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# Influence of Sterically Demanding Carbene Ligation on Catalytic Behavior and Thermal Stability of Ruthenium Olefin Metathesis Catalysts

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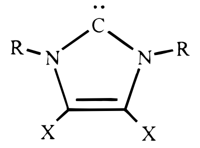
The exchange reaction of one phosphine ligand in $Cl_2(PCy_3)_2Ru{=}CHPh$ (**1**; Cy = cyclohexyl, $C_6H_{11}$) with the sterically demanding carbene ligands 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), 1,3-bis(4-methylphenyl)imidazol-2-ylidene (ITol), and 1,3-bis(4-chlorophenyl)imidazol-2-ylidene (IpCl) leads to the isolation of the new complexes $(PCy_3)(IMes)Cl_2Ru{=}CHPh$ (**2**), $(PCy_3)(ITol)Cl_2Ru{=}CHPh$ (**3**), and $(PCy_3)(IpCl)Cl_2Ru{=}CHPh$ (**4**). Similarly, one IMes ligand can be substituted for one $PCyp_3$ ligand in $Cl_2(PCyp_3)_2Ru{=}CHCH{=}C(CH_3)_2$ (**5**; Cyp = cyclopentyl, $C_5H_9$) to produce $(PCyp_3)(IMes)Cl_2Ru{=}CHPh$ (**6**) in high yield. X-ray structure analysis of **6** confirmed a near-square-pyramidal coordination sphere around the metal center. Improved catalytic properties and thermal stability are observed for **2** and **6** in comparison to the parent **1** and **5**.

## Introduction

Olefin metathesis reactions are proving to be useful tools in organic and macromolecular synthesis.[1] One early example of these metal-mediated transformations is ring-opening metathesis polymerization (ROMP) of cyclic olefins.[1a,2] Ring-closing metathesis (RCM), acyclic diene metathesis (ADMET), cross metathesis (CM), ring-opening metathesis (ROM), and combinations of these more recently explored transformations have now developed into powerful methods leading to previously difficult to reach synthetic targets.[1b−d] As the number of applications involving olefin metathesis catalysts has grown in the 1990s, the interest in catalyst design and performance continues to be of significant interest to the organic and pharmaceutical community.

Catalysts of the Grubbs type (benzylidene and vinylalkylidene) are of special interest, since they are only moderately sensitive to air and moisture and show significant tolerance of functional groups.[3] These five-coordinated Ru complexes adopt a distorted-square-pyramidal structure. A large variety of metathesis reactions proceed rapidly with high selectivity using these catalysts.[3f,h,k] Their catalytic activity originates from the coordination of the olefin substrate at the empty site and simultaneous liberation of one phosphine.[3k] The C−C bond is formed via a 14-electron metallacyclic intermediate.[4] The nature of the carbene moiety has been shown to influence not only the initiation but also the propagation of the catalytic reaction.[3f] Sterically demanding and highly donating phosphine ligands (e.g. $PCy_3$) favor the stabilization of the intermediate catalytic species. Despite its widespread use, this catalyst type still suffers from a relatively low thermal stability as a consequence of phosphine loss and subsequent easily accessible bimolecular decomposition pathway which renders it only sparingly suitable for use at elevated temperatures.[5]

Nucleophilic carbene ligands of the imidazol-2-ylidene type have proven to be phosphine mimics.[6]



