexpensive (compared to second generation Grubbs catalysts) phosphorus containing ligands such as phosphabicyclononane ligands, which have been used in hydroformylation reactions, provide excellent stability, product yields and selectivities when used in a homogeneous metathesis catalyst. In addition, it has surprisingly been found that metathesis catalysts incorporating these phosphorus containing ligands in at least some cases show enhanced resistance to feed impurities. Furthermore, in at least some cases these catalysts afford superior performance for ring closing metathesis, ring opening metathesis polymerization and cross metathesis when compared to the standard first generation Grubbs catalyst (**1a**). When compared to the rather expensive standard second generation Grubbs catalyst (**1b**), in at least some cases their activity is comparable while the reaction selectivity is often superior.

15

20

Summary of the invention

According to a first aspect of the present invention there is provided the use of a phosphorus containing ligand as a
5 ligand for a metathesis catalyst in a catalysed metathesis reaction wherein the phosphorus containing ligand is a heterocyclic organic compound in the form of a phosphabicycloalkane with a ligating phosphorus atom as an atom in the heterocyclic ring structure of the
10 heterocyclic organic compound.

According to a second aspect of the present invention there is provided the use of a phosphorus containing ligand in the preparation of a catalyst containing the
15 ligand, which catalyst is for use in a metathesis reaction, wherein the phosphorus containing ligand is a heterocyclic organic compound in the form of a phosphabicycloalkane with a ligating phosphorus atom as an atom in the heterocyclic ring structure of the
20 heterocyclic organic compound.

According to a third aspect of the present invention there is provided a metathesis catalyst which includes a phosphorus containing ligand which is a heterocyclic
25 organic compound in the form of a phosphabicycloalkane with a ligating phosphorus atom as an atom in the heterocyclic ring structure of the heterocyclic organic compound.

30 In one embodiment, the metathesis reaction is a homogenous metathesis reaction.

In another embodiment, the ligating phosphorus atom is also bound to a further moiety which is not part of the
35 heterocyclic ring structure.

In a further embodiment, the phosphorus containing ligand

comprises a phosphine ligand. In a preferred form of the invention, the phosphorus containing ligand comprises a secondary or tertiary phosphine ligand. In an even more preferred form, the phosphorus containing ligand comprise
5 a tertiary phosphine ligand. The further moiety bound to the ligating phosphorus atom may be an atom, and preferably it is H. In an alternative and preferred embodiment of the invention the said moiety may comprise an organyl. The organyl may comprise an alkyl, alkenyl,
10 alkynyl, aryl, cycloalkyl, cycloalkenyl, cycloalkynyl and optionally it may be substituted. In subsequent embodiments it comprises alkyl, cycloalkyl or aryl.

According to one embodiment, the heterocyclic organic
15 compound comprises a single heteroatom in the form of the ligating phosphorus atom.

The heterocyclic organic compound may comprise a bicyclic organic compound. In one embodiment the heterocyclic
20 organic compound includes no unsaturated carbon to carbon bonds. The two ring structures may have at least 3 shared atoms. The two ring structures may not have more than 12 ring atoms. For instance in one preferred embodiment, they have nine ring atoms.

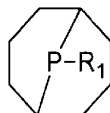
25 In another embodiment of the invention the phosphine ligand comprises a bicyclic tertiary phosphine having a ligating phosphorus atom which is preferably bound to two first atoms (preferably carbon atoms) in the ring
30 structure with each of said first atoms being bound to two other second atoms (preferably carbon atoms) in the ring structure. Both the second atoms may be carbon atoms.

It will be appreciated that in this embodiment each first
35 atom is bound to three ring atoms.

In another embodiment of the invention the heterocyclic

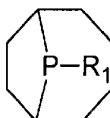
organic compound comprises a phosphabicyclononane, each of which optionally may be substituted. In further embodiments, it comprises a monophosphacycloalkane, such as a monophosphabicycloalkane, and preferably a
5 monophosphabicyclononane. The compound may comprise a tertiary phosphine.

In a further embodiment of the invention, the phosphabicyclononane is a 9-phosphabicyclo[3.3.1]nonane of
10 formula 2a or a 9-phosphabicyclo[4.2.1]nonane of formula 2b or mixtures thereof:



15

..... (2a)



..... (2b)

20

wherein R_1 is H or an organyl. Preferably R_1 is an optionally substituted alkyl, or optionally substituted aryl, or an optionally substituted cycloalkyl.

25 The phosphabicyclononane may be a compound of formula 2a.

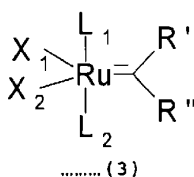
In one embodiment of the invention R_1 is alkyl, preferably $-C_{20}H_{41}$ also known as eicosyl. In this instance the ligand is known as eicosyl phoban (that is for both compounds of
30 formula 2a and 2b where R_1 is $-C_{20}H_{41}$).

In one embodiment of the invention R_1 is cyclohexyl. In this instance the ligand is known as cyclohexyl phoban (that is for both compounds of formula 2a and 2b where R_1 is cyclohexyl).

The catalyst or metathesis catalyst may comprise a transition metal based catalyst, preferably a group VIII metal based catalyst, preferably a Ru based catalyst. The catalyst may comprise ligands as defined below.

The metathesis reaction may comprise cross metathesis (including self metathesis and ethenolysis), ring-opening metathesis polymerisation or ring-closing metathesis.

According to another aspect of the present invention there is provided a compound formula 3:



wherein L_1 is a neutral electron donor ligand;
 L_2 is a phosphorus containing ligand in the form of a heterocyclic organic compound in the form of a phosphabicycloalkane with a ligating phosphorus atom as an atom in the heterocyclic ring structure of the heterocyclic organic compound;
 X_1 and X_2 are independently selected from an anionic ligand; and
 R' and R'' are independently selected from H or an organyl.

The compound may comprise a catalyst, such as a metathesis catalyst. In a preferred embodiment the compound comprises a homogeneous metathesis catalyst.

