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Mixed Isobutylphobane/N-Heterocyclic Carbene Ruthenium-Indenylidene Complexes: Synthesis and Catalytic Evaluation in Olefin Metathesis Reactions

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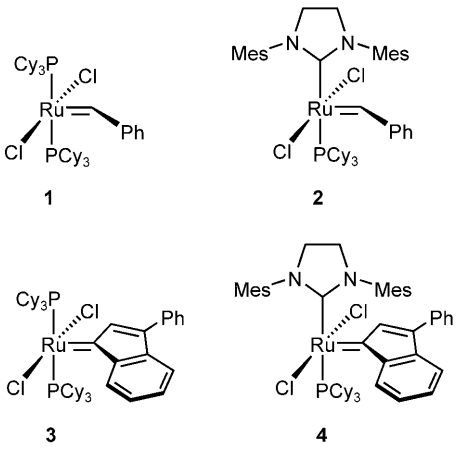
Abstract: Two new second generation ruthenium(II) dichloride-indenylidene complexes [$RuCl_2$(9-isobutylphosphabicyclo[3.3.1]nonane)(NHC)(3-phenyl-1-indenylidene)], where NHC = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene (SIMes) or its unsaturated imidazol-2-ylidene analogue (IMes), were isolated in high yields upon heating a tetrahydrofuran (THF) solution of the diphosphane complex [$RuCl_2$(isobutylphobane)$_2$(3-phenyl-1-indenylidene)] with a two-fold excess of the corresponding imidazol(in)ium-2-carboxylate zwitterions. Both products were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, and the molecular structure of [$RuCl_2$(isobutylphobane)(SIMes)(3-phenyl-1-indenylidene)] was determined by X-ray diffraction analysis. A close inspection of the packing structure revealed the presence of different types of intra- and intermolecular interactions that enhanced the global stability of the crystals, while low temperature NMR experiments showed the existence of two distinct rotational isomers due to the unsymmetrical nature of the phobane ligand. The catalytic activity of both compounds was assessed in olefin metathesis using benchmark ring-opening metathesis polymerization, ring-closing metathesis (RCM), and cross-metathesis reactions, and compared with those of related first and second generation ruthenium-benzylidene and indenylidene catalyst precursors. Kinetic studies confirmed the high thermal stability of the mixed isobutylphobane/N-heterocyclic carbene complexes, which suffered from a slow initiation efficiency compared to other catalytic systems based on the tricyclohexylphosphane ligand. However, the remarkable robustness of [$RuCl_2$(isobutylphobane)(SIMes)(3-phenyl-1-indenylidene)] was beneficial for performing the RCM of diethyl 2,2-bis(2-methylallyl)malonate. Monitoring the formation of the ruthenium-methylidene active species [$RuCl_2$(isobutylphobane)(SIMes)(=CH_2)] derived from this precursor further demonstrated its ability to sustain long reaction times and high temperatures required to carry out the RCM of tetrasubstituted olefins.

Keywords: ethenolysis; homogeneous catalysis; N-heterocyclic carbenes; phosphane ligands; ring-closing metathesis; ruthenium

Introduction

Thanks to the development of well-defined ruthenium-alkylidene catalysts initiated by Grubbs in the late 1990s,[1] olefin metathesis has become a key methodology in organic synthesis and in polymer chemistry.[2] Most catalytic systems investigated so far derive from the Grubbs first generation ruthenium-benzylidene complex [$RuCl_2$(=CHPh)(PCy_3)$_2$] (**1**) (PCy_3 is tricyclohexylphosphane) (Scheme 1).[3] Countless structural alterations have been made to this archetypal compound in order to tailor its activity,[4,5] stability,[6] water-solubility,[7] recoverability,[8] or latency[9] toward specific catalytic processes, sometimes in an asymmetric fashion.[10] Replacement of one phosphane ligand with an N-heterocyclic carbene (NHC) was quickly recognized to increase the catalyst stability and efficiency, thereby affording a new subset of ruthenium

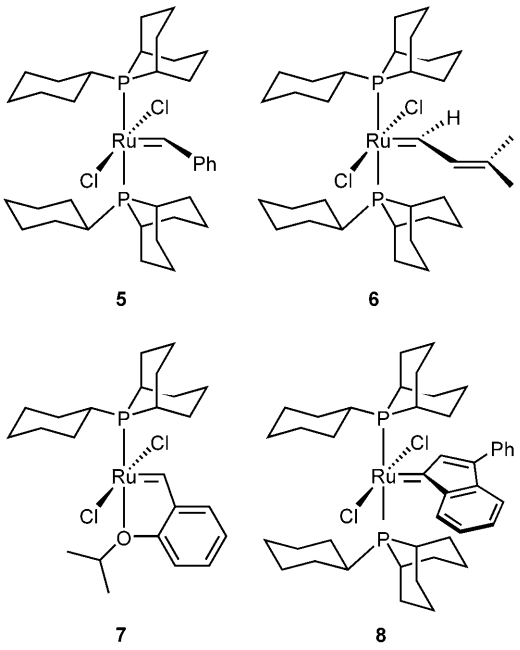


Scheme 1. First and second generation ruthenium-benzylidene and indenylidene complexes bearing tricyclohexylphosphane ligands.

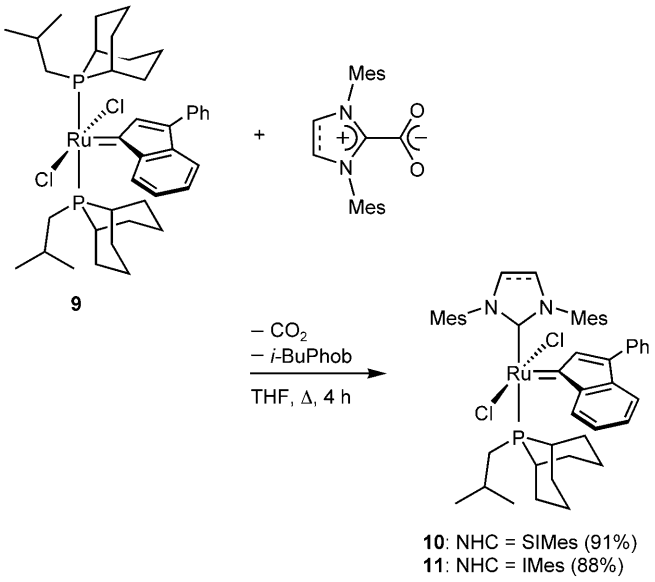
metathesis initiators, exemplified by the second generation Grubbs catalyst, [$RuCl_2$(=CHPh)(PCy_3)(SIMes)] (**2**) [SIMes is 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene].[11] Numerous variations on the alkylidene fragment have also been performed.[12] Among other things, they led to the emergence of first and second generation ruthenium-indenylidene complexes, such as **3** and **4**, whose straightforward synthesis makes them an attractive alternative to benzylidene-based precatalysts.[13]

Although the dissociation of a phosphane ligand is supposed to be a crucial step in the mechanism of olefin metathesis initiated by complexes **1**–**4**,[14] only a few studies have aimed at modifying this key component. Early reports from Grubbs and co-workers[15] and related work from our group[16] showed that both strongly basic and bulky phosphanes were required to achieve high catalytic efficiencies. Hence, tricyclohexylphosphane has been the ligand of choice for most of the ruthenium catalyst precursors investigated so far. Recently, however, another class of phosphane ligands displaying similar steric and electronic properties has generated much interest as a viable alternative to PCy_3 in olefin metathesis catalysts. The first representatives of this family known collectively as 9-phosphabicyclononanes or phobanes date back to 1966.[17] They are prepared on a large scale *via* the radical addition of 1,5-cyclooctadiene to PH_3 or primary alkylphosphanes and are usually obtained as a mixture of [3.3.1]- and [4.2.1]-bridged isomers in variable proportions.[17,18] These relatively inexpensive ligands are currently used industrially in the cobalt-catalyzed hydroformylation process developed by Shell.[19] They have also found applications in other transition metal-catalyzed reactions, such as the oligomerization of ethylene (with Ni),[20] the hydrocarbonylation of alkenes (with Pd),[21] the arylation of heterocycles (with Rh),[22] or various atom transfer radical reactions (with Ru),[23] to name just a few.