R = alkyl, aryl, amine, ether... X = alkyl, H, halide

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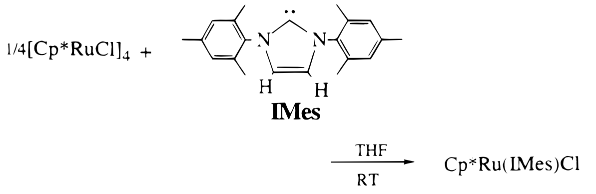
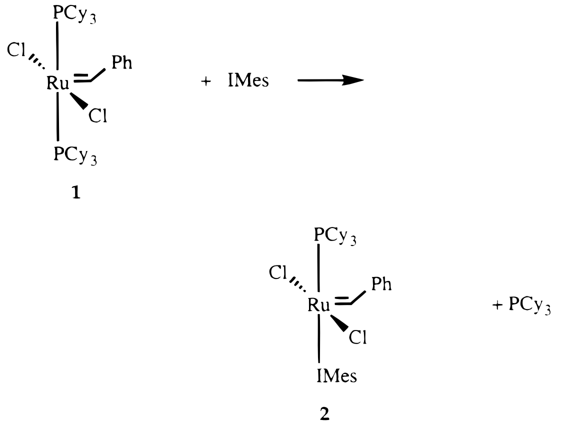
Late-transition-metal complexes have been synthesized bearing these ligands. Palladium systems bearing these phosphine mimics have been employed to mediate Heck[7] and Suzuki[8] couplings. Ruthenium complexes bearing these ligand types have been reported to possess a high catalytic activity in ROMP and ADMET reactions.[9] Of special interest are the sterically demanding carbenes developed by Arduengo, which bear aryl groups on the nitrogen positions and are less sensitive to carbene degradation.[10] Thermodynamic studies of the reaction involving [Cp*RuCl]$_4$ and nucleophilic carbenes have shown this ligand family to possess better donating properties than the common bulky, electron-donating phosphine ligands PCy$_3$ and P$^i$Pr$_3$ (eq 1).



(1)

Data from single-crystal X-ray studies of these Cp*RuCl(L) (L = nucleophilic carbene) complexes indicate a high steric protection of the metal center.[11] Recently, we have isolated an olefin metathesis catalyst bearing one sterically demanding carbene and one phosphine ligand ((PCy$_3$)(IMes)Cl$_2$Ru=CHPh, IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene). This was achieved by simple ligand exchange reaction from the ruthenium benzylidene complex **1** (eq 2).

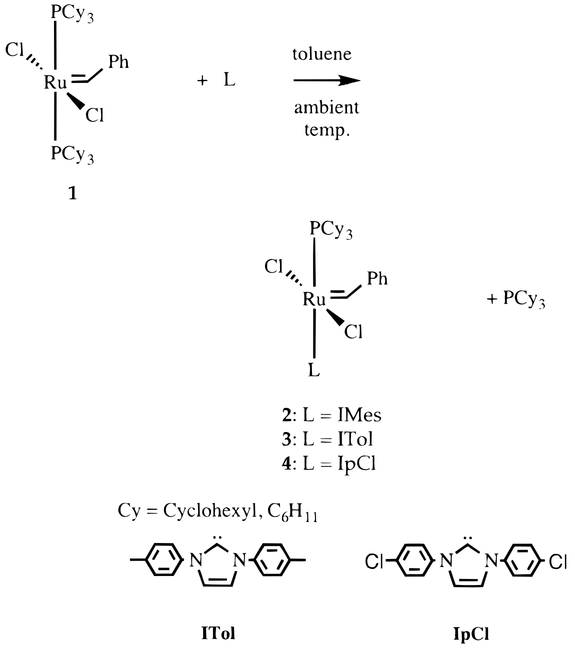


(2)

We have investigated the thermal stability as well as the catalytic activity of such complexes and compared them to those of their phosphine relatives.[12] On the basis of our initial results indicating improved thermal stability as well as enhanced catalytic activity, we now wish to report on the synthesis and thermal stability of phosphine–nucleophilic carbene mixed catalysts as well as their activity in olefin metathesis processes.

## Results and Discussion

**Synthesis.** The exchange reaction (eq 3) of one phosphine ligand in Cl$_2$(PCy$_3$)$_2$Ru=CHPh (**1**; Cy = cyclohexyl, C$_6$H$_{11}$) with the sterically demanding carbene ligands 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes), 1,3-bis(4-methylphenyl)imidazol-2-ylidene (ITol), and 1,3-bis(4-chlorophenyl)imidazolylid-2-ene (IpCl) leads to the isolation of the new complexes (PCy$_3$)(IMes)Cl$_2$Ru=CHPh (**2**), (PCy$_3$)(ITol)Cl$_2$Ru=CHPh (**3**), and (PCy$_3$)(IpCl)Cl$_2$Ru=CHPh (**4**). Similarly, one IMes can be substituted for one PCyp$_3$ in Cl$_2$(PCyp$_3$)$_2$-Ru=CH–CH=C(CH$_3$)$_2$ (**5**; Cyp = cyclopentyl, C$_5$H$_9$) to produce (PCyp$_3$)(IMes)Cl$_2$Ru=CHPh (**6**) in high yield.