5

Ligand L₁

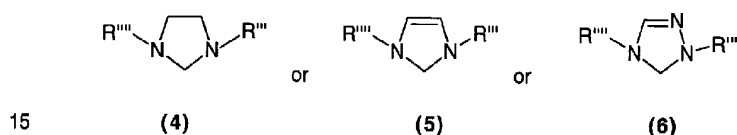
L₁ may be selected from the group consisting of phosphine, sulfonated phosphine, phosphite, phosphinite, phosphonite, 10 arsine, stibine, amine, amide, imine, nitrosyl, carbene and pyridine. In a preferred embodiment of the invention L₁ may be any neutral phosphine ligand or carbene ligand. L₁ may be a _____

phosphine preferably a phosphine of the formula $PR^3R^4R^5$, wherein R^3 , R^4 and R^5 are each independently aryl, $C_1 - C_{10}$ alkyl or cycloalkyl. Preferably L_1 is selected from the group consisting of $-P(\text{cyclohexyl})_3$; $-P(\text{cyclopentyl})_3$; $-P(\text{isopropyl})_3$; and $-P(\text{phenyl})_3$. Preferably it comprises a neutral phosphine ligand as

5 defined in respect of L_2 . Accordingly L_1 may be the same as L_2 .

In another embodiment of the invention L_1 may be selected from a group of heterocyclic compounds containing substituted or unsubstituted five membered rings which may be saturated or unsaturated and which may include at least two

10 adjacent or non adjacent nitrogen atoms as part of the group. Examples of such ligands are illustrated as formulas 4, 5 and 6:



wherein R''' and R'''' may be any group such as H or an organyl, including alkyl, aryl, cycloalkyl, adamantyl or the like, and may be further substituted with

20 functional groups.

Ligand L_2

L_2 is preferably a phosphorus containing ligand as already described above.

25 Namely, the phosphorus containing ligand may comprises a phosphine ligand,

preferably a secondary or tertiary phosphine ligand, preferably a tertiary phosphine ligand. The ligating phosphorus atom may also be bound to a further moiety which is not part of the heterocyclic ring structure. The further moiety bound to the ligating phosphorus atom may be an atom, and preferably it is H. In
5 an alternative and preferred embodiment of the invention the said moiety may comprise an organyl. The organyl may comprise an alkyl, alkenyl, alkynyl, aryl, cycloalkyl, cycloalkenyl, cycloalkylenyl and optionally it may be substituted. Preferably it comprises alkyl, cycloalkyl or aryl.

10 Preferably the heterocyclic organic compound has a single heteroatom in the form of the ligating phosphorus atom.

The heterocyclic organic compound may comprise a bicyclic organic compound. Preferably the heterocyclic organic compound includes no unsaturated carbon to
15 carbon bonds. Preferably the two ring structures have at least 3 shared atoms. Preferably the two ring structures do not have more than 12 ring atoms, preferably they have nine ring atoms.

In a preferred embodiment of the invention the phosphine ligand comprises a
20 bicyclic tertiary phosphine having a ligating phosphorus atom which is preferably bound to two first atoms (preferably carbon atoms) in the ring structure with each of said first atoms being bound to two other second atoms (preferably carbon atoms) in the ring structure. Preferably both the second atoms are

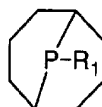
carbon atoms. It will be appreciated that in this embodiment each first atom is bound to three ring atoms.

In a preferred embodiment of the invention the heterocyclic organic compound
5 comprises a phosphacycloalkane, preferably a phosphabicycloalkane, preferably a phosphabicyclononane, each of which optionally may be substituted. Preferably it comprises a monophosphacycloalkane, preferably a monophosphabicycloalkane, preferably a monophosphabicyclononane. Preferably the compound comprises a tertiary phosphine.

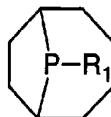
10

In a preferred embodiment of the invention, the phosphabicyclononane is a 9-phosphabicyclo-[3.3.1]nonane of formula 2a or a 9-phosphabicyclo[4.2.1] nonane of formula 2b or mixtures thereof:

15



..... (2a)



..... (2b)

20 wherein R₁ is H or an organyl. Preferably R₁ is an organyl, preferably an optionally substituted alkyl, or optionally substituted.

aryl, or an optionally substituted cycloalkyl. The phosphabicyclononane may be a compound of formula 2a.

In one embodiment of the invention the organyl comprises alkyl, preferably $-C_{20}H_{41}$ also known as eicosyl. In this instance the
5 ligand is known as eicosyl phoban (that is for both compounds of formula 2a and 2b where R_1 is $-C_{20}H_{41}$).

In one preferred embodiment of the invention R_1 is cyclohexyl. In this instance the ligand is known as cyclohexyl phoban (that is for
10 both compounds of formula 2a and 2b where R_1 is cyclohexyl).

Ligands X_1 and X_2

X_1 and X_2 may be independently selected from hydrogen; halide; or a compound
15 selected from the group consisting of $C_1 - C_{20}$ alkyl; aryl; $C_1 - C_{20}$ alkoxide; aryloxy; $C_3 - C_{20}$ alkyldiketonate; aryldiketonate; $C_1 - C_{20}$ carboxylate; arylsulfonate; $C_1 - C_{20}$ alkylsulfonate; $C_1 - C_{20}$ alkylthiol; aryl thiol; $C_1 - C_{20}$ alkylsulfonyl; and $C_1 - C_{20}$ alkylsulfinyl, the compound being optionally
20 $C_1 - C_{10}$ alkyl; $C_1 - C_{10}$ alkoxy; aryl and halide. Preferably X_1 and X_2 are each independently selected from the group consisting of halide; CF_3CO_2 ; CH_3CO_2 ; CFH_2CO_2 ; $(CH_3)_3CO$; $(CF_3)_2(CH_3)CO$; $(CF_3)(CH_3)_2CO$; PhO; MeO; EtO; tosylate; mesylate; and trifluoromethanesulfonate. Preferably X_1 and X_2 are each independently selected from halide. Preferably X_1 and X_2 are each chloride.

