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Imidazol(in)ium-2-carboxylates as N-Heterocyclic Carbene Precursors for the Synthesis of Second Generation Ruthenium Metathesis Catalysts

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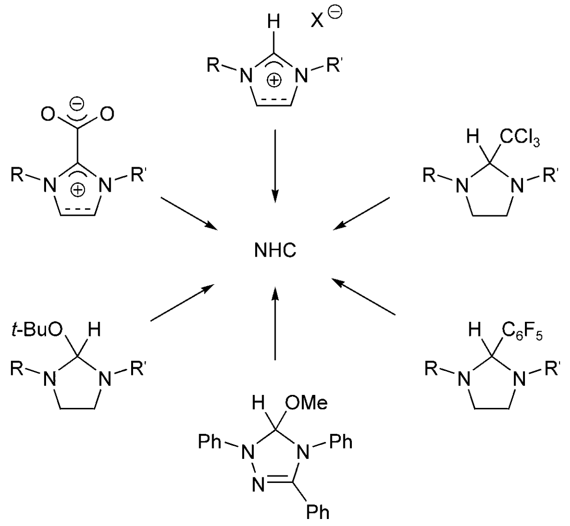
Abstract: Five well-known ruthenium-N-heterocyclic carbene (NHC) catalysts for olefin metathesis and related reactions, including the second generation Grubbs and Hoveyda–Grubbs catalysts, were prepared by phosphane exchange between first generation ruthenium-benzylidene or indenylidene complexes and NHCs generated *in situ* upon thermolysis of imidazol(in)ium-2-carboxylates. Because N-heterocyclic carbene carbon dioxide adducts (NHC·CO_2) are stable zwitterionic compounds that can be stored and handled with no particular precautions, this procedure is particularly attractive from a practical point of view. Reaction courses were conveniently monitored by ^{31}P NMR spectroscopy and the experimental conditions were carefully adjusted to obtain high yields of pure products within short periods of time.

Keywords: alkene metathesis; homogeneous catalysis; N-heterocyclic carbenes; phosphane ligands; ruthenium; zwitterions

Introduction

N-Heterocyclic carbenes (NHCs)[1] have found numerous applications as organocatalysts[2] and as ligands in both organometallic catalysis[3] and coordination chemistry.[4] Currently, the NHCs most commonly encountered are imidazolin-2-ylidene and imidazolidin-2-ylidene species, in which both nitrogen atoms are substituted with alkyl or aryl groups either in symmetrical ($R=R'$) or in asymmetrical fashion ($R\neq R'$).[5] The most popular route for the preparation of NHCs involves the deprotonation of imidazolium or imidazolinium salts with strong bases such as sodium hydride,[6] potassium *tert*-butoxide,[7] or potassium bis(trimethylsilyl)amide.[8,9]

Because most NHCs are air- and moisture-sensitive, several strategies were developed to generate these species *in situ* from more stable precursors (Scheme 1). The simplest option is to add both an imidazol(in)ium salt and a strong base to the reaction mixture.[10] In this case, a slight excess of base is generally employed, which may further interact with organic or organometallic compounds, thereby leading to unwanted side-reactions.[11] Another method consists in the release of free carbenes upon thermolysis of labile imidazolidine adducts. Indeed, NHCs form stable adducts with a wide range of main group elements[12] and non-metal compounds.[13] So far, the formation of four different types of adducts has been identified to be thermoreversible. Thus, the chloroform and pentafluorobenzene adducts of 1,3-dimesitylimidazolidin-2-ylidene (nicknamed SIMes) are stable at room temperature but release the corresponding NHC when heated.[14] Alcohol adducts of



Scheme 1. Strategies for the *in situ* generation of NHCs.

triazolin-5-ylidene and imidazolidin-2-ylidene derivatives were also reported to be efficient carbene precursors.[15] For instance, SIMes(H)(O-*t*-Bu) decomposed at room temperature and was used for the *in situ* generation of SIMes in sensitive reaction media.[16]

An equally important strategy to obtain transition metal-carbene complexes[17] or organocatalysts[18] involves the reaction of an imidazol(in)ium salt with a silver(I) source. The intermediate Ag(I)-NHC complex formed can readily transfer its carbene ligand to another late transition metal *via* transmetalation, or decompose upon thermolysis, thereby affording the desired final products. Although very general, this method requires the use of a precious metal in stoichiometric amount and is not exempt from failure.[19]