(3)

Because of the improved electron donor properties characterizing bulky carbene ligands, these are able to substitute for one phosphine ligand in ruthenium complexes. Unlike the results reported by Herrmann in their study of related complexes,[9a,b] a second carbene substitution could not be achieved even in the presence of a 10-fold excess of the nucleophilic carbene ligand. This presumably is disfavored because of steric reasons. The ligand substitution reactions were conducted in nonpolar solvents such as toluene (for the isolation of **2**–**4**) or hexane (**6**). The formation of complex **6** (eq 4) shows high sensitivity to these parameters. The heterogeneous reaction proceeds in hexane at elevated temperature (60 °C). The advantage of this method is

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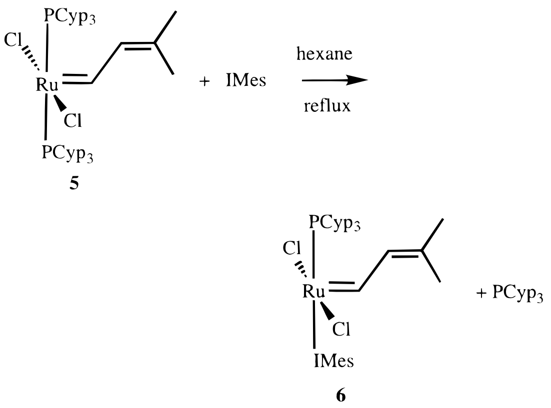

(4)

Cyp = Cyclopentyl, $C_5H_9$

that provided by the lower solubility of the IMes-ligated complex **6** compared to its precursor **5**. The workup procedure is straightforwardly carried out by simply cooling the reaction solution to −78 °C, affording an almost complete precipitation of the product without removal of the solvent. Filtration at this temperature and washing with cold pentane (−78 °C) gives the analytically pure product as an orange-brown powder. The same conditions can be used for the conversion of compound **1** into **2**. However, due to the better solubility of **2** in hexane lower yields are obtained compared to the previously reported method.[12] The best procedure for isolation of **2** involved substitution at room temperature in toluene with 1.1 equiv of IMes. Removal of the solvent and filtration of a cooled pentane suspension (−78 °C) affords compound **2** in high yields. Compounds **3** and **4** were obtained in high yields by analogous procedures.

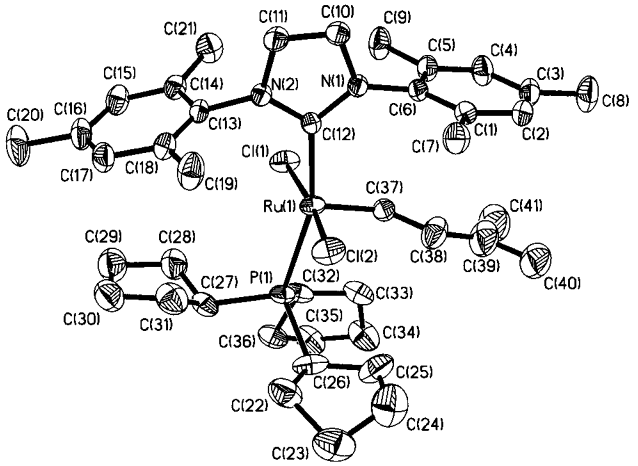

**Figure 1.** ORTEP diagram of $Cl_2(IMes)(PCyp_3)Ru(=CHCH=CMe_2)$ (**6**) with ellipsoids drawn in at 50% probability.

**Table 1. Crystallographic Data for the Complex $(PCyp_3)(IMes)Cl_2Ru(=CHCH=CMe_2)$ (6)**

| | |
|---|---|
| formula | $C_{41}H_{59}Cl_2N_2PRu$ |
| fw | 782.84 |
| color | orange |
| space group | monoclinic, $P2_1/c$ |
| $a$, Å | 12.1385(14) |
| $b$, Å | 14.2694(16) |
| $c$, Å | 23.344(3) |
| α, deg | 90 |
| $\beta$, deg | 98.829(2) |
| $\gamma$, deg | 90 |
| $\mu$(Mo), cm$^{-1}$ | 5.96 |
| $Z$ | 4 |
| $R$ | 0.0493 |
| $R_w$ | 0.1192 |
| no. of refined params | 549 |
| no. of data collected | 49 422 |
| no. of unique data, $I > 3\sigma$ | 11 646 |
| $R_{merge}$ | 0.1260 |

**Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 2 and 6**

| | **2**[a] | **6**[b] |
|---|---|---|
| Ru−C(carbene) | 1.84 | 1.76 |
| Ru−(IMes) | 2.07 | 2.08 |
| Ru−P | 2.42 | 2.45 |
| Ru−Cl(1,2) | 2.38, 2.39 | 2.40, 2.39 |
| C(carbene)−Ru−C(IMes) | 99.5 | 102.5 |
| C(carbene)−Ru−P | 89.5 | 95.6 |
| C(carbene)−Ru−Cl(1,2) | 87.1, 104.3 | 91.2, 97.4 |
| IMes−Ru−Cl(1,2) | 90.4, 86.9 | 90.0, 86.8 |
| P−Ru−Cl | 89.9, 89.5 | 93.3, 87.3 |

[a] Taken from ref 11. [b] This work.

**Structural Discussion.** Complex **6** was crystallized from a saturated hexane/$CH_2Cl_2$ solution by slow evaporation as orange-brown prisms (for crystal data see Table 1). X-ray data of compounds **2**[12] and **6** (for an ORTEP diagram of **6** see Figure 1[13]) show similar bond distances and angles around the metal center. Selected bond lengths and angles are given in Table 2. The coordination sphere around the metal center forms a distorted square pyramid with the benzylidene and vinylmethylene moiety at the apex. However, the pyramid base of complex **6** is more planar than for complex **2**; the distance of the apical vinylmethylene carbene carbon atom from the metal center (1.76 Å) is shorter by 0.08 Å than the distance for the apical benzylidene carbene carbon atom (1.84 Å). From this shorter distance, it might be concluded that the vinylmethylene moiety is more strongly bonded to ruthenium than the benzylidene. All other bond distances around the metal center are slightly longer in complex **6** than in complex **2** (0.01 Å for Ru−Cl(1,2) and Ru−C(IMes); 0.03 Å for Ru−P). All bond angles in a square-pyramidal structure with the metal placed in the center of the basal plane should be 90°. Unsurprisingly large deviations are formed by C(IMes)−Ru−C(carbene) angle in both complexes (99.5° for **2** and 102.5° for **6**). The fence created by the IMes ligand[11] which interferes sterically with the carbene moiety causes this disturbance. Whereas the adjacent angle C(carbene)−Ru−P seems not to be affected in compound **2** (89.5°), this angle is also widened in compound **6** (95.6°). Significantly enlarged is the angle C(carbene)−Ru−Cl(2) (104.3° for **2** and 97.4° for **6**) sterically enforced by the cis orientation of the carbene moieties. All other angles do not deviate more than 4° from the ideal 90°.

**Thermal Stability.** When toluene solutions of compounds **1**, **2**, **5**, and **6** are subjected to elevated temperatures, signs of decomposition, as monitored by NMR spectroscopy, afford a straightforward gauge of the thermal stability of the carbene complexes. The initial step of thermal decomposition is presumably the elimination of one phosphine ligand from the metal center. Since the IMes ligand is the stronger binder to the metal center and provides better steric protection than the

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[13] Crystals of compound **6** contain two symmetric isomers. Only one is shown in the ORTEP drawing.

**Table 3. RCM Activity of (IMes)(PCy)$_3$Cl$_2$Ru(=CHPh) (2) with Diethyl Diallylmalonate in the Presence of Additives**[a]

| additive (amt, equiv) | $N_t$ (equiv/h) | rel activity (%) |
|---|---|---|
| | 44.1 | 100 |
| HCl (1.0) | 93.7 | 216 |
| PCy$_3$ (0.06) | 10.8 | 24.2 |
| IMes (0.25) | 0 | 0 |

[a] Protocol is presented in the Experimental Section.