Substituents R' and R''

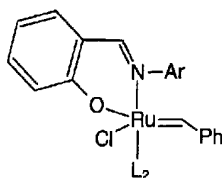
R' and R'' are each independently selected from hydrogen or an organyl selected
5 from the group consisting of C₁-C₂₀ alkyl; C₂-C₂₀ alkenyl; C₂-C₂₀ alkynyl; aryl; C₁-
C₂₀ carboxylate; C₁-C₂₀ alkoxy; C₂-C₂₀ alkenyloxy; C₂-C₂₀ alkynyloxy; aryloxy; C₂-
C₂₀ alkoxy-carbonyl; C₁-C₂₀ alkylthio; aryl thiol; C₁-C₂₀ alkylsulfonyl and C₁-C₂₀
10 alkylsulfinyl, the organyl being optionally substituted with one or more moieties
preferably selected from the group consisting of C₁-C₁₀ alkyl; C₁-C₁₀ alkoxy; aryl;
and a functional group selected from the group consisting of hydroxyl; thiol;
thioether; ketone; aldehyde; ester; ether; amine; imine; amide; nitro; carboxylic
acid; disulfide; carbonate; isocyanate; carbodiimide; carboalkoxy; carbamate; and
halogen. Preferably R' is hydrogen and R'' is phenyl or vinyl, optionally
substituted with one or more moieties selected from the group consisting of C₁-C₅
15 alkyl; C₁-C₅ alkoxy; phenyl; and a functional group selected from the group
consisting of hydroxyl; thiol; thioether; ketone; aldehyde; ester; ether; amine;
imine; amide; nitro; carboxylic acid; disulfide; carbonate; isocyanate;
carbodiimide; carboalkoxy; carbamate; and halogen. Preferably R' is H and R'' is
phenyl or -C=C(CH₃)₂.

20

In some cases some of the ligands X₁, X₂, L₁, L₂, R' and R'' may be linked to
each other, for example:

25

L₁ to X₁ for example to form a bidentate Schiff base ligand such as:



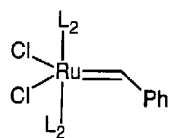
5

wherein L_2 is as defined above.

In a preferred embodiment of the invention, the catalyst may be of the structure of formula 7, wherein L_2 is the same or different and is as defined above.

10 Preferably L_2 are the same and preferably L_2 is a phosphabicyclononane ligand.

In a preferred embodiment L_2 may be a 9-phosphabicyclononane ligand of formula 2a or 2b. Preferably L_2 is cyclohexyl phoban.



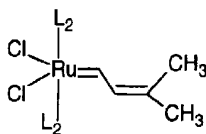
.....(7)

15

In another preferred embodiment of the invention, the catalyst may be of the structure of formula 8, wherein L_2 is the same or different and is as defined above. Preferably L_2 are the same and preferably L_2 is a phosphabicyclononane ligand. In a preferred embodiment L_2 may be a 9-phosphabicyclononane ligand

20 of formula 2a or 2b. Preferably L_2 is cyclohexyl phoban.

17



.....(8)

According to another aspect of the invention there is provided the use of a
5 catalyst of formula 3 above in a metathesis reaction, preferably a homogeneous
metathesis reaction.

The reaction is preferably a homogeneous metathesis reaction of preferably at
least one olefinic compound and the reaction conditions for the metathesis
10 reaction wherein the catalyst of formula 3 is used may be in accordance to
conditions which are well known to a person skilled in the art of metathesis
reactions.

The at least one olefinic compound may comprise an olefin with one or more
15 double bonds or a compound which includes an olefinic moiety with one or more
double bonds. Preferably the olefinic compound has a single double bond in the
case of a cross-metathesis reaction. Preferably the olefinic compound has two
double bonds in the case of a ring-closing metathesis reaction. Preferably the
olefinic compound is a cyclic olefin in the case of a ring-opening metathesis
20 polymerisation reaction.

According to a further aspect of the invention there is provided a metathesis product produced by a metathesis reaction using a catalyst substantially as described hereinabove.

- 5 The metathesis catalyst may be a Grubbs catalyst of formula 3 hereinbefore, preferably a homogeneous metathesis catalyst.

According to yet a further aspect of the invention there is provided a catalysed metathesis reaction wherein at least one olefinic compound is subjected to
10 metathesis in the presence of a catalyst of the type described hereinbefore. Preferably the metathesis reaction is a homogeneous metathesis reaction.

According to yet a further aspect of the invention there is provided a process for a ring closing metathesis reaction in the presence of a catalyst of the type
15 described hereinbefore. According to yet a further aspect of the invention there is provided a process for a ring opening metathesis polymerization reaction in the presence of a catalyst of the type described hereinbefore. According to yet a further aspect of the invention there is provided a process for a cross or self metathesis reaction in the presence of a catalyst of the type described
20 hereinbefore. The cross metathesis reaction may specifically be an ethenolysis reaction (where one of the two olefinic compounds is ethylene). The metathesis reactions preferably comprise homogeneous metathesis reactions.

- The process may further be characterised therein that the catalyst may be formed in situ. The process may then include the steps of adding together sufficient quantities of a source of ruthenium which may be an inorganic salt of ruthenium e.g. $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$, a source of ligand in the form of L_2 described above,
- 5 a precursor which would form the carbene structure on the central Ru atom for example an alkyne like butynedioldiacetate and a requisite starting material for the metathesis reaction.
- 10 Without thereby limiting the scope of the invention it will now be further described with reference to the following examples.

Example 1

15 IN SITU FORMED CATALYSIS

- This example is in respect of the homogeneous metathesis of 1-octene to form 7-tetradecene using an *in situ* formed catalyst system with a ruthenium concentration of 100ppm. The comparison is between the phosphine ligands
- 20 eicosyl phoban (EP) and PCy_3 as ligands in an *in situ* formed metathesis catalyst.