In the field of olefin metathesis, the first report on the use of ruthenium-alkylidene complexes bearing phobane ligands originated from the group of Forman in 2004.[24] Thus, complexes **5** and **6** were synthesized by ligand exchange between [$RuCl_2$(=CHPh)(PCy_3)$_2$] (**1**) or [$RuCl_2$(=CH−CH=CMe_2)(PPh_3)$_2$] and 9-cyclohexyl-9-phosphabicyclo[3.3.1]nonane (Scheme 2). The catalytic activity of benzylidene precatalyst **5** was evaluated in various types of metathetical reactions, including ring-closing metathesis (RCM),[24,25] cross-metathesis (CM),[24,26] self-metathesis (SM),[24,25] and ethenolysis.[24] In many cases, the first generation phobane complex **5** outperformed its tricyclohexylphosphane-based analogue (**1**) and behaved more like the second generation Grubbs catalyst (**2**). Indeed, DFT calculations showed that the substrate-induced decomposition of propagating species decreased in the order **1** > **5** > **2**, in good agreement with experimental observations.[27] Further enhancement of the catalytic efficiency of **5** could be achieved by the addition of diverse co-catalysts, such as phenols,[28] tin and iron halogenides,[29] or ionic liquids.[30] A stoichiometric reaction of **5** with 2-isopropoxystyrene afforded the chelated alkoxybenzylidene compound **7**, which was found to be highly active at promoting the RCM of *N,N*-diallyltosylamide.[31] In the indenylidene series, the first generation di(cyclohexylphobane) complex **8** was synthesized and characterized by Forman et al. in 2006, starting from [$RuCl_2$(3-phenyl-1-indenylidene)-



Scheme 2. First generation ruthenium-alkylidene complexes bearing cyclohexylphobane ligands.



Scheme 3. Synthesis of second generation ruthenium-indenylidene catalysts bearing isobutylphobane ligands.

$(PPh_3)_2$] and an isomeric mixture of cyclohexylphobanes.[32] It should be pointed out that the related compound **9** bearing two isobutylphobane ligands (see Scheme 3) is commercially available but, to the best of our knowledge, its preparation has not been described in the open literature. Catalyst precursors **8** and (to a lesser extent) **9**, were found to be more efficient promoters for the SM of terminal alkenes or the RCM of a wide variety of α,ω-dienes and enynes than the Grubbs first generation catalyst (**1**).[25] In addition, ruthenium-indenylidene complex **8** was also successfully applied to SM and ethenolysis reactions of methyl oleate under low catalyst loading conditions.[32]

Surprisingly, the synthesis and catalytic evaluation of second generation ruthenium-alkylidene catalyst precursors bearing phobane ligands has not been documented yet. Thus, in this contribution, we report on the preparation and characterization of two new mixed isobutylphobane/NHC Ru-indenylidene complexes and we assess their catalytic activity in various types of olefin metathesis transformations using benchmark reactions. In order to shed light on their remarkable stability, we have also monitored their decomposition rate in the presence of ethylene.

Results and Discussion

Synthesis and Characterization of Complexes 10 and 11

Recently, we have shown that imidazol(in)ium-2-carboxylates could act as convenient NHC ligand precursors for the synthesis of second generation ruthenium metathesis catalysts.[33] Because these stable zwitterionic adducts can be stored and handled with no particular precautions, they are particulary attractive surrogates to air and moisture-sensitive free carbenes. In order to further illustrate their potentials in organometallic chemistry,[34] we used them as NHC ligand precursors for this work. Thus, we have performed a phosphane/NHC ligand exchange starting from [RuCl_2(isobutylphobane)$_2$(3-phenyl-1-indenylidene)] (Neolyst™ M11) (**9**) and a two-fold excess of either SIMes·CO_2 or IMes·CO_2 [IMes is 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene] (Scheme 3). The reactions were carried out in refluxing THF using a round-bottom flask fitted with a reflux condenser topped with a gas bubbler and flushed by a slow stream of argon. We reasoned that this experimental set-up would help displace carbon dioxide and speed up the decarboxylation process.[35] Attempts to monitor the phosphane exchange by ^{31}P NMR analysis of samples removed from the reaction media at various time intervals remained largely unsuccessful. Indeed, both the substrate and the products gave very broad resonances at room temperature (*vide infra*), and only the signal assigned to free isobutylphobane was observed at −39.1 ppm in ^{31}P NMR spectra acquired from a few scans in THF spiked with C_6D_6. Yet, the remarkable stability of the first and second generation ruthenium-phobane complexes under investigation allowed us to use TLC analysis to monitor the reaction course. With both SIMes·CO_2 and IMes·CO_2, a quantitative conversion was achieved within 4 h. The products were then separated and purified by flash chromatography on silica gel. Mixed isobutylphobane/NHC complexes **10** and **11** bearing, respectively, the saturated ligand SIMes and its unsaturated counterpart IMes, were isolated as red powders in high yields (*ca.* 90%) and purities. These results were deemed very satisfactory. Therefore, we did not investigate the direct reactions between complex **9** and a stoichiometric amount of the IMes or SIMes free carbenes, although we are confident that they would lead to similar outcomes.

Compounds **10** and **11** proved to be particularly stable in the solid state, as well as dissolved in aprotic solvents. These observations are in good agreement with previous work by Nolan et al., who found that indenylidene complexes **3** and **4** bearing PCy_3 ligands did not show any sign of decomposition in toluene-d_8 at 80 °C for at least 10 days.[36] The ^{13}C{^{1}H} NMR spectrum of [RuCl_2(isobutylphobane)(IMes)(3-phenyl-1-indenylidene)] (**11**) featured a doublet at 186.9 ppm for the C-2 carbon of the NHC ligand bound to the metal center. The corresponding signal in complex **10** was found at 217.9 ppm. Hence, saturation of the imidazole ring caused a 31 ppm shift of the carbene carbon to lower field, consistent with a

higher anisotropy due to a lower population of the carbene p_π-orbital.[37] This difference of chemical shift between coordinated IMes and SIMes ligands is slightly larger than the values computed for the free 1,3-dimesitylimidazol(in)-2-ylidenes ($\Delta\delta = 24$ ppm) and their imidazol(in)ium salt precursors ($\Delta\delta = 25$ ppm).[38] In both complexes, the $^2J_{C,P}$ coupling constant measured for the (S)IMes C-2 carbon was greater than 80 Hz, indicative of a *trans* relationship between the phobane and the NHC ligand. Another doublet located at 294.9 ppm in both complexes was assigned to the indenylidene C-1 carbon atom. In this case, the $^2J_{C,P}$ coupling constant was reduced to *ca.* 4 Hz, due to a *cis* arrangement relative to the phobane ligand.

At room temperature, the $^{31}P\{^1H\}$ NMR spectrum of complex **10** consisted of a very broad singlet centered at 7.8 ppm. A likely shaped signal was observed at 10.2 ppm for complex **11**. This difference of chemical shift might be explained by a stronger σ-donor ability of the saturated imidazolin-2-ylidene ligand compared to its aromatic imidazol-2-ylidene counterpart, which would increase the electron density around the phosphorus nucleus *via* a *trans* effect. Detailed investigations of the steric and electronic properties of NHCs suggest, however, that saturated heterocycles are slightly less electron-donating than their unsaturated analogues,[39] in apparent contradiction with our correlation. At this point, we prefer not to draw any definite conclusion from these data, although we note that the tendency observed here for mixed phobane/NHC ruthenium-indenylidene complexes is in line with the ^{31}P chemical shift gap observed between various other second generation ruthenium-alkylidene catalysts, where the IMes or IDip ligands always lead to a more pronounced deshielding of the *trans*-phosphane than SIMes or SIDip, even if the difference is sometimes less than 1 ppm [IDip is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene, SIDip is 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene].[36,40–43]

It should be noted that the interpretation of ^1H and ^{13}C NMR spectra was complicated by the presence of many hardly differentiable signals in the aliphatic and aromatic regions due to the phobane and indenylidene ligands, respectively.[44] Yet, elemental analysis confirmed the identity and purity of complexes **10** and **11**. Moreover, we were able to grow crystals of [$RuCl_2$(isobutylphobane)(SIMes)(3-phenyl-1-indenylidene)] (**10**) suitable for X-ray diffraction analysis by slow diffusion of isopropyl alcohol into a saturated dichloromethane solution at room temperature. Their molecular structure is depicted in Figure 1, along with selected bond lengths and angles. The coordination geometry around the ruthenium center is a distorted square pyramid with the indenylidene moiety occupying the apical position, while the two chloro substituents and the donor atoms of the phobane and NHC ligands form the basal plane. Bond lengths and angles are similar to those observed in first generation complexes **6**[24] and **8**,[32] or in related second generation ruthenium-indenylidene catalysts bearing PCy_3 and