**Table 4. Relative Catalytic Activities (% Conversion) of Complexes 1, 2, 5, and 6**[a]

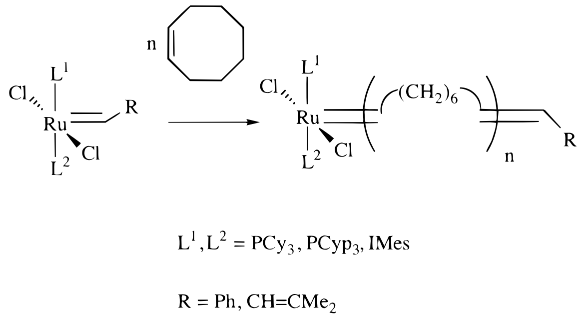
| | 1 | 2 | 5 | 6 |
|---|---|---|---|---|
| ROMP of COE | 86 | 100 | 12 | 15 |
| RCM of diethyl 2,2-diallyl malonate | 91 | 100 | 48 | 10 |
| isomerization of *cis*-2-pentene | 45 | 100 | 1 | 25 |

[a] Protocols are given in the Experimental Section.

phosphine ligands, the lifetime of the resulting 14-electron intermediate and therefore the thermal stability of the mixed phosphine/carbene compounds **2** and **6** should be enhanced compared to those of **1** and **5**. This is proved by parallel experiments heating toluene solutions of **1**, **2**, **5**, and **6** to 60 and 100 °C and recording their $^{31}$P{$^1$H} NMR spectra signals as a function of time. At 60 °C compound **1** shows the highest sensitivity. Significant amounts of the material have already decomposed after 1 h, as judged by new $^{31}$P{$^1$H} NMR shifts at $\delta$ 29.2 and 23.7 ppm. Significant degradation in complex **5** was observed after 2 h. Due to the presence of high amounts of free phosphine (no other $^{31}$P{$^1$H} NMR signal was observed), it can be concluded that no P−C bond degeneration takes place in this complex. The elimination of the phosphine most likely leads to the formation of an insoluble ruthenium-containing product, and the resulting excess phosphine slows down further phosphine elimination from starting material. In a 24 h period, the IMes complexes **2** and **6** show no sign of decomposition. Subjecting toluene solutions to 100 °C for 1 h leads to major decomposition in compounds **1** (75% decomposed) and **5** (90% decomposed), whereas **2** and **6** show no degradation. A large amount of new $^{31}$P{$^1$H} NMR signals between $\delta$ 20 and 95 ppm indicate a variety of degradation processes for complexes **1** and **5** at this temperature. Compounds **2** (33% decomposed after 48 h) and **6** (15% after 4 h) eventually decompose, but significantly more slowly, due to better steric and electronic stabilization of the 14-electron species. This protection leads to exceptional stability of complex **6** (or its related 14-electron intermediate) even in refluxing diglyme solution (165 °C!). Complex **6** shows no sign of decomposition after 10 min under these conditions.

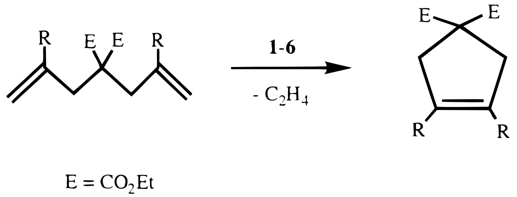
**Metathesis Reactions.** Catalytic conversion for the following typical metathesis reactions for catalysts Cl$_2$Ru(PR$_3$)(L)(=CHR′) were monitored: ring-opening metathesis polymerization (ROMP) of cyclooctene (COE), ring-closing metathesis (RCM) for diethyl diallylmalonate, and cross-metathesis of *cis*-2-pentene. Table 4 illustrates the relative activities according to catalyst used. The general trend shows faster conversion rates for the benzylidene complexes **1** and **2** compared to the vinylmethylene complexes **5** and **6** due to the presumably weaker bond strength of the carbene moieties. This hypothesis is supported by X-ray data for **2** and **6**. It was also observed that the IMes ligation in compounds **2** and **6** influences the initiation process, with slower initiation. Once the complex has been initiated, then catalytic properties appear superior to the phosphine complexes.