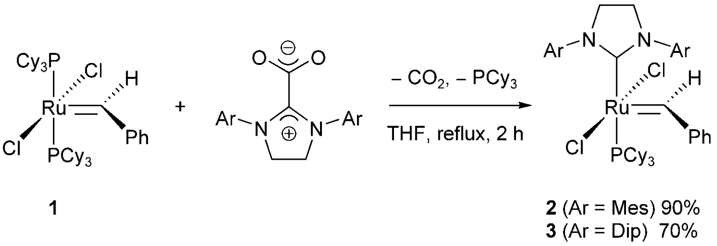
Recently, carbon dioxide adducts of NHCs were successfully employed for the synthesis of several organometallic complexes[20] and in organocatalysis.[21,22] From all the methods investigated so far for generating NHCs *in situ*, the decarboxylation of imidazol(in)ium-2-carboxylate betaines is the most convenient and versatile one (Scheme 1). Indeed, NHC·CO_2 zwitterions are easily obtained by bubbling carbon dioxide into a free carbene solution, followed by solvent evaporation.[23] They are air-stable and they may be stored for more than one year without any sign of decomposition. Furthermore, the formation of carboxylate adducts is virtually possible with every type of NHC, whereas adducts with haloalkanes and alcohols are strictly limited to saturated NHCs.

We have already taken advantage of imidazol(in)ium-2-carboxylate betaines to generate active species *in situ* for the palladium-catalyzed Suzuki–Miyaura cross-coupling of aryl halides with *trans*-2-phenylvinylboronic acid[24] and for ruthenium-promoted olefin metathesis and cyclopropanation reactions.[25] We have also reported the preparation of various ruthenium-arene complexes bearing NHC ligands, starting from $[RuCl_2(p\text{-cymene})]_2$ and imidazolium-2-carboxylates.[26] Herein, we describe the synthesis of five well-known ruthenium-NHC catalysts of prime importance for olefin metathesis and related reactions,[27] by phosphane exchange between first generation ruthenium-benzylidene or indenylidene complexes and NHCs generated *in situ* upon thermolysis of imidazol(in)ium-2-carboxylates. We also emphasize the usefulness of ^{31}P NMR spectroscopy as a convenient tool for monitoring the progress of these reactions.

Results and Discussion

To begin our study, we first investigated the reaction of $[RuCl_2(PCy_3)_2(=CHPh)]$ (**1**)[28] with SIMes·CO_2 (Scheme 2). Preliminary experiments were conducted in toluene at 80 °C 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 increase the decarboxylation rate. The ligand exchange was conveniently monitored by ^{31}P NMR analysis of samples withdrawn from the crude reaction mixture and diluted with a small amount of C_6D_6 (Figure 1). Spectra recorded at regular time intervals showed the progressive disappearance of the resonance at 36.8 ppm for the first generation Grubbs catalyst and the simultaneous emergence of two new sharp singlets located at 30.0 ppm and 10.4 ppm for the second generation Grubbs catalyst (**2**)[29] and free tricyclohexylphosphane (PCy_3), respectively (Table 1). It should be noted that, because no internal or external reference was added, slight variations of these chemical shifts occurred from one experiment to another. After 1 h, integration of the various peaks indicated a 78% conversion of complex **1** into product **2**, while the transformation was almost quantitative after about 2 h (Figure 1).

When the reaction temperature was lowered from 80 to 60 °C, NMR spectroscopy revealed that conversion of catalyst **1** into the second generation benzylidene complex **2** remained limited to 40% after 4 h in toluene. Such sluggishness is most likely due to a poor solubility of SIMes·CO_2 in the aromatic hydrocarbon. In order to better dissolve the zwitterionic NHC precursor in the reaction medium, we decided to replace toluene by THF. Under reflux in this latter solvent, the reaction proceeded faster than in toluene at 80 °C, although the temperature was reduced (the boiling point of THF is 66 °C), and a quantitative conversion was reached within 2 h, as shown by ^{31}P NMR analysis (Table 1). The ruthenium benzylidene com-



Scheme 2. Synthesis of second generation ruthenium-benzylidene catalysts.