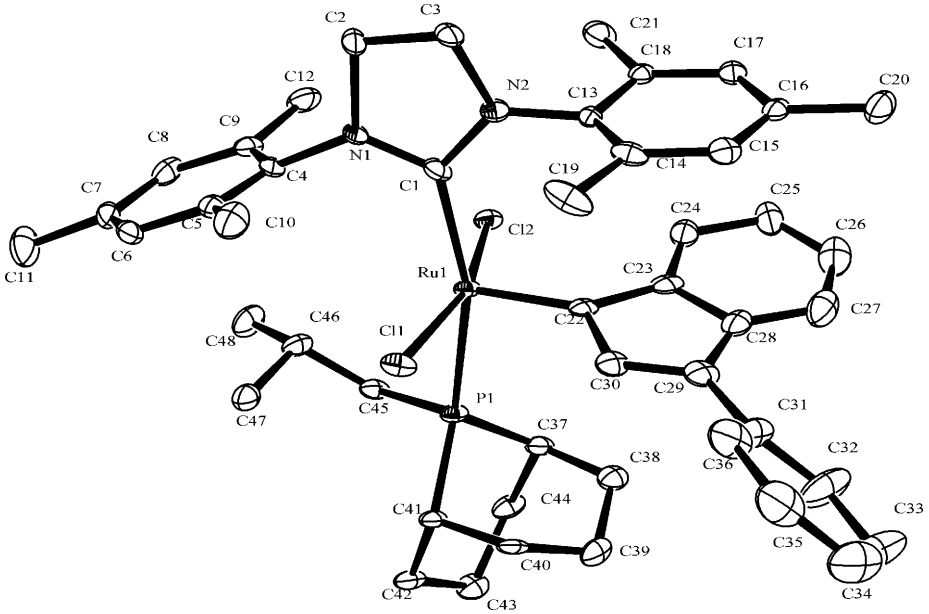


Figure 1. ORTEP representation of complex **10** with thermal ellipsoids drawn at the 50% probability level. Hydrogen atoms were omitted for the sake of clarity. Selected bond lengths (Å) and angles (deg): Ru1–Cl1 2.3911(16), Ru1–Cl2 2.3999(15), Ru1–C1 2.090(6), Ru1–P1 2.4161(15), Ru1–C22 1.874(6), C1–Ru1-C22 102.4(2), C1–Ru1-Cl1 87.91(16), C1–Ru1–Cl2 91.57(16), C1–Ru1–P1 161.61(17), C22–Ru1–P1 96.01(16), Cl1–Ru–Cl2 162.68(5).

the IDip or SIDip ligands.[36,43] It is noteworthy, however, that the 3-phenyl group and the cyclopentene ring of the indenylidene ligand in complex **10** are in the opposite orientation with respect to the other compounds examined. Indeed, the 3-phenyl group lies in front of another terminal phenyl group from an adjacent molecule, whereas in compound **8** and in [$RuCl_2$(isobutylphobane)(SIDip)(3-phenyl-1-indenylidene)], it is in front of the core six-membered ring of the indenylidene ligand from an adjacent molecule. Inspection of the packing structure of complex **10** further reveals the presence of two intramolecular hydrogen bonds between the indenylidene hydrogen atoms flanking the Ru=C bond and the chlorine atoms, and an intermolecular hydrogen bond between the *para*-hydrogen of the terminal phenyl group and the Cl(1) atom of an adjacent molecule. More important is the existence of intramolecular π-π stacking interactions between the indenylidene ligand and the mesityl group of the NHC above it, a common feature in ruthenium-alkylidene complexes bearing NHC ligands with aromatic substituents, which may have important implications in terms of catalyst stability and activity.[45] Terminal phenyl rings of two adjacent molecules are also involved in a weak intermolecular π-π stacking interaction, whereas various aliphatic C–H bonds interact with aromatic rings either intra- or intermolecularly (see the Supporting Information for more details about the crystallographic analysis of complex **10** and color illustrations).

In 2006, researchers from Sasol have shown that the very broad peak observed in $^{31}P\{^1H\}$ NMR spectroscopy at room temperature for the first generation di(cyclohexylphobane) ruthenium-benzylidene complex **5** and related compounds was due to the slow rotation of its unsymmetrical phobane ligands around the Ru–P bonds.[46] Three distinct rotational isomers were detected at −40 °C in 72/25/3 proportions. Based on experimental results and DFT calculations, they were assigned, respectively, to structures with (*transoid*, *transoid*), (*transoid*, *cisoid*), and (*cisoid*, *cisoid*) orientations of the cyclohexyl groups relative to the benzylidene unit. In the case of second generation complex **10** bearing only one isobutylphobane ligand, lowering the temperature to −40 °C led to the replacement of the broad signal observed at room temperature by two sharp singlets at 9.7 and −0.3 ppm in a 87/13 ratio (Figure 2). Thus, we tentatively assign the major peak to the *transoid* conformer **10a** and the minor one to its *cisoid* congener **10b**. The same explanation also holds true for complex **11**, whose ^{31}P NMR spectrum at −40 °C comprised a major peak at 11.3 ppm and a minor one at 0.5 ppm in a 92/8 ratio (not shown). It is supported by the crystal structure depicted in Figure 1, which shows that the isobutyl chain of the phobane ligand points in the opposite direction of the indenylidene fragment, thereby suggesting that the conformer with a *transoid* orientation of the isobutyl group relative to the indenylidene moiety is more stable than the *cisoid* one in the solid state.

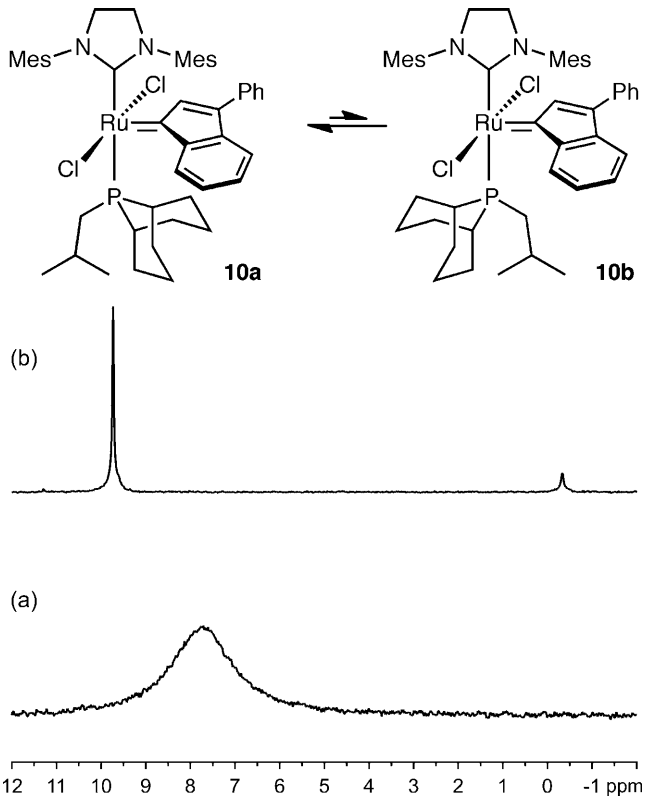
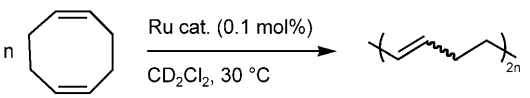


Figure 2. ^{31}P NMR spectra of complex **10** in $CDCl_3$ (**a**) at 25 °C and (**b**) at −40 °C.

Catalytic Tests

In order to assess the ability of complexes **10** and **11** to promote olefin metathesis, we have tested them in benchmark ROMP, RCM, and CM reactions using standard protocols defined by Grubbs and co-workers to ease the comparison between different catalytic systems.[47] Thus, in a first series of experiments, we have carried out the ROMP of 1,5-cyclooctadiene in CD_2Cl_2 at 30 °C using 0.1 mol% of various ruthenium



(1)

initiators [Eq. (1)]. As observed previously by the group of Verpoort,[42] consumption of the monomer occurred much faster with the second generation benzylidene catalyst **2** than with the known bis(tricyclohexylphosphane) ruthenium-indenylidene complex **3**

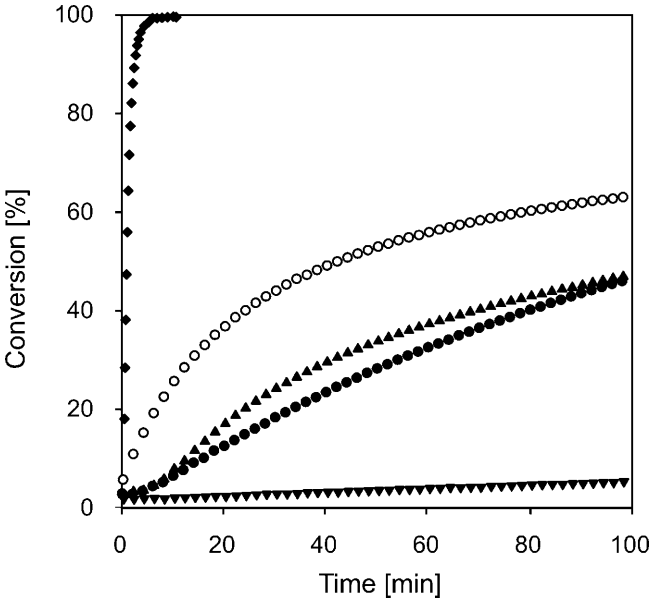
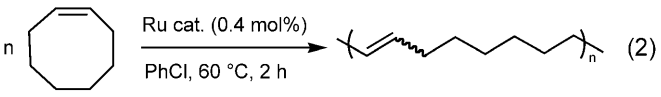


Figure 3. Time course of the ROMP of 1,5-cyclooctadiene using various catalyst precursors (0.1 mol%) in CD_2Cl_2 at 30 °C (**2**: ◆, **3**: ○, **9**: ●, **10**: ▲, **11**: ▼).