General experimental procedure:

- Reactions were carried out in a 100 ml three-necked flask fitted with a reflux
- 25 condenser, thermometer and septum. The reflux condenser was connected to a

cooling bath to ensure a constant flow of chilled water through the jacket, thereby preventing loss of octene. The top of the condenser was connected to a cold trap and bubbler in order to monitor liquid losses and gas emissions. The thermometer was positioned below the level of the reaction solution to ensure correct temperature monitoring. The reaction flask was purged with argon to ensure removal of oxygen. The reagents [EP or PCy₃, RuCl₃.xH₂O and 1,4-butyne-1,3-diol diacetate (BDD) and 1-octene] were added to the flask under inert conditions, then a slow hydrogen sparge (2 bubbles per second) was started and maintained during the reaction. The reaction mixture was heated, with stirring, to the desired temperature. Samples were taken at regular intervals with a syringe through the septum and quenched with a mixture of toluene and two drops of *t*-butylhydroperoxide. Samples were analyzed by GC using a Pona column. Unless otherwise stated, 20 ml of octene was employed in all experiments, and catalyst, solvent and additive amounts were calculated relative to this. Octadecane in an amount of 0.5ml was used as internal standard. The conversion percentages (as molar%) of 1-octene to 7-tetradecene are provided in Figures 1 and 2.

1.1 Comparison of EP and PCy₃ as ligands in the metathesis reaction at 50°C

20

It is evident from the graph in Figure 1 that EP performs far better than PCy₃ at 50°C, affording higher reaction rates and conversions.

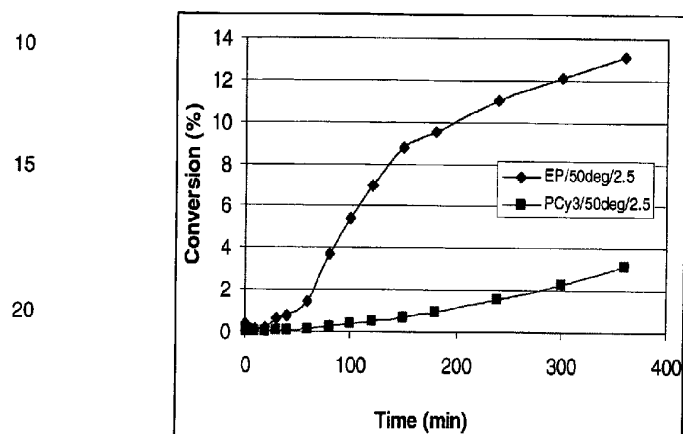
Reaction conditions:

100 ppm Ru

2.5:1 phosphine ligand :ruthenium (molar ratio)

10:1 BDD:Ru (molar ratio)

5 T = 50°C

Figure 11.2 Comparison of EP and PCy₃ as ligands in the metathesis reaction at25 110°C.

It is evident from the graph in Figure 2 that at high temperatures, EP shows similar reaction rates and affords higher yields at lower ligand concentrations (1.5:1 molar ratio for EP versus 2.5:1 molar ratio for PCy₃).

30

Reaction conditions:

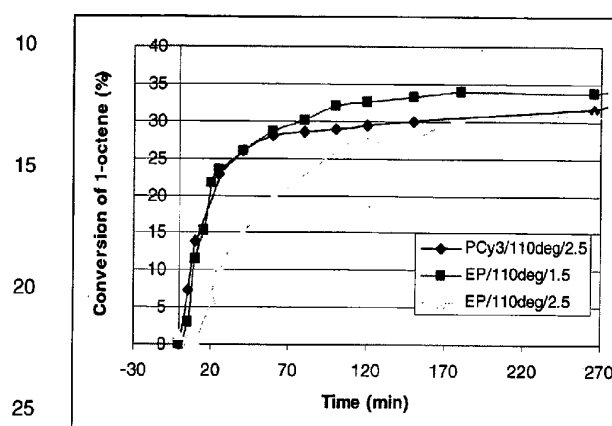
100 ppm Ru

2.5:1 and 1.5:1 phosphine ligand :ruthenium (molar ratio)

10:1 BDD:Ru (molar ratio)

5 T = 110°C

Figure 2



At higher temperatures with a 2:5 molar ratio of phosphine ligand to ruthenium, PCy₃ affords improved reaction rates compared to the corresponding EP reaction which is slower. However EP catalyst stability is sustained over a far longer period, and the end of run conversions are the same for both. This suggests that EP coordinates more strongly to the metal center, thereby giving added catalyst stability but slowing reaction rates as phosphine dissociation is hindered.

[According to the generally accepted reaction mechanism, phosphine dissociation is required before metathesis can proceed].

In order to further explore this, less ligand was added (EP or PCy₃: Ru molar ratio
5 of 1.5:1). In the case of PCy₃ [not shown] lower ligand concentrations led to poorer yields of the desired metathesis product, presumably due to lower catalyst stabilities. However in the case of EP, lower ligand concentrations afforded improved reaction rates and yields. Thus at 110°C, only 1.5 equivalents of EP
10 are required to get similar reaction rates and improved yields of desired product relative to those obtained with 2.5 equivalents of PCy₃. The reduced amount of ligand required allows a tremendous reduction in process costs.

Example 2

15 PREFORMED CATALYSTS

Preparation of cyclohexyl phoban is as follows:

A 3-neck round bottomed flask equipped with pressure-equalising dropping
20 funnel was charged with 1,5-cyclooctadiene (de-oxygenated, 5.3 mL, 4.663 g, 4.31×10^{-2} mols) and cyclohexylphosphine (6.0 mL, 5.250 g, 4.52×10^{-2} mols) and heated to 105°C. A toluene (d/d/d, 20 ml) solution of VAZO® (VAZO® = 1,1'-Azobis(cyclohexanecarbonitrile; 3 g) was then added dropwise to the vigorously stirred solution over 2 hours and the solution heated at 105°C for a further 21

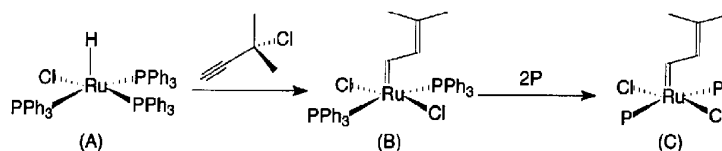
hours. At this point a further 0.5 g of VAZO® (as a solid) was added to the reaction mixture and heating continued for a further 8 hours. After this time the volatiles were removed *in vacuo* to leave a viscous, pale yellow, oil.