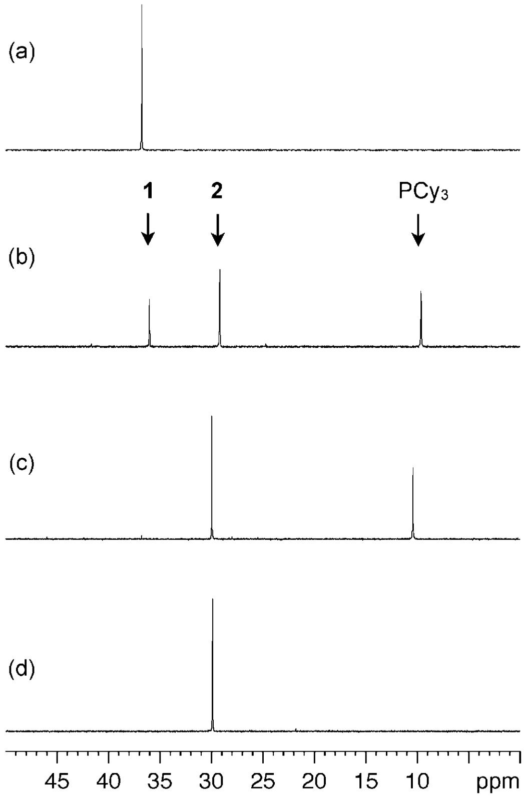


Figure 1. ^{31}P NMR monitoring of the synthesis of complex **2** from [RuCl$_2$(PCy$_3$)$_2$(=CHPh)] (**1**) and SIMes·CO$_2$ in toluene at T=80°C: (**a**) t=0, (**b**) t=1 h (78% conversion), (**c**) t=2 h (98% conversion), (**d**) after work-up.

plex [RuCl$_2$(PCy$_3$)(SIMes)(=CHPh)] (**2**) was purified by flash chromatography on silica gel using a 92/8 v/v mixture of petroleum ether (bp 40–60°C) and diethyl ether as eluent. All the imidazolinium by-products stayed on top of the column and the Grubbs II precatalyst could be isolated in both high yield (90%) and high purity.

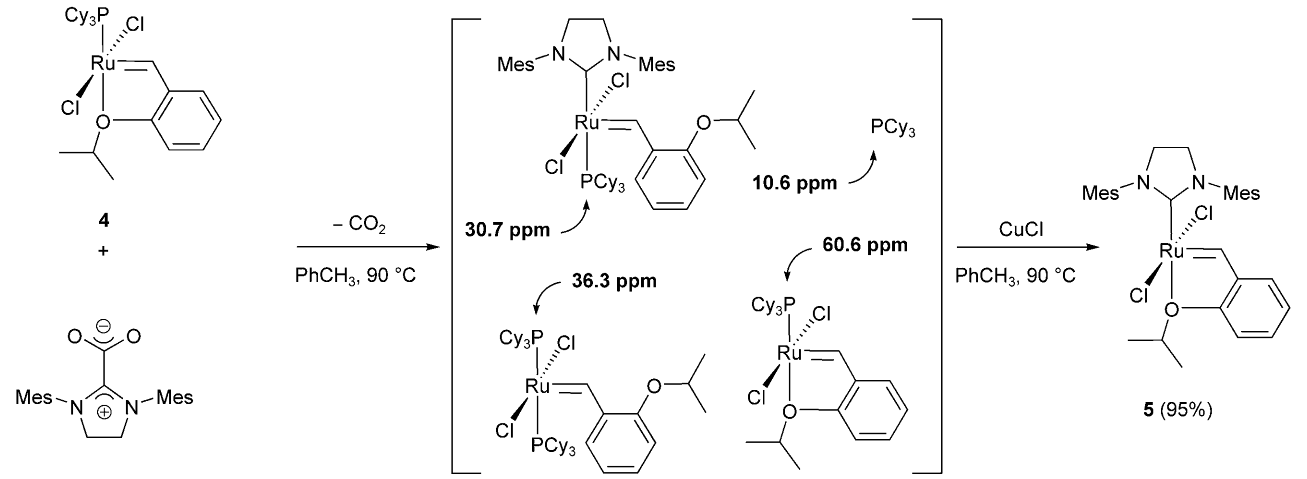
The known [RuCl$_2$(PCy$_3$)(SIDip)(=CHPh)] complex (**3**)[30] was obtained from the first generation Grubbs catalyst (**1**)[28] and SIDip·CO$_2$ in 70% yield using the same experimental procedure as described above [SIDip is 1,3-bis(2,6-diisopropylphenyl)imidazolidin-2-ylidene] (Scheme 2). The ^{31}P NMR signature peak for compound **3** was detected at 27.1 ppm, almost identical to the corresponding signal in SIMes-based complex **2** (Table 1). Although great care was taken to prevent the introduction of oxygen and moisture in the reaction mixture, the formation of tricyclohexylphosphane oxide could not be completely repressed and led to a small peak at 46.2 ppm in addition to the main line due to free PCy$_3$ at 10.4 ppm. It should be noted that complex **3** is significantly less stable in solution than its sibling **2** and totally decomposed on silica gel plates used for TLC analysis. Therefore, it was purified by a quick wash with methanol instead of column chromatography. Although this work-up worked fine in our hands and afforded pure product **3**, we noticed that prolonged contact with the alcohol led to the formation of a new, unidentified by-product, whose ^{31}P NMR resonance was located at 55.8 ppm, but we did not further investigate the structure of this compound. The lower stability in solution of ruthenium-benzylidene or indenylidene complexes bearing the SIDip ligand compared to analogous species containing IMes or IDip, such as complexes **2** or **8**, was already pointed out by Clavier and Nolan, who suggested that the more sterically demanding SIDip ligand should ease phosphane dissociation.[31]