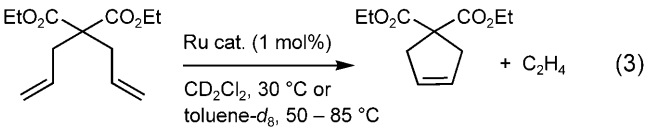
(Figure 3). The analogous first generation Ru-indenylidene complex **9** bearing two isobutylphobane ligands was even less active. Introduction of the SIMes ligand in second generation complex **10** slightly increased the polymerization rate compared to **9**, whereas substitution of an isobutylphobane ligand with the unsaturated IMes donor led to a dramatic reduction of activity. Complete consumption of 1,5-cyclooctadiene was, however, achieved within 24 h with complexes **3**, **9**, and **10**. In the case of complex **11**, it took 9 days to reach a 78% conversion. Although we stopped the experiment at this point, the catalyst was still active, which indicates a great stability and a poor initiation efficiency.

Because no information on the polymer microstructure could be obtained from the NMR kinetic measurements, we decided to perform the ROMP of cyclooctene on a millimolar scale and to characterize the polyoctenamer formed using catalyst precursors **10** and **11**. The standard procedure used in our laboratory to appraise new catalytic systems was applied.[48] Polymerizations were carried out in chlorobenzene at



60 °C and the monomer-to-catalyst ratio was 250 [Eq. (2)]. Under these conditions, no significant difference was observed in the polymerization outcome, whether complex **10** or **11** was employed as catalyst precursor. In both cases, a high molecular weight polymer with a polydispersity index close to 1.5 and a backbone that contained mostly *trans* double bonds was isolated in almost quantitative yield (Table 1).

Next, we have investigated the RCM of diethyl 2,2-diallylmalonate [Eq. (3)]. Preliminary experiments



were carried out using 1 mol% of ruthenium initiator and a 0.1 M stock solution of substrate in CD_2Cl_2 at 30 °C, as recommended by Grubbs et al. for the comparative evaluation of catalyst precursors in the RCM of α,ω-dienes.[47] Under these conditions, complexes **10** and **11** were considerably less active than their first generation parent **9** (Figure 4). The latter catalyst afforded a 96% conversion after 30 min. Within the same period of time, consumption of the starting material did not exceed 6% with complex **10** and 3% with complex **11**. Yet, with these two compounds, satisfactory conversions were eventually reached after a few days. The same trend was already observed by Clavier and Nolan when comparing first and second generation ruthenium-indenylidene catalysts based on the tricyclohexylphosphane ligand (**3** and **4**, respectively).[49] Subsequent work by Verpoort et al. confirmed that first generation catalysts **1** and **3** afforded higher conversions of diethyl 2,2-diallylmalonate in shorter reaction times than their second generation analogues **2** and **4** when the RCM was carried out at 20 °C.[42,44]

To compensate for the slow initiation rate displayed by complexes **10** and **11** at 30 °C, we decided to per-

Table 1. ROMP of cyclooctene catalyzed by complexes **10** and **11**.[a]

Complex	Monomer Conversion [%][b]	Polymer Yield [%]	M_n [kg mol^{-1}][c]	M_w/M_n[c]	σ_{cis}[d]
10	>99	91	195	1.6	0.18
11	>99	88	207	1.5	0.14

[a] *Experimental conditions:* Ru catalyst (0.03 mmol), PhCl (5 mL), cyclooctene (7.5 mmol), 2 h at 60 °C.
[b] Determined by GC using the cyclooctane impurity of cyclooctene as an internal standard.
[c] Determined by SEC in THF with polystyrene calibration.
[d] Fraction of *cis* double bonds within the polyoctenamer, determined by ^{13}C NMR.

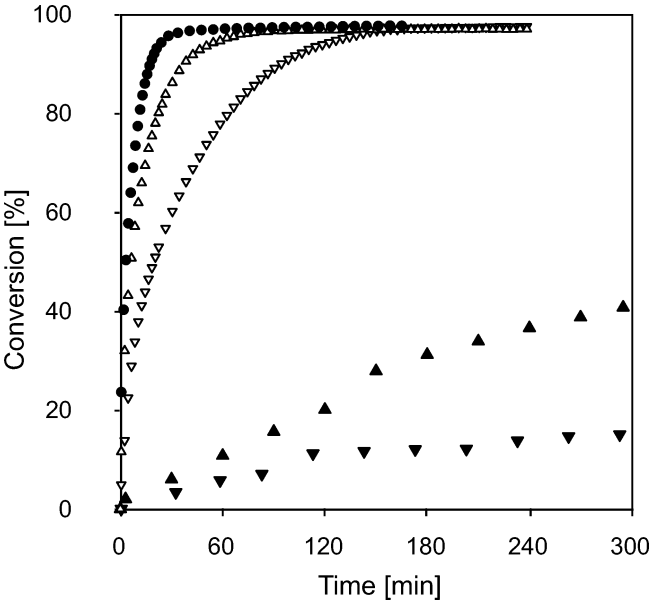
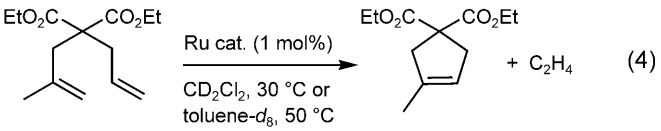


Figure 4. Time course of the RCM of diethyl 2,2-diallylmalonate using various catalyst precursors (1 mol%) in CD_2Cl_2 at 30 °C (**9**: ●, **10**: ▲, **11**: ▼) or in toluene-d_8 at 50 °C (**10**: △, **11**: ▽).

form the RCM of diethyl 2,2-diallylmalonate at higher temperatures. Because the boiling point of CD_2Cl_2 is only 40 °C, we replaced it with toluene-d_8 (bp 111 °C) in these experiments. A first data set was recorded at 50 °C (Figure 4). At this temperature, it took approximately 1 h to achieve an almost quantitative conversion with complex **10**, whereas complex **11** required *ca.* 140 min to reach equilibrium. A further kinetic plot was recorded with this latter catalyst precursor at 80 °C. At this temperature, the reaction took place almost instantaneously and led to a complete conversion of the substrate before the first NMR analysis could be performed. In order to quantify the activities of the two complexes under scrutiny, we have determined the rate constants observed in the RCM of diethyl 2,2-diallylmalonate (DEDAM) at 50 °C. The formalism proposed by Grubbs et al. was employed to extract the pseudo-first order rate constants from the plot of ln([DEDAM]) *vs.* time.[47,50] As expected, the k_{obs} value computed for complex **10** (0.0010 s^{-1}) was greater than for its counterpart **11** (0.0004 s^{-1}), but lagged significantly behind the one obtained with complex **9** at 30 °C (0.0019 s^{-1}).

Replacement of one allyl group with a branched 2-methylallyl substituent in DEDAM affords diethyl 2-allyl-2-(2-methylallyl)malonate, which is a standard substrate to probe metathesis catalysts in the formation of trisubstituted cycloolefins [Eq. (4)].[47] Due to steric effects, this reaction is more demanding than the corresponding RCM to form the disubstituted cyclopentene shown in Eq. (3). Thus, we chose to perform the reaction with second generation isobutylphobane complexes **10** and **11** (1 mol%) in toluene-d_8 at 50 °C instead of 30 °C with the more active diphobane precursor **9**. Under these conditions, an almost quantitative conversion of the β-substituted α,ω-diene took place within 4 h with all three catalysts (Figure 5). Small differences in reaction rates were, nevertheless, clearly visible from the kinetic plots. They confirmed the trends already observed for the RCM of DEDAM, as complex **9** displayed a higher catalytic activity at 30 °C than complex **10** at 50 °C, which was in turn slightly more efficient than its sibling **11**. It should be pointed out that metathesis reactions are limited to an equilibrium that does not always allow a 100% conversion to be reached (especially when RCM is performed in a closed system that does not allow removal of the ethylene by-product), thereby explaining the levelling off at *ca.* 95% observed with complexes **9** and **10**.