- 5 The oil was subjected to a short-path distillation (fraction distilling at >96°C collected) to leave a white, waxy solid (analysis showed this to be contaminated with VAZO decomposition products). This solid was then subjected to a Kugelrohr distillation and the fraction distilling at ~110°C recovered (4.570 g, 47 % as a white, waxy solid). The ligand was isolated as a 3:1 mixture of [3.3.1] and [4.2.1] isomers; ³¹P NMR (C₆D₆): 13.6, -25.3 ppm. That is cyclohexyl phoban formed, that is the compound of formula 2a and 2b wherein R₁ is cyclohexyl.
- 10

The catalysts were prepared according to the following reaction scheme.

Complex B was prepared using the known literature method of Fogg et al [D.

- 15 Amoroso, J. L. Snelgrove, J. C. Conrad, S. D. Drouin, G. P. A. Yap and D. E. Fogg, *Adv.Synth. Catal.*, **2002**, *344*, 757].



- 20 A specific procedure for preparation of the compound of formula 8 wherein L₂ is cyclohexyl phoban from complex B via this route is as follows:

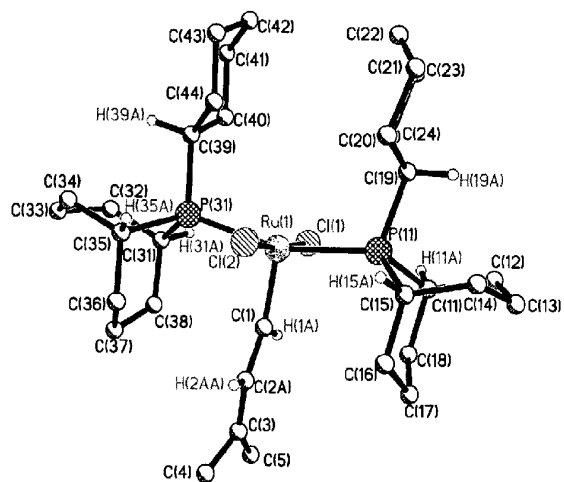
25

A solution of cyclohexyl phoban (0.65 mmol) in CH_2Cl_2 (10 ml) was added dropwise to complex (B) (0.26 mmol) in CH_2Cl_2 (10 ml) and stirred overnight at room temperature. The solution turned from dark brown to purple. The solvent was removed *in vacuo* followed by the addition of petroleum ether (20 ml). The solution was cooled to $-15\text{ }^\circ\text{C}$ to precipitate the product of formula 8 wherein L_2 is cyclohexyl phoban as a purple solid (0.14 mmol, 55% yield). ^{31}P NMR (121.4 MHz, CD_2Cl_2) δ 22 (very broad); ^1H NMR (300 MHz, CD_2Cl_2) δ 19.6 (d, Ru=CH, 1H, $^3\text{J}_{\text{HH}} = 11.52$ Hz), 8.2 (d, Ru=CHCH, 1H, $^3\text{J}_{\text{HH}} = 11.7$ Hz). ^{13}C NMR (75.4 MHz, CD_2Cl_2) δ 284 (m, Ru=C). The X-ray crystal structure for this complex is shown below in Figure 3. Selected bond length and angle data is shown in the Table 1.

15

20

Figure 3



5

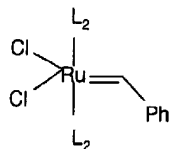
10

15

Table 1. Bond lengths [Å] and angles [°] for the compound of Figure 3

Bond	Lengths and Angles
Ru(1)-C(1)	1.795(7)
Ru(1)-P(11)	2.3834(16)
Ru(1)-P(31)	2.3842(17)
Ru(1)-Cl(1)	2.3963(17)
Ru(1)-Cl(2)	2.4025(16)
C(1)-Ru(1)-P(11)	99.6(2)
C(1)-Ru(1)-P(31)	98.2(2)
P(11)-Ru(1)-P(31)	162.23(6)
C(1)-Ru(1)-Cl(1)	93.0(3)
P(11)-Ru(1)-Cl(1)	90.24(6)
P(31)-Ru(1)-Cl(1)	88.36(6)
C(1)-Ru(1)-Cl(2)	93.3(3)
P(11)-Ru(1)-Cl(2)	88.94(6)
P(31)-Ru(1)-Cl(2)	90.50(6)
Cl(1)-Ru(1)-Cl(2)	173.66(7)

- 5 One possible preparation of such catalysts where the alkylidene is specifically a benzylidene group (that is a compound of (formula 7), involves the displacement of tricyclohexyl phosphine (PCy₃) from the standard first generation Grubbs catalyst (1a). A specific example for the preparation of the benzylidene complex of formula 7 (wherein L₂ is cyclohexyl phoban) is as follows:



10

.....(7)

To a suspension of the Grubbs catalyst of formula 1a (10 mmol) and cyclohexyl phoban (40 mmol) was added degassed DCM (15 ml). After stirring at room temperature for 16 h, the solvent was removed, and degassed pentane was added to the residue. The mixture was sonicated for 1 min, and the solid filtered.

- 5 To the solid was added degassed cold MeOH. The suspension was sonicated again for 1 min and filtered. The complex of formula 7 wherein L₂ is cyclohexyl phoban was isolated as a purple solid (5.8 mmol, 58%). ¹H NMR (300 MHz, d⁸ Toluene): 20.2 ppm (s, 1H, Ru=CH), 9.7 ppm (bs, 1H, o-H of C₆H₅), 7.5 ppm (bs, 1H, o-H of C₆H₅), 7.1 ppm (t, ³J_{HH} = 7.6 Hz, p-H of C₆H₅), 2.6 ppm (4H, P-C-H of Phoban), 2.20-0.70 ppm (m, 46H). ³¹P NMR (121 MHz, d⁸ Toluene): 24 ppm (bs). Mass Spec: (TOF MS ES+); 733.728 (M + Na)⁺, 710.74 (M⁺).
- 10

CATALYSIS EXPERIMENTS WITH PREFORMED CATALYSTS

- 15 The performance of the novel catalysts was compared with the standard first generation Grubbs catalyst (1a) and in some cases with the standard second generation catalyst (1b) in homogeneous metathesis reactions.