Besides the variation in dielectric constant and its influence on the solubility, we suspected that the convection of fluids induced by the reflux of THF had a beneficial influence on the elimination of gaseous CO$_2$ and contributed to shifting the equilibrium existing in solution between an imidazol(in)ium-2-carboxylate and the corresponding free carbene toward the latter. In order to support this assumption, we tried to assess the thermolysis rate of NHC·CO$_2$ adducts in solution by following the evolution of their characteristic $\tilde{\nu}$(CO$_2$) bands *vs.* time using *in situ* FT-IR spectros-

Table 1. List of chemical shifts used to monitor the synthesis of second generation ruthenium metathesis catalysts by *in situ* ^{31}P NMR spectroscopy.[a]

Reaction	Solvent	δ ^{31}P Reagent [ppm]	δ ^{31}P Product [ppm]	δ ^{31}P Free PCy$_3$ [ppm]	δ ^{31}P Cy$_3$P=O [ppm]
(**1**)→(**2**)	toluene	36.8	30.0	10.4	–
(**1**)→(**2**)	THF	34.0	27.2	7.6	–
(**1**)→(**3**)	THF	36.8	27.1	10.4	46.2
(**4**)→(**5**)	toluene	60.1	–[b]	10.6	–
(**6**)→(**7**)	THF	29.7	23.7	8.3	43.0
(**6**)→(**8**)	toluene	29.7	25.3	7.6	42.9
(**6**)→(**8**)	THF	28.5	27.9	10.7	45.7

[a] Spectra were recorded on 0.5 mL aliquots taken from the reaction media + 0.1 mL C$_6$D$_6$ under an inert atmosphere.
[b] Product (**5**) did not include a phosphane ligand, see Scheme 3 for the chemical shifts of phosphorus-containing intermediates formed during this reaction.

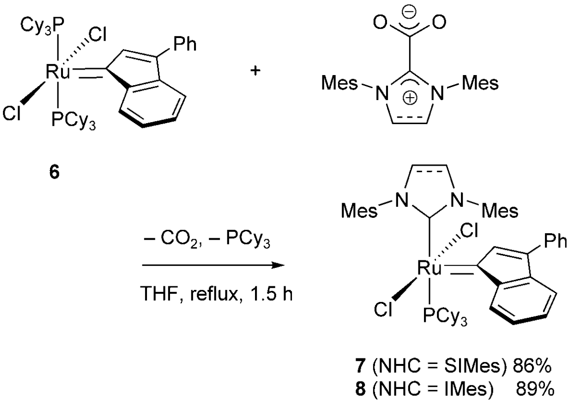


Scheme 3. Synthesis of the second generation isopropoxybenzylidene Hoveyda–Grubbs catalyst.

copy, as described recently by Lu et al. for IDip·CO$_2$ in dichloromethane [IDip is 1,3-bis(2,6-diisopropylphenyl)imidazolin-2-ylidene].[21] Unfortunately, the solubility of NHC·CO$_2$ zwitterions in both toluene and THF was too low for acquiring meaningful data by standard IR techniques (in THF at 25 °C, for instance, the solubility of IMes·CO$_2$ is lower than 5×10^{-5} M). Because of their robustness toward nucleophilic attack, toluene and THF are, nevertheless, solvents of choice for the manipulation of both NHC precursors and ruthenium-alkylidene complexes, so we kept using them in all our subsequent syntheses.