(4)

In a final series of RCM experiments, we have investigated the cyclization of diethyl 2,2-bis(2-methylallyl)malonate into the corresponding tetrasubstituted cycloolefin [Eq. (5)]. The considerable steric hindrance of the β,ψ-disubstituted α,ω-diene makes this reaction very challenging for most ruthenium initiators currently available.[47] Because an important thermal activation is required to perform the cyclization,

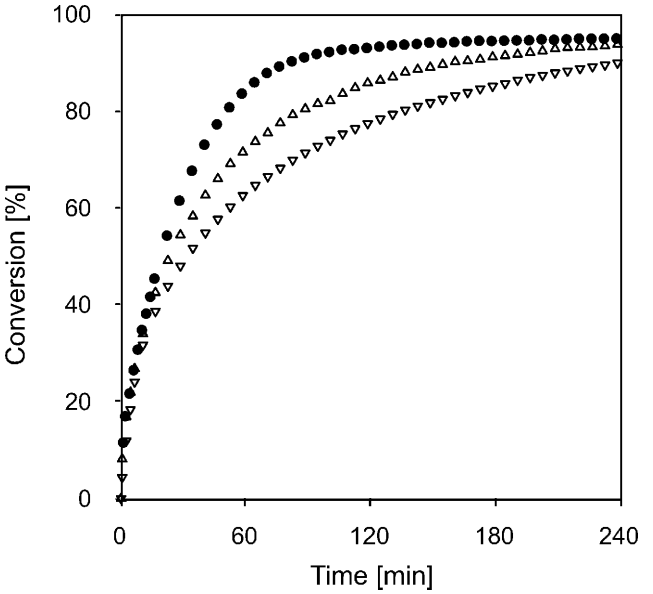
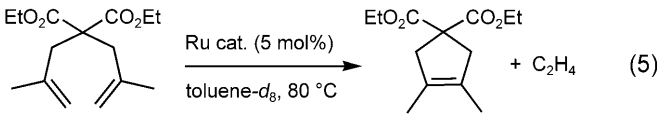


Figure 5. Time course of the RCM of diethyl 2-allyl-2-(2-methylallyl)malonate using various catalyst precursors (1 mol%) in CD_2Cl_2 at 30 °C (**9**: ●) or in toluene-d_8 at 50 °C (**10**: △, **11**: ▽).



rapid degradation of the active species is a major issue in this transformation, and the second generation complexes that are more able to withstand elevated temperatures usually give better results than their first generation analogues.[5,36,40] In our hands, despite the use of rather forcing conditions (5 mol% catalyst loading at 80 °C), conversions remained, however, far from quantitative using common SIMes-based catalyst precursors, such as complexes **2** and **4** (Figure 6). To overcome these limitations, Grubbs et al. have successfully introduced a new family of second generation ruthenium-benzylidene and isopropoxybenzylidene catalyst precursors based on NHC ligands designed to reduce the steric pressure around the metal center (Scheme 4). Thus, in compounds **12** and **13**, free *ortho* positions on the *N*-bound 2-tolyl substituents provide more space around the ruthenium atom, which is thought to account for their increased activity toward sterically challenging substrates.[51]

We reasoned that another strategy to achieve the same goal would be to increase the catalyst stability through a modification of the phosphane ligand and that complexes **10** and **11** were ideal candidates to probe the validity of this approach. Hence, we were very pleased to note that the two mixed isobutylphobane/NHC catalyst precursors were more active than

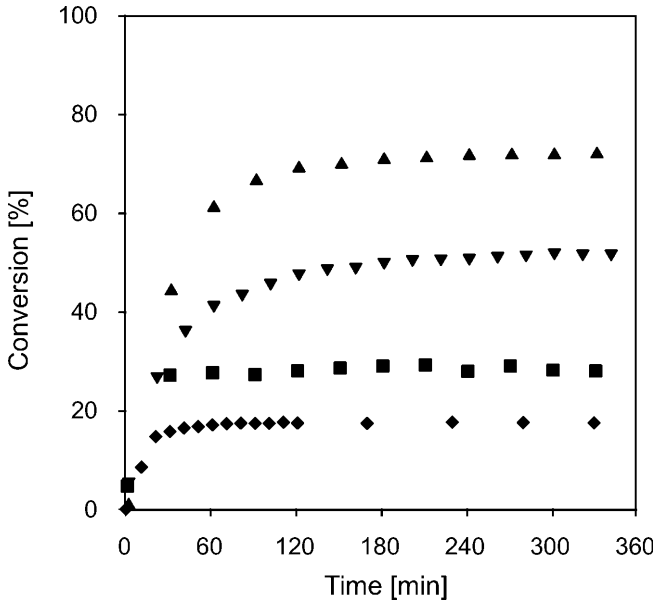
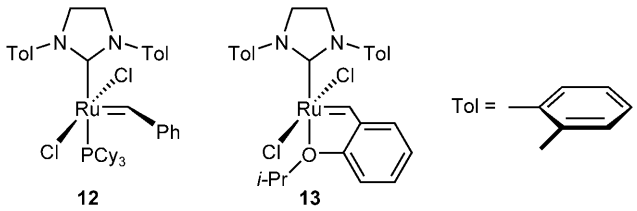


Figure 6. Time course of the RCM of diethyl 2,2-bis(2-methylallyl)malonate using various catalyst precursors (5 mol%) in toluene-d_8 at 80 °C (**2**: ◆, **4**: ■, **10**: ▲, **11**: ▼).

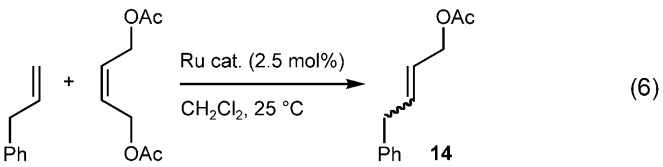


Scheme 4. Unhindered second generation ruthenium-alkylidene complexes.

the corresponding ruthenium-benzylidene or indenylidene complexes **2** and **4** bearing the PCy_3 ligand (Figure 6). The validity of our approach was further strenghtened by recent reports from the groups of Plenio and Nolan that appeared while this manuscript was under review.[52] The two teams showed that ruthenium-benzylidene or indenylidene catalyst precursors bearing two distinct NHC ligands were highly active for the RCM of tetrasubstituted cycloolefins. In both cases, an increased stability due to the strong interaction between the NHCs and the metal center was held responsible for the slow generation of active species at elevated temperatures.

The kinetic plots of our systems revealed that once again, the SIMes-based complex **10** outperformed its IMes-based sibling **11**: within 2 h at 80 °C, conversion reached 72% with the former catalyst but did not exceed 55% with the latter one. No more evolution was recorded after that period of time, indicating a complete decomposition of the active species. Comparatively, complexes **2** and **4** were far less resistant to thermal degradation and stopped working after 30 to 60 min under the experimental conditions adopted. Adding the ruthenium initiator in small portions over time and venting the ethylene produced upon RCM of diethyl 2,2-bis(2-methylallyl)malonate should further enhance the resilience of complexes **10** and **11**, but such modifications of the benchmark protocols used to compare various catalytic systems fell outside the scope of this study.

Last but not least, we have investigated the cross-metathesis between allylbenzene and *cis*-1,4-diacetoxy-2-butene [Eq. (6)]. Because these two starting



materials display similar high reactivities toward self-metathesis, and their homodimers or cross-products are prone to undergo secondary metathesis events, a statistical mixture containing six different products

(*E/Z*-heterocoupled 4-phenyl-2-buten-1-yl acetate, *E/Z*-1,4-diacetoxy-2-butene, and *E/Z*-homocoupled 1,4-diphenyl-2-butene) is obtained.[53] In order to increase the statistical yield for the desired heterocoupled monoester **14**, 2 equiv. of *cis*-1,4-diacetoxy-2-butene (corresponding to 4 equiv. of allyl acetate) were introduced relative to allylbenzene. The benchmark procedure proposed by Grubbs et al.[47] (2.5 mol% of catalyst in CH_2Cl_2 at 25 °C) was followed and the reaction course was monitored by GC using *n*-tetradecane as internal standard. The conversions to heterocoupled product **14** *vs.* time were recorded using various ruthenium-indenylidene catalyst precursors (Figure 7). The results of this kinetic study confirmed the trends already deduced from the RCM experiments. Thus, the replacement of tricyclohexylphosphane in complex **3** with the isobutylphobane ligand in the analogous first generation catalyst **9** led to a small albeit significant reduction of activity. A fine distinction was also made between complexes **10** and **11**, but the difference was less pronounced than in RCM reactions. With these two catalysts, conversions did not exceed 5% after 5 h. When the reactions were prolonged overnight, the yield of cross-product **14** reached 79% with SIMes-based complex **10** and 76% with its counterpart **11**. In both cases, formation of the thermodynamically more stable *trans*-4-phenyl-2-buten-1-yl acetate was favored over its *cis* isomer (*E/Z* ratio = 6.7 with **10** and 6.3 with **11**). Most strikingly, second generation complexes **10** and **11** were far less active than the first generation catalysts **3** and **9**. This is in sharp contrast with previous results from the literature that demonstrated the superior activity of second generation ruthenium-benzylidene or indenylidene catalysts based on the PCy_3 ligand, such as **2** or **4**, over their first generation counterparts (**1** and **3**, respectively) in several types of CM reactions.[47,54] This discrepancy further suggests that complexes **10** and **11** are particularly stable in solution and are much slower initiators for olefin metathesis than most ruthenium-alkylidene species investigated so far.