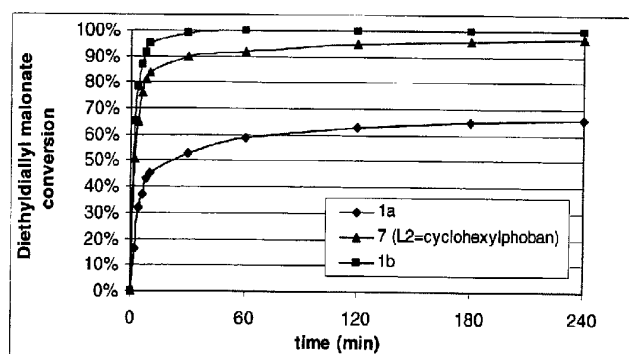
2.1 RING CLOSING METATHESIS WITH COMPOUND 7 (L₂ = Cyclohexyl Phoban)

20

Reactions were carried out in a 250 ml three-necked flask fitted with a reflux condenser, thermometer and septum. A needle inserted through the septum and connected to a gas supply *via* a needle valve was used to

ensure a slow and steady stream of argon through the reaction solution. Dry, degassed toluene (80 ml) was added, followed by diethyldiallylmalonate (4g, 16.8 mmol) and the reaction was heated at 50°C. The catalyst of formula 7 wherein L₂ is cyclohexyl phoban (0.01 mmol) was weighed into a custom-made aluminum weighing tray and added to the reaction mixture. Samples were taken at regular intervals *via* syringe through the septum. Samples were analysed by GC with a Pona column using an FID. Results are shown in Figure 4 below.

10 Figure 4



It is evident that the catalyst of formula 7 (L₂ = cyclohexyl phoban) performs ring-closing metathesis of diethyldiallylmalonate to form cyclopent-3-ene-1,1-dicarboxylic acid diethyl ester (at a substrate to catalyst molar ratio of 1680/1, 50 deg, 0.01 M in toluene) significantly faster than the catalyst of formula 1a and

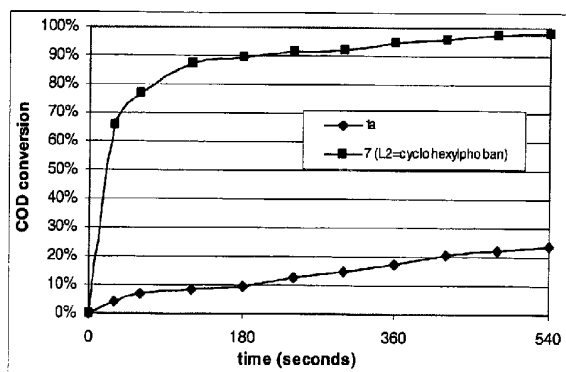
compares favourably to results obtained with the much more expensive catalyst of formula **1b**.

2.2 RING OPENING METATHESIS POLYMERIZATION WITH COMPOUND

5 7 (L₂ = Cyclohexyl Phoban)

Into a glass vial was added 2ml of dry, degassed toluene, followed by decane (900 μl, internal standard for GC) COD (0.46 g, 4.63 mmol) was added, followed by toluene. A solution of catalyst (0.001838 mmol) in
10 toluene (100 μl) was added and the reaction was monitored by GC by taking samples at regular intervals. Results are shown Figure 5 below.

Figure 5



15

It is clear that the catalyst of formula 7 (L_2 =cyclohexyl phoban) catalyses ROMP of 1,5-cyclooctadiene (COD) to form 1,4-polybutadiene faster than the catalyst for formula 1a at a substrate to catalyst molar ratio (S/C) of 2500/1

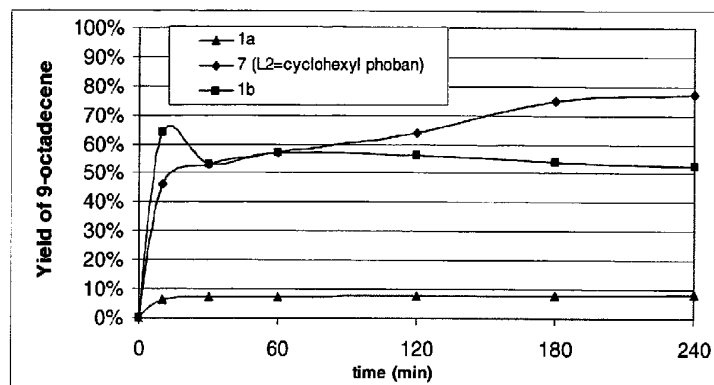
5 2.3 CROSS METATHESIS WITH COMPOUND 7 (L_2 = Cyclohexyl Phoban)

2.3.1 1-DECENE METATHESIS, 65°C.

10 Reactions were carried out in a 250 ml three-necked flask fitted with a reflux condenser, thermometer and septum. A needle inserted through the septum and connected to a gas supply *via* a needle valve was used to ensure a slow and steady stream of argon through the reaction solution. Dry, degassed 1-decene (24 ml) was added, and the reaction was heated at 65°C. The catalyst (0.014 mmol) was weighed into a custom-made
15 aluminum weighing tray and added to the reaction mixture. Samples were taken at regular intervals *via* syringe through the septum. Samples were analysed by GC using a Pona column. Results are shown in Figure 6 below.

20

Figure 6



5

Under identical conditions, the catalyst of formula 1a showed a poor performance, for the 1-decene metathesis to 9-octadecene while the catalyst of formula 1b showed lower final yields of the desired product due to extensive formation of side products. The catalyst of formula 7 (L₂=cyclohexylphoban) gave the highest yield of desired product.

10

2.3.2 1-OCTENE METATHESIS, 50 DEGREES.