Next, we investigated the formation of the second generation Hoveyda–Grubbs catalyst (**5**)[32,33] starting from the first generation isopropoxybenzylidene complex [RuCl$_2$(PCy$_3$)(=CH-*o*-O-*i*-PrC$_6$H$_4$)] (**4**)[34] and a small excess of SIMes·CO$_2$ (Scheme 3). After 3 h in toluene at 90 °C, we noticed the persistence of a residual small peak at 60.6 ppm in the ^{31}P NMR spectrum of the reaction mixture, assigned to the starting complex (**4**), and the formation of a prominent new resonance at 30.7 ppm corresponding to the mixed phosphane-NHC complex [RuCl$_2$(PCy$_3$)(SIMes)(=CH-*o*-O-*i*-PrC$_6$H$_4$)].[35] This intermediate was accompanied by a small amount of free PCy$_3$, as evidenced by a weak absorption at 10.6 ppm. An additional minor peak at 36.3 ppm was tentatively attributed to the complex [RuCl$_2$(PCy$_3$)$_2$(=CH-*o*-O-*i*-PrC$_6$H$_4$)] as we had also observed it during the preparation of the first generation Hoveyda–Grubbs catalyst. The brown reaction mixture was further heated at 90 °C for 1 h before 1.2 equivalents of CuCl were added to help displace PCy$_3$.[36] Because this phosphane scavenger is paramagnetic, it was not possible anymore to monitor the reaction course by NMR spectroscopy. After 2 h at 90 °C, the final chelated product (**5**) was isolated as a green microcrystalline solid in almost quantitative yield.

Encouraged by the success encountered in the preparation of ruthenium-benzylidene catalysts, we decided to study the formation of second generation ruthenium-indenylidene complexes using imidazol(in)ium-2-carboxylate betaines as ligand precursors. The phosphane/NHC exchange reaction of the complex [RuCl$_2$(PCy$_3$)$_2$(3-phenyl-1-indenylidene)] (**6**)[37,38] with SIMes·CO$_2$ was investigated in refluxing THF (Scheme 4). The ^{31}P NMR analysis of an aliquot taken from the reaction mixture after 30 min showed a 60% conversion of the starting complex resonating at 29.7 ppm, the formation of a new species giving a sharp signal at 23.7 ppm, and the release of a stoichiometric amount of free phosphane in solution (Table 1). After 1.5 h, the starting material had been fully consumed and the product was isolated and purified by flash column chromatography to afford the Neolyst™ M2 catalyst [RuCl$_2$(PCy$_3$)(SIMes)(3-phenyl-1-indenylidene)] (**7**)[39] in 86% yield. A small



Scheme 4. Synthesis of second generation ruthenium-indenylidene catalysts.

peak at 43.0 ppm was also observed while monitoring the reaction by *in situ* ^{31}P NMR spectroscopy. It was assigned to tricyclohexylphosphane oxide formed upon oxidation of the free phosphane ligand in solution. When pure complex (**6**) was dissolved in THF-d_8 under normal atmosphere, NMR spectra recorded after two days at room temperature also revealed the appearance of a new peak at 43.1 ppm due to $Cy_3P{=}O$. It should be pointed out, however, that this impurity was formed in minute amount only during the synthesis of complex (**7**) and could be efficiently removed during work-up.

The synthesis of [$RuCl_2(PCy_3)$(IMes)(3-phenyl-1-indenylidene)] (**8**) was achieved by replacing a tricyclohexylphosphane ligand in catalyst (**6**)[37,38] with IMes generated *in situ* from IMes·CO_2 instead of adding the free NHC ligand to the starting complex, as originally described in the literature.[40] The reaction course was monitored by ^{31}P NMR spectroscopy in both toluene and THF as solvents (Table 1). Yet, in order to minimize the slow degradation of the complex [$RuCl_2(PCy_3)_2$(3-phenyl-1-indenylidene)] (**6**) discussed above, we chose to optimize the experimental procedure in refluxing THF, because it involved a shorter reaction time compared to toluene. Under these conditions, a full conversion of the starting material took place within 1.5 h and catMETium® IMesPCy catalyst (**8**) was isolated in 89% yield after purification by flash chromatography to remove the excess of carboxylate reagent, tricyclohexylphosphane, and its oxide (Scheme 4).