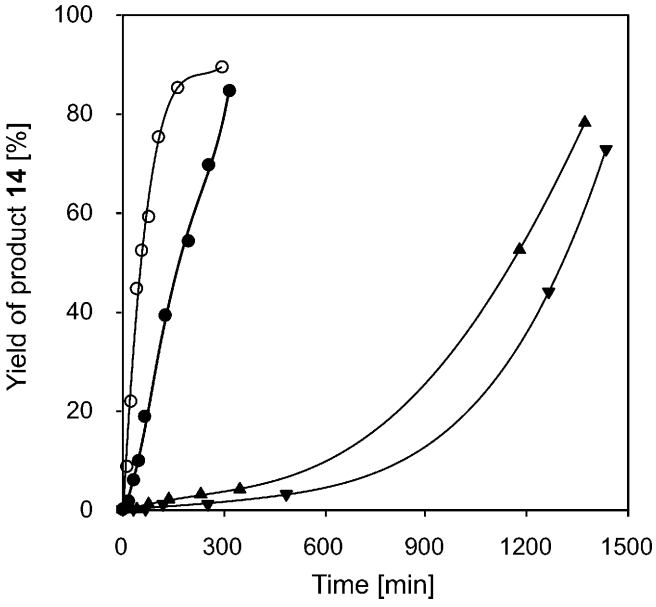
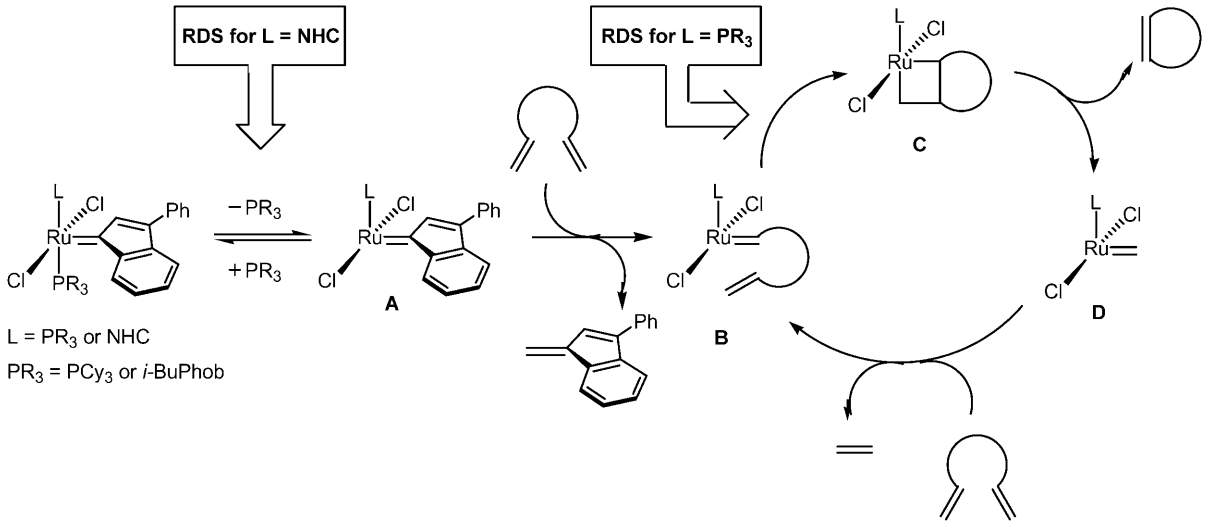


Figure 7. Time course of the CM between allylbenzene and *cis*-1,4-diacetoxy-2-butene using various catalyst precursors (2.5 mol%) in CH_2Cl_2 at 25 °C (**3**: ○, **9**: ●, **10**: ▲, **11**: ▼). Lines are intended as visual aids only, not as curve fits.

Mechanistic Indications

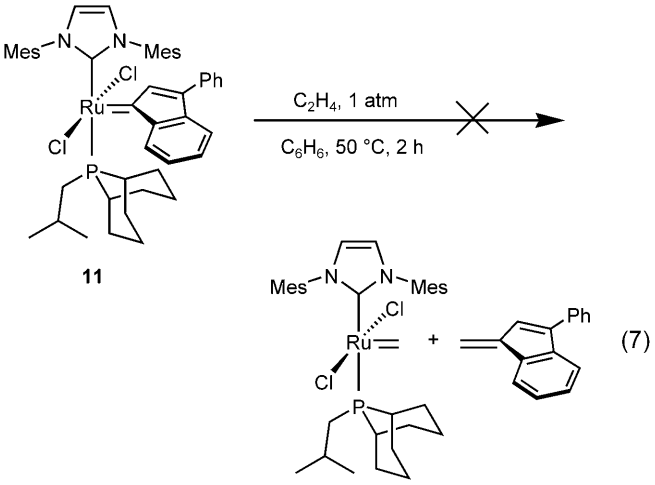
According to the well-established mechanism postulated for olefin metathesis, 16-electron ruthenium-alkylidene catalyst precursors must lose a phosphane ligand in order to generate 14-electron complexes **A** and **D**, which are the true active species leading to the key metallacyclobutane intermediate **C** (Scheme 5).[55] The formation of **A** precedes the olefin coordination and a first metathesis event that leads to complex **B**. The initial phosphane dissociation is not related to the nature of the substrate and corresponds to the limiting step for NHC-containing precatalysts.[14] This explains why a thermal activation of second generation ruthenium-indenylidene complexes **10** and **11** was required to perform the RCM of diethyl 2,2-diallylmalonate and diethyl 2-allyl-2-(2-methylallyl)malonate, in sharp contrast with their diphosphane parent **9**, which reacted faster at lower temperature (*cf.* Figure 4 and Figure 5). Conversely, the formation of the metallacyclobutane **C**, and its conversion to the methylidene species **D** upon extrusion of the RCM product constitute the limiting step for first generation precatalysts, which are therefore much more sensitive to the steric hindrance of the substrate and fail to accomplish the RCM of tetrasubstituted olefins.[56]

We have no explanation to account for the superior activity exhibited by SIMes-based complex **10** in comparison with its IMes-containing sibling **11** in the vast majority of our catalytic tests. We note, however, that related precursors **2** and **4** were also found better catalysts than the corresponding PCy_3/IMes ruthenium-alkylidene compounds for many RCM or CM reactions.[47,49] Based on DFT calculations, Jensen and coworkers attributed this difference of behavior to both electronic and steric effects.[57] The specific σ-donor and π-acceptor properties of the NHC ligand are expected to have a large impact on the stability of 14-electron complexes **A** and **D**. The non-planarity of the imidazoline backbone in SIMes and differences in the tilt angle of the mesityl groups may also be responsible for subtle steric modifications of the ruthenium coordination sphere. Likewise, our investigations have shown that the replacement of tricyclohexylphosphane with isobutylphobane had a dramatic in-



Scheme 5. Proposed mechanism and rate-determining steps (RDS) for the RCM of α,ω-dienes catalyzed by ruthenium-indenylidene complexes.

fluence on the stability and activity of second generation ruthenium-indenylidene complexes. This result was hardly predictable based on simple steric and electronic considerations. As a matter of fact, tricyclohexylphosphane is slightly more bulky than isobutylphobane, as expressed by the Tolman cone angle ($\theta =$ 170° for PCy_3[58] and 163° for *i*-BuPhob[59]). For non-obvious reasons, it is also a better electron donor, as measured from the values of ν(CO) in *trans*-$[RhCl(CO)(PR_3)_2]$ complexes (1943 cm^{-1} for PCy_3[60] *vs.* 1950 cm^{-1} for *i*-BuPhob[61]).

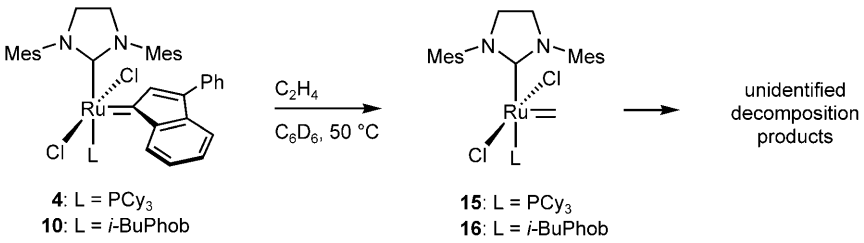


(7)

Decomposition Studies

The steric and electronic robustness of the indenylidene unit, together with the strong binding of PCy_3 and NHC ligands are responsible for the high thermal stability of ruthenium complexes **3** and **4**, as pointed out by the groups of Nolan[36] and Verpoort.[42] The catalytic tests that we have carried with isobutylphobane-based compounds **10** and **11** suggest that they are even more stable. Because ruthenium-methylidene species are key propagating agents in many metathetical transformations and represent the thermally least stable intermediates within the catalytic cycle,[62] we reasoned that assessing their stability and decomposition pathways would help us to better rank their indenylidene precursors in terms of catalytic efficiency. Thus, we tried to prepare the $[RuCl_2$(isobutylphobane)(IMes)$(=CH_2)]$ complex by reacting indenylidene compound **11** with ethylene in benzene at 50 °C for 2 h [Eq. (7)]. This procedure was successfully applied by Forman et al. for the synthesis of methylidene complexes derived from first generation cyclohexylphobane catalyst precursors **5** and **6**.[24] With the second generation isobutylphobane complex **11**, no sign of reaction was detected by ^1H NMR analysis and the starting material was recovered unchanged upon work-up. This lack of reactivity confirms the remarkable stability and the poor initiation efficiency of the isobutylphobane/NHC ruthenium-indenylidene template.