15

Reactions were carried out in a 100 ml three-necked flask fitted with a reflux condenser, thermometer and septum. A needle inserted through the septum and connected to a gas supply *via* a needle valve was used to ensure a slow and steady stream of argon through the reaction solution.

Dry, degassed 1-octene (20 ml) was added, and the reaction was heated at 50°C. The catalyst (0.014 mmol) was weighed into a custom-made aluminum weighing tray and added to the reaction mixture. Samples were taken at regular intervals *via* syringe through the septum. Samples were analysed by GC using a Pona column. Results are shown in the Table 2 below.

Table 2

Time (min)	Product Yield (molar %)	
	Catalyst 1a	Catalyst 7 (L ₂ =cyclohexyl phoban)
120	34%	57%
360	34%	84%

10

Complex 7 (L₂=cyclohexylphoban) efficiently catalyses the self-metathesis of 1-octene to 7-tetradecene, affording significantly higher yields under the same conditions as 1a. Under the reaction conditions, little visible decomposition is observed, and conversions are significantly higher than those achievable with commercial Grubbs 1st generation catalyst of formula 1a. It is evident that catalyst 1a decomposes within the first two hours of reaction, as no further product formation is observed, while complex 7 (L₂=cyclohexyl phoban) shows activity over at least 6 hours. Thus complex 7 (L₂=cyclohexyl phoban) has a superior catalyst lifetime.

20

2.3.3 ETHENOLYSIS OF 2-OCTENE

A 50ml Parr autoclave was fitted with a 50 ml addition vessel connected via a needle valve to the autoclave diptube. The autoclave was sealed and thoroughly flushed with ethylene. 2-Octene (16.5ml) was introduced to the addition vessel via syringe. It was then introduced to the autoclave by applying 10 bar of ethylene pressure to the addition vessel and opening the needle valve on the diptube. Stirring (1000rpm) was started immediately, and the reactor contents were heated to 45°C. The catalyst (0.018 mmol) was dissolved in the octane (8.5ml), and when the reactor contents were at the desired temperature, the catalyst solution was introduced to the autoclave by applying 15 bar of ethylene pressure to the addition vessel and opening the needle valve on the diptube. Once the reactor pressure had stabilised, the needle valve was closed and the reaction was stirred at 45°C for 2 hours. Samples were taken at intervals and monitored by GC using a Pona column. Results are shown in Table 3 below.

Table 3

Time (min)	2-octene conversion (molar%)	
	Catalyst 1a	Catalyst 7 L ₂ =cyclohexyl phoban
20	17%	27%
40	17%	38%
120	18%	45%

It is evident that complex 7 (L₂=cyclohexylphoban) affords faster reaction rates and higher conversions than catalyst 1a for the reaction of 2-octene and ethylene to form 1-heptene. Catalyst activity is also sustained over a longer period with complex 7 (L₂=cyclohexyl phoban).

2.3.4 CROSS METATHESIS OF SASOL 1-HEPTENE FEED

Fischer-Tropsch-derived olefins contain a multitude of impurities which have a deleterious effect on many homogeneous catalysts. A Fischer-Tropsch (FT) derived C₇ feed with the following composition was employed (percentages expressed as molar%):

Linear 1-alkene	86%
Linear internal alkene	1-1.5%
Branched alkene (incl. internal)	5-7%
Cyclic alkene	1-2%
Diene	1%

Oxygenate	<100ppm
Paraffins, aromatics & other	5-7%

Reactions were carried out in a 100 ml three-necked flask fitted with a reflux condenser, thermometer and septum. A needle inserted through the septum and connected to a gas supply via a needle valve was used to ensure a slow and steady stream of argon through the reaction solution. Dry, degassed 1-heptene feed (20 ml) was added, and the reaction was heated at 50°C. The catalyst (0.014 mmol) was then added as a solid to the preheated reaction mixture. Samples were taken at intervals via syringe through the septum. Samples were analysed by GC using a Pona column. Results are shown in Table 4 below.

Table 4

15

Time (min)	1-heptene conversion (molar%)	
	Catalyst 1a	Catalyst 7 (L ₂ =cyclohexyl phoban)
20	19%	39%
60	19%	52%
360	19%	70%

It is evident from these results that complex 7(L₂=cyclohexyl phoban) affords far superior results to catalyst 1a for the metathesis of a Fischer Tropsch derived 1-heptene feed to form 6-dodecene . It

is also clear that catalyst 1a is poisoned very quickly by trace impurities, as it shows no further conversion of substrate after 20 minutes, and does not reach the conversion obtained with pure 1-octene feed (34%). In comparison, complex 7 (L₂=cyclohexyl phoban) affords much higher conversions of substrate, and catalyst activity is maintained over a longer period. The catalyst therefore shows a greater tolerance to feed impurities.

2.4 CROSS METATHESIS OF 1-OCTENE WITH COMPLEX 8 (L₂=Cyclohexyl Phoban)

Reactions were carried out in a 250 ml three-necked flask fitted with a reflux condenser, thermometer and septum. A needle inserted through the septum and connected to a gas supply *via* a needle valve was used to ensure a slow and steady stream of argon through the reaction solution. Dry, degassed 1-octene (20 ml) was added, and the reaction was heated at 50°C. The catalyst (0.014 mmol) was weighed into a custom-made aluminum weighing tray and added to the reaction mixture. Samples were taken at regular intervals *via* syringe through the septum. Samples were analysed by GC using a Pona column. Results are shown in Table 5 below.

Table 5

Time (min)	Product Yield (molar%)	
	Catalyst 1a	Catalyst 8 (L ₂ =cyclohexyl phobane)
120	34%	44%
360	35%	82%

5

It is evident from these results that complex 8 (L₂ = cyclohexyl phobane) affords superior results to catalyst 1a for the metathesis of 1-octene to 7-tetradecene.

10 From the above examples it can be seen that the catalysts including ligands according to the present invention may have improved performance over the prior art catalysts in at least one of the following aspects:

- 15 i) higher reaction rates;
ii) higher conversions;
iii) improved catalyst stability;
iv) improved rates/yields at lower ligand concentrations;
and
20 v) higher yields of desired products.