Conclusions

The synthesis of five NHC-containing ruthenium-benzylidene or indenylidene complexes was successfully achieved using imidazol(in)ium-2-carboxylates as carbene ligand precursors. The products obtained are well-known catalysts for olefin metathesis and related reactions that have attracted a lot of attention from both industrial and academic scientists. Their preparation starting from stable zwitterionic adducts that can be stored and handled with no particular precautions instead of using air- and moisture-sensitive free carbenes is particularly attractive from a practical point of view. Experimental conditions were carefully adjusted to obtain high yields of pure products within short periods of time. In this respect, ^{31}P NMR spectroscopy proved to be a very convenient tool for monitoring the progress of the reactions. We are currently applying the decarboxylation of NHC·CO_2 betaines to prepare new ruthenium-NHC complexes and we shall report on their synthesis and catalytic properties in due course.

Experimental Section

General Information

All reactions were carried out using standard Schlenk techniques under an argon atmosphere. Organic solvents were distilled from standard drying agents and degassed prior to use. The first generation Grubbs catalyst (**1**) and copper(I) chloride were purchased from Aldrich and used as received. The first generation Hoveyda–Grubbs catalyst (**4**),[34b] IMes·CO_2,[25] SIMes·CO_2,[25] and SIDip·CO_2[25] were prepared according to literature procedures. Indenylidene complex **6** was obtained from Umicore. Flash chromatography was performed on silica gel 60 (60 Å nominal pore diameter, 0.04–0.063 mm particle size) supplied by ROCC. Petroleum ether refers to the hydrocarbon fraction of bp 40–60 °C and was purchased from Labotec. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker DRX 400 or a Bruker Avance 250 spectrometer at 25 °C.

Synthesis of [$RuCl_2(PCy_3)$(SIMes)(=CHPh)] (2) (Second Generation Grubbs Catalyst)

A flame-dried, 100-mL round-bottom flask containing a magnetic stirring bar and fitted with a reflux condenser topped with a gas bubbler was charged with the complex [$RuCl_2(PCy_3)_2$(=CHPh)] (**1**) (0.99 g, 1.2 mmol) and SIMes·CO_2 (0.63 g, 1.8 mmol). The reactor was purged of air by applying three vacuum/argon cycles before dried and degassed THF (40 mL) was added. The resulting suspension was stirred and refluxed for 3 h in an oil bath at 80 °C under a slow stream of argon. The reaction progress was monitored by ^{31}P NMR spectroscopy. After cooling to room temperature, the solvent was removed under vacuum and the remaining solid was purified by flash chromatography on silica gel with petroleum ether/diethyl ether (92/8 v/v) as eluent. Evaporation of the volatiles under reduced pressure followed by drying under high vacuum afforded the title compound (**2**) as a red solid; yield: 0.92 g (90%). ^{1}H and ^{31}P NMR spectra were identical to those reported earlier in the literature.[29,41]

Synthesis of [$RuCl_2(PCy_3)$(SIDip)(=CHPh)] (3)

A flame-dried, 100-mL round-bottom flask containing a magnetic stirring bar and fitted with a reflux condenser topped with a gas bubbler was charged with the complex [$RuCl_2(PCy_3)_2$(=CHPh)] (**1**) (0.99 g, 1.2 mmol) and SIDip·CO_2 (0.78 g, 1.8 mmol). The reactor was purged of air by applying three vacuum/argon cycles before dried and degassed THF (40 mL) was added. The resulting suspension was stirred and refluxed for 2 h in an oil bath at 80 °C under a slow stream of argon. The reaction progress was monitored by ^{31}P NMR spectroscopy. After cooling to room temperature, the solvent was removed under vacuum. The remaining brownish violet product was quickly washed with dried and degassed MeOH (4 × 5 mL) under an argon atmosphere and dried under high vacuum to afford the title compound (**3**) as a violet solid; yield: 0.79 g (70%). ^{1}H and ^{31}P NMR spectra were identical to those reported earlier in the literature.[30]