We then decided to compare the ethenolysis rates of two second generation ruthenium-indenylidene complexes bearing, respectively, a tricyclohexylphosphane and an isobutylphobane ligand. For these experiments, complexes **4** and **10** were dissolved in C_6D_6 saturated with ethylene at 25 °C and then heated to 50 °C in sealed NMR tubes (Scheme 6). The disappearance of the indenylidene H-8 protons in the starting materials was followed by ^1H NMR spectroscopy using triptycene as an internal standard. Concomitantly, we also monitored the appearance of new signals at higher field (*ca.* 18.5 ppm), due to the formation of



Scheme 6. Decomposition path of ruthenium-indenylidene complexes under ethylene atmosphere.

ruthenium-methylidene active species **15** or **16** (Figure 8). A rapid consumption of PCy_3-based indenylidene complex **4** took place as soon as ethylene was added to the reaction mixture. It led to the formation of the corresponding methylidene species **15**, whose maximum concentration peaked after 7 h and corresponded to 45% of the initial precatalyst. Due to bimolecular decomposition processes, this intermediate then slowly decomposed into unidentified products and almost totally disappeared after 2 days. The decomposition path of isobutylphobane complex **10** was completely different. An induction period of *ca.* 9 h was observed before it started reacting with ethylene to afford a small amount of [$RuCl_2$(isobutylphobane)(SIMes)(=CH_2)] (**16**). Although the molar proportion of this complex never exceeded 2%, it persisted after almost 3 days, when the measurements were interrupted. This behavior explains why complex **10** initiates RCM and CM reactions very slowly, but leads to robust active species that are able to sustain the long reaction times and high temperatures required to carry out the RCM of tetrasubstituted olefins.

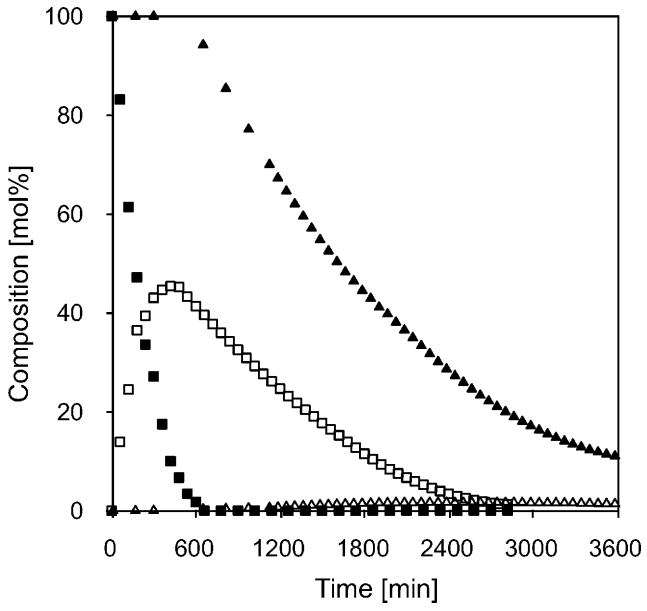


Figure 8. Time course of the decomposition of ruthenium-indenylidene complexes (**4**: ■, **10**: ▲) and ruthenium-methylidene species derived thereof (**15**: □, **16**: △) in C_6D_6 saturated with ethylene at 50 °C.

Conclusions

By heating a THF solution of the commercially available [$RuCl_2$(isobutylphobane)$_2$(3-phenyl-1-indenylidene)] catalyst precursor (**9**) with a two-fold excess of either SIMes·CO_2 or IMes·CO_2, we were able to isolate two new second generation ruthenium-indenylidene complexes bearing mixed isobutylphobane/NHC ligands (**10** and **11**) in high yields. These compounds were highly stable in the solid state, as well as dissolved in aprotic solvents. They were characterized by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, and the molecular structure of [$RuCl_2$(isobutylphobane)(SIMes)(3-phenyl-1-indenylidene)] (**10**) was determined by X-ray diffraction analysis. A close inspection of the packing structure revealed the presence of different types of intra- and intermolecular interactions that enhance the global stability of the crystals, while low temperature NMR experiments showed the existence of two distinct rotational isomers due to the unsymmetrical nature of the phobane ligand.

The catalytic activity of compounds **10** and **11** was probed in various types of ROMP, RCM, and CM reactions, and compared with those of related first and second generation ruthenium-benzylidene and indenylidene catalyst precursors. Kinetic studies confirmed the high thermal stability of isobutylphobane complexes **10** and **11**, which suffered from a slow initiation efficiency compared to other catalytic systems based on the tricyclohexylphosphane ligand. However, the remarkable robustness of [$RuCl_2$(isobutylphobane)(SIMes)(3-phenyl-1-indenylidene)] (**10**) turned out to be beneficial for performing the RCM of diethyl 2,2-bis(2-methylallyl)malonate, a challenging reaction that holds previously developed ruthenium-indenylidene catalysts in check. Monitoring the formation of the ruthenium-methylidene active species [$RuCl_2$(isobutylphobane)(SIMes)(=CH_2)] (**16**) derived from this precursor further demonstrated its ability to sustain long reaction times and high temperatures required to carry out the RCM of tetrasubstituted olefins. Other types of metathetical processes,

such as the self-metathesis or ethenolysis of renewable fatty acid esters, are also in dire need for economical, selective, and long-lived catalysts to be applied on a large scale, and we envision that mixed phobane/NHC ruthenium-indenylidene complexes might be promising candidates to fulfill these duties.

Experimental Section

General Information

All reactions were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were distilled from appropriate drying agents and deoxygenated prior to use. Diethyl 2-allyl-2-(2-methylallyl)malonate,[63] diethyl 2,2-bis(2-methylallyl)malonate,[63] IMes·CO_2,[35a] and SIMes·CO_2[35a] were synthesized according to published procedures. Indenylidene complex **9** (Neolyst™ M11) was obtained from Umicore. Silica gel 60 (60 Å nominal pore diameter, 0.04–0.063 mm particle size) supplied by ROCC was used for flash chromatography. Petroleum ether refers to the hydrocarbon fraction of bp 40–60 °C and was purchased from Labotec. All the other chemicals were purchased from Aldrich. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded with a Bruker DRX 400 or a Bruker Avance 250 spectrometer. Chemical shifts are listed in parts per million downfield from TMS and are referenced from the solvent residual peaks (^{1}H, ^{13}C) or external H_3PO_4 (^{31}P). Gas chromatography was carried out with a Varian 3900 instrument equipped with a flame ionization detector and a WCOT fused silica column (stationary phase: CP-Sil 5CB, column length: 15 m, inside diameter: 0.25 mm, outside diameter: 0.39 mm, film thickness: 0.25 μm). Size-exclusion chromatography (SEC) was performed in THF at 45 °C with a SFD S5200 autosampler liquid chromatograph equipped with a SFD 2000 refractive index detector and a battery of 4 PL gel columns fitted in series (particle size: 5 μm; pore sizes: 10^5, 10^4, 10^3, and 10^2 Å; flow rate: 1 mL min^{-1}). The molecular weights (not corrected) are reported *versus* monodisperse polystyrene standards used to calibrate the instrument. Elemental analyses were carried out in the Laboratory of Pharmaceutical Chemistry at the University of Liège.