It will be appreciated that many variations in detail are possible without thereby departing from the spirit and scope of the invention.

25

It is to be understood that, if any prior art publication is referred to herein; such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any
30 other country.

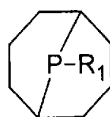
In the claims which follow and in the preceding
description of the invention, except where the context
5 requires otherwise due to express language or necessary
implication, the word "comprise" or variations such as
"comprises" or "comprising" is used in an inclusive sense,
i.e. to specify the presence of the stated features but
not to preclude the presence or addition of further
10 features in various embodiments of the invention.

CLAIMS

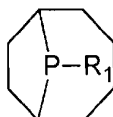
- 5
1. The use of a phosphorus containing ligand as a ligand
for a metathesis catalyst in a catalysed metathesis
reaction wherein the phosphorus containing ligand is a
heterocyclic organic compound in the form of a
10 phosphabicycloalkane with a ligating phosphorus atom as
an atom in the heterocyclic ring structure of the
heterocyclic organic compound.
 2. The use of a phosphorus containing ligand in the
15 preparation of a catalyst containing the ligand, which
catalyst is for use in a metathesis reaction, wherein
the phosphorus containing ligand is a heterocyclic
organic compound in the form of a phosphabicycloalkane
with a ligating phosphorus atom as an atom in the
20 heterocyclic ring structure of the heterocyclic organic
compound.
 3. The use of either one of claims 1 or 2 wherein the
25 metathesis reaction is a homogenous metathesis
reaction.

4. The use of any one of the preceding claims wherein the phosphorus containing ligand comprises a phosphine ligand.
5. The use of claim 4 wherein the ligating phosphorus atom is also bound to a further moiety which is an organyl and which is not part of the heterocyclic ring structure.
6. The use of any one of claims 1 to 4 wherein the phosphorus containing ligand is a 9-phosphabicyclo[3.3.1]nonane of formula 2a or a 9-phosphabicyclo[4.2.1]nonane of formula 2b or mixtures thereof:

15



..... (2a)



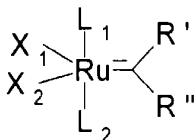
..... (2b)

20

- 41 -

wherein R_1 is H or an organyl.

7. The use of claim 6 wherein R_1 is $-C_{20}H_{41}$.
8. The use of claim 6 wherein R_1 is cyclohexyl.
9. The use of any one of the preceding claims wherein the metathesis reaction is a reaction selected from the group consisting of cross metathesis, ring-opening metathesis polymerisation and ring-closing metathesis.
10. A metathesis catalyst which includes a phosphorus containing ligand which is a heterocyclic organic compound in the form of a phosphabicycloalkane with a ligating phosphorus atom as an atom in the heterocyclic ring structure of the heterocyclic organic compound.
11. A compound of formula 3:



..... (3)

wherein

L_1 is a neutral electron donor ligand;

L_2 is a phosphorous containing ligand in the form of a heterocyclic organic compound in the form of a phosphabicycloalkane with a ligating phosphorus atom as an atom in the heterocyclic ring structure of the heterocyclic organic compound;

X_1 and X_2 are independently selected from an anionic ligand; and

R' and R'' are independently selected from H and an organyl.

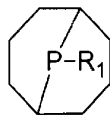
12. The compound of claim 11 which is a homogeneous metathesis catalyst.

13. The compound of either one of claims 11 or 12 wherein L_1 is the same as L_2 .

14. The compound of any one of claims 11 to 13 wherein the phosphorus containing ligand of L_2 comprises a phosphine ligand.

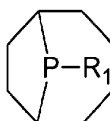
15. The compound of claim 14 wherein L_2 is a 9-phosphabicyclo[3.3.1]nonane, of formula 2a, or a

9-phosphabicyclo[4.2.1]nonane of formula 2b or mixtures thereof:



5

..... (2a)



10

..... (2b)

wherein R_1 is H or an organyl.

16. The compound of claim 15 wherein R_1 is $-C_{20}H_{41}$.

15

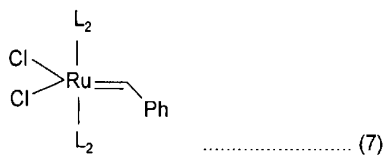
17. The compound of claim 15 wherein R_1 is cyclohexyl.

18. The compound of any one of claims 11 to 17

20

wherein X_1 and X_2 are each independently selected from halide.

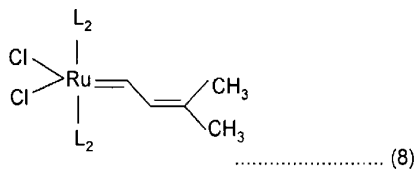
19. The compound of claim 11 which is a compound of formula 7:



5 wherein L₂ is the same or different and is as defined in claim 11.

20. The compound of claim 11 which is a compound of formula 8

10



wherein L₂ is the same or different and is as defined in claim 11.

15

21. The compound of either one of claims 19 or 20 wherein L₂ is as defined in claim 15.

22. The use of a compound of any one of claims 11 to
20 in a metathesis reaction.

23. The use of claim 22 wherein the metathesis reaction is
5 a homogeneous metathesis reaction selected from the
group consisting of cross metathesis ring-opening
metathesis polymerisation and ring-closing
metathesis.

10 24. A catalysed metathesis reaction wherein at least
one olefinic compound is subjected to metathesis
in the presence of a compound of claim 11.

25. The reaction of claim 24 wherein the compound of
15 claim 11 is formed *in situ*.

26. A metathesis product formed by the reaction of
either one of claims 24 or 25.

20 27. A compound substantially as hereinbefore
described and with reference to the accompanying
examples.

28. The use of a phosphorus containing ligand substantially as hereinbefore described with reference to the accompanying examples.

5 29. A catalysed metathesis reaction substantially as hereinbefore described and with reference to the accompanying examples.

30. A metathesis catalyst substantially as
10 hereinbefore described with reference to the accompanying examples.

31. A metathesis product substantially as
15 hereinbefore described and with reference to the accompanying examples.