Synthesis of [RuCl$_2$(SIMes)(=CH-*o*-O-*i*Pr-C$_6$H$_4$)] (5) (Second Generation Hoveyda–Grubbs Catalyst)

A flame-dried, 100-mL round-bottom flask containing a magnetic stirring bar and fitted with a reflux condenser topped with a gas bubbler was charged with the complex [RuCl$_2$(PCy$_3$)(=CH-*o*-O-*i*-PrC$_6$H$_4$)] (**4**) (0.43 g, 0.71 mmol) and SIMes·CO$_2$ (0.30 g, 0.85 mmol, 1.2 equiv.). The reactor was purged of air by applying three vacuum/argon cycles before dried and degassed toluene (20 mL) was added. The resulting suspension was heated in an oil bath at 90 °C until complete disappearance of the starting complex was observed either by ^{31}P NMR spectroscopy or by TLC (*ca.* 4 h). After cooling to room temperature, CuCl (0.084 g, 0.82 mmol, 1.2 equiv.) was added and the reaction mixture was heated at 90 °C for 2 h. It was then concentrated under vacuum and the resulting dark green solid was dissolved in a minimum amount of petroleum ether/dichloromethane (1/1 v/v). Insoluble phosphane-copper chloride complexes were removed by filtering the suspension through a Pasteur pipette containing a cotton plug while loading it onto a short silica gel column. Elution of the green band with 1/1 petroleum ether/dichloromethane (1/1 v/v) and removal of the solvent under vacuum afforded the title compound (**5**) as a green microcrystalline solid; yield: 0.43 g (95%). ^{1}H and ^{13}C NMR spectra were identical to those reported earlier in the literature.[32]

Synthesis of [RuCl$_2$(PCy$_3$)(SIMes)(3-phenyl-1-indenylidene)] (7) (Neolyst™ M2 Catalyst)

A flame-dried, 100-mL round-bottom flask containing a magnetic stirring bar and fitted with a reflux condenser topped with a gas bubbler was charged with the complex [RuCl$_2$(PCy$_3$)$_2$(3-phenyl-1-indenylidene)] (**6**) (0.4 g, 0.43 mmol) and SIMes·CO$_2$ (0.27 g, 0.78 mmol, 1.8 equiv.). The reactor was purged of air by applying three vacuum/argon cycles before dried and degassed THF (15 mL) was added. The resulting suspension was stirred and refluxed for 1.5 h in an oil bath at 80 °C under a slow stream of argon. After cooling to room temperature, the solvent was removed under vacuum and the remaining red solid was dry-loaded onto silica gel and purified by flash chromatography using hexanes (100 mL) followed by hexanes/diethyl ether (92/8 v/v) as eluents. The deep red solution was concentrated under reduced pressure to afford the title compound (**7**) as a red powder; yield: 0.35 g (86%). ^{1}H, ^{13}C, and ^{31}P NMR spectra were identical to those reported earlier in the literature.[39,42]

Synthesis of [RuCl$_2$(PCy$_3$)(IMes)(3-phenyl-1-indenylidene)] (8) (CatMETium® IMesPCy Catalyst)

A flame-dried, 100-mL round-bottom flask containing a magnetic stirring bar and fitted with a reflux condenser topped with a gas bubbler was charged with the complex [RuCl$_2$(PCy$_3$)$_2$(3-phenyl-1-indenylidene)] (**6**) (0.4 g, 0.43 mmol) and IMes·CO$_2$ (0.27 g, 0.78 mmol, 1.8 equiv.). The reactor was purged of air by applying three vacuum/argon cycles before dried and degassed THF (15 mL) was added. The resulting suspension was stirred and refluxed for 1.5 h in an oil bath at 80 °C under a slow stream of argon. After cooling to room temperature, the solvent was removed under vacuum and the remaining red solid was dry-loaded onto silica gel and purified by flash chromatography using hexanes (100 mL) followed by hexanes/diethyl ether (92/8 v/v) as eluents. The deep red solution was concentrated under reduced pressure to afford the title compound (**8**) as a red powder; yield: 0.37 g (89%). ^{1}H and ^{31}P NMR spectra were identical to those reported earlier in the literature.[40]

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