Synthesis of {Dichloro(9-isobutylphosphabicyclo-[3.3.1]nonane)[1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene](3-phenyl-1-indenylidene)-ruthenium(II)} (10)

A 100-mL, two-neck, round-bottom flask containing a magnetic stirring bar and fitted with a reflux condenser topped with an oil bubbler was charged with [$RuCl_2$(isobutylphobane)$_2$(3-phenyl-1-indenylidene)] (**9**) (0.4 g, 0.53 mmol) and SIMes·CO_2 (0.369 g, 1.05 mmol, 2 equiv.). The reactor was purged of air by applying three vacuum/argon cycles before dry THF (20 mL) was added. The dark red solution was refluxed in an oil bath at 80 °C under a slow stream of argon. The reaction progress was monitored by TLC on silica gel plates using petroleum ether/diethyl ether (92/8 v/v) as eluent. When conversion of the starting complex was complete (*ca.* 4 h), the solution was cooled down and the solvent was removed under vacuum. The residue was purified by flash chromatography on a silica gel plug using the same eluent that was used for TLC to afford the title compound (**10**) as a red powder; yield: 0.42 g (91%). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 9.18 (d, $^4J_{7,8}$ = 7.2 Hz, 1H, H-8), 7.87 (s, 1H, Ph), 7.85 (s, 1H, Ph), 7.80 (s, 1H, H-2), 7.33–7.30 (m, 2H), 7.24–7.20 (m, 3H), 7.12–7.08 (m, 1H), 6.95 (s, 2H, CH_{ar} Mes), 6.48 (s, 1H, CH_{ar}), 6.04 (s, 1H, CH_{ar}), 3.39–3.33 (m, 2H, CH_2 NHC), 3.27–3.13 (m, 2H, CH_2 NHC), 2.88, 2.83, 2.39, 2.22, 2.17, 1.76 (aliphatic part); ^{13}C NMR (101 MHz, C_6D_6, 298 K): δ = 294.9 (d, $^2J_{P,C}$ = 3.9 Hz, C-1 indenylidene), 217.9 (d, $^2J_{P,C}$ = 80.9 Hz, C-2 NHC), 145.1, 141.8, 139.5, 139.4, 138.4, 138.0, 137.7, 137.6, 137.4, 137.2, 137.0, 136.9, 136.1, 130.3, 130.2, 129.4, 129.1, 128.9, 126.8, 116.5, 52.4, 52.0, (other aliphatic signals not listed); ^{31}P NMR (101 MHz, C_6D_6, 298 K): δ = 7.8 (br s); anal. calcd. for $C_{48}H_{59}Cl_2N_2PRu$ (866.95): C 66.50, H 6.86, N 3.23; found: C 66.80, H 7.06, N 3.59.

Synthesis of {Dichloro(9-isobutylphosphabicyclo-[3.3.1]nonane)[1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene](3-phenyl-1-indenylidene)-ruthenium(II)} (11)

Using the same procedure as described above, [$RuCl_2$(isobutylphobane)$_2$(3-phenyl-1-indenylidene)] (**9**) (0.4 g, 0.53 mmol) was reacted with IMes·CO_2 (0.367 g, 1.05 mmol, 2 equiv.) to afford the title compound (**11**) as a red powder; yield: 0.40 g (88%). ^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 9.13 (d, $^4J_{7,8}$ = 7.2 Hz, 1H, H-8), 7.87 (s, 1H, Ph), 7.85 (s, 1H, Ph), 7.82 (s, 1H, H-2), 7.31–7.24 (m, 2H), 7.23–7.19 (m, 3H), 7.13–6.93 (m, 1H), 6.93 (s, 2H, CH_{ar} NHC), 6.47 (s, 1H, CH_{ar} NHC), 6.18 (s, 2H, H-4,5 NHC), 6.03 (s, 1H, CH_{ar} NHC), (other aliphatic signals not listed); ^{1}H NMR (400 MHz, CD_2Cl_2, 223 K): δ = 0.7 (br s, CH_3 phobane, 6H), 1.50–2.50 (m, CH_2 + CH phobane, 17H), 1.77 (s, CH_3, 3H), 1.80 (s, CH_3, 3H), 1.96 (s, CH_3, 3H), 2.37 (s, CH_3, 6H), 2.89 (s, CH_3, 3H), (aliphatic part only); ^{13}C NMR (101 MHz, C_6D_6, 298 K): δ = 294.9 (d, $^2J_{P,C}$ = 3.5 Hz, C-1 indenylidene), 186.9 (d, $^2J_{P,C}$ = 85.9 Hz, C-2 NHC), 145.2, 141.8, 139.1, 138.7, 138.5, 137.7, 137.5, 137.2, 136.3, 129.5, 129.3, 129.0, 128.3, 126.8, 126.6, 125.6, 125.3, 124.7, 116.6, (other aliphatic signals not listed); ^{13}C NMR (101 MHz, CD_2Cl_2, 223 K): δ = 17.7 [s, P–CH_2–$CH(CH_3)_2$], 18.15, 18.23, 19.1, 19.2 (s, *ortho*-CH_3, IMes), 20.8 (d, $^3J_{P,C}$ = 3.7 Hz, P–CH–CH_2–CH_2), 20.9, 21.3 (s, *para*-CH_3, IMes), 21.4 (d, $^3J_{P,C}$ = 4.5 Hz, P–CH–CH_2–CH_2), 23.2 [d, $^1J_{P,C}$ = 22 Hz, P–CH_2–$CH(CH_3)_2$], 24.3 (d, $^3J_{P,C}$ = 6.3 Hz, P–CH–CH_2), 25.1 (d, $^3J_{P,C}$ = 8.9 Hz, P–CH–CH_2), 26.8 [m, P–CH–CH_2, P–CH_2–$CH(CH_3)_2$], 27.2 (d, $^2J_{P,C}$ = 16.1 Hz, P–CH), 32.9 (d, $^2J_{P,C}$ = 16.1 Hz, P–CH), (aliphatic part only); ^{31}P NMR (101 MHz, C_6D_6, 298 K): δ = 10.2; anal. calcd. for $C_{48}H_{57}Cl_2N_2PRu$ (864.93): C 66.65, H 6.64, N 3.24; found: C 66.69, H 6.82, N 3.39.

X-Ray Crystal Structure Determination

Orange crystals of complex **10** suitable for X-ray diffraction analysis were obtained by slow diffusion of isopropyl alcohol into a saturated dichloromethane solution at room temperature. Crystal data (d = 0.95 Å) were collected on a Bruker APPEX II diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) from a fine-focus sealed

tube source at 100 K. Computing data and reduction was made with the APPEX II software.[64] The structure was solved using DIRDIF,[65] and finally refined by full-matrix, least-squares based on F^2 by SHELXL.[66] An empirical absorption correction was applied using SADABS.[67] All non-hydrogen atoms were anisotropically refined and the hydrogen atom positions were calculated and refined using a riding model.

Crystal Data for [$RuCl_2$(isobutylphobane)(SIMes)(3-phenyl-1-indenylidene)] (10): $C_{48}H_{59}Cl_2N_2PRu$, $M=866.95$, crystal dimensions: $0.09\times0.08\times0.05$ mm, monoclinic, $a=13.2609(10)$, $b=19.0101(12)$, $c=17.2004(11)$ Å, $\beta=102.419(4)°$, $V=4234.6(5)$ Å^3, $T=100$ K, space group $P2_1/c$, $Z=4$, λ(Mo-$K\alpha$)$=0.71073$ Å, $\mu=0.57$ mm^{-1}, 48381 measured reflections, 5178 independent reflections ($R_{int}=0.1262$), 3646 independent reflections with $I>2s(I)$, 499 parameters refined, GOF$=1.015$, $R_1=0.046$ [$I>2s(I)$] and 0.084 (for all data), $wR_2=0.089$ [$I>2s(I)$] and 0.103 (for all data), residual electron density $\rho_{max}=0.897$ e Å^{-3}, $\rho_{min}=-0.48$ e Å^{-3}.

CCDC 766617 contains the supplementary crystallographic data (excluding structure factors) for the structure reported in 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 or on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax.: (internat.) +44-1223/336-033].

Catalytic Tests

Standard benchmark procedures were followed to perform the ROMP of cyclooctene[48] and all the other ROMP, RCM, or CM catalytic tests.[47] Full details are given in the Supporting Information.

Decomposition of Ruthenium-Indenylidene Catalysts Precursors in the Presence of Ethylene

A 20-mL Schlenk tube was charged with dry and degassed C_6D_6 (5 mL) and ethylene was bubbled for 10 min at 25 °C. An NMR tube equipped with a screw-cap septum was charged with a ruthenium complex (13.8 μmol) and triptycene (3 mg, 11.8 μmol). Air was expelled by flushing with argon for 10 min before C_6D_6 saturated with ethylene (0.6 mL) was added with a syringe. The reaction mixture was thermostatted at 50 °C in the NMR probe and experimental data points were collected using Bruker automation software. The concentrations in ruthenium-indenylidene and ruthenium-methylidene species were determined by comparing the integrals of the indenylidene H-8 protons (**4**: $\delta=8.85$, d, $^3J_{H,H}=7.4$ Hz, 1H; **10**: $\delta=9.19$, d, $^3J_{H,H}=6.9$ Hz, 1H) or methylidene protons (**15**: $\delta=18.51$, s, 2H; **16**: $\delta=18.82$, s, 2H) with those of the aliphatic protons in triptycene ($\delta=5.2$, s, 2H).

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