**Ring-Opening Metathesis Polymerization (ROMP) of Cyclooctene (COE).** The IMes-containing derivatives **2** ($N_t = 2.8 \times 10^3$ equiv/h) and **6** ($N_t = 4.3 \times 10^2$ equiv/h) perform well as catalysts for the polymerization of cyclic olefins such as cyclooctene (COE) (eq 5). They show a slightly enhanced polymerization propagation compared to their precursors **1** ($N_t = 2.4 \times 10^3$ equiv/h) and **5** ($N_t = 3.3 \times 10^2$ equiv/h) as determined by $^1$H NMR. The improved electron donor properties of the IMes ligand lead to a better stabilization of the reactive site, which is formed by phosphine abstraction from the metal center. As noted above, the PCy$_3$−benzylidene complexes **1** and **2** display a significantly more rapid polymerization behavior than the PCyp$_3$−vinylmethylene complexes **5** and **6**, which is obviously caused by the replacement of the benzylidene versus the vinylmethylene moiety at the metal center. The polymers obtained from reaction of the compounds **2** and **6** with 50 equiv of COE show a relatively high polydispersity (PDI; $M_w/M_n = 1.80$, data obtained from GPC analysis of polymeric materials).



(5)

**Ring-Closing Metathesis (RCM) of Diethyl Diallylmalonate and Diethyl Bis(2-methylallyl)malonate.** Ring-closing metathesis (RCM) has become a very popular method for the formation of unsaturated cyclic compounds from α,ω-dienes and is now widely used in organic chemistry.[1b−d] In one example, a prototypical RCM reaction, 4,4-diethylcarboxycyclopent-1-ene derivatives are formed by elimination of ethylene (eq 6).



(6)

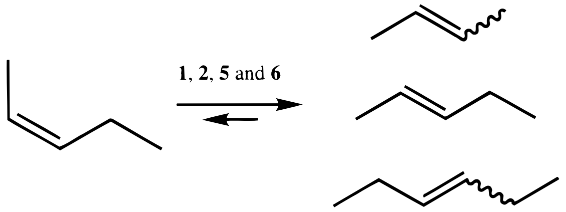
For the RCM of diethyl diallylmalonate (R = H, eq 6) using complexes **1** and **2** leads to a turnover number (CH$_2$Cl$_2$, 20 °C) of $N_t = 44.1$ equiv/h for complex **2** compared to $N_t = 40.2$ equiv/h for **1** (Table 3). The ITol (**3**; $N_t = 14.4$ equiv/h) and IpCl (**4**; $N_t = 17.0$ equiv/h) ligands lead to significantly slower reactions. This can be attributed to a combination of poorer electron donation from the ligand to the ruthenium center and smaller steric protection from the lack of substituents at the aryl ortho positions. Similar to the ROMP experimental results, the PCyp$_3$–vinylmethylene complexes **5** ($N_t$ = 20.8 equiv/h) and especially **6** ($N_t$ = 4.2 equiv/h) perform significantly more slowly under these conditions.

The high RCM activity for compound **2** is illustrated by the reaction with the sterically hindered substrate diethyl bis(2-methylallyl)malonate (eq 6, R = Me). After 1 h in toluene (80 °C) under reduced pressure (refluxing solvent), the NMR analysis shows a 75% conversion of a 20:1 (substrate/catalyst) mixture into the corresponding cyclopentene derivative. As ethylene is formed in this reaction, reduced pressure favors completion of the reaction. Otherwise, large amounts of the catalyst are converted into what appears to be a very stable methylene derivative. The reaction in benzene at 80 °C for the same substrate/catalyst ratio in a sealed tube affords only a 25% conversion and the formation of 70% of the new methylidene catalyst after 2 h, as estimated by $^1$H NMR spectroscopy.

**Acceleration and Inhibition of Ring-Closing Metathesis (RCM) of Diethyl Diallylmalonate by Additives.** The turnover number varies as a function of the concentration of the reactive 14-electron species formed by phosphine liberation from the starting complex. This concentration in the equilibrium can be influenced by addition of Lewis or Brønsted acids[14] or ligand.[2f] We investigated the catalytic activities for RCM of diethyl diallylmalonate mediated by complex **2** in the presence of additives: e.g. addition of HCl, PCy$_3$, and IMes. Strong acids such as HCl in dioxane work as "phosphine sponges" by formation of the phosphonium salt by quaternizing the liberated phosphine ligand in the first step of the catalytic reaction. Thus, the concentration of free phosphine is reduced and the concentration of the catalytic active species is increased. Therefore, the catalytic reaction is accelerated. There is a precedent for spectroscopic evidence for the formation of a phosphonium salt upon acid addition to Grubbs' catalyst.[14b] The addition of 1 equiv of HCl in dioxane to the catalyst/substrate solution results in a 2.2-fold increase in turnover number ($N_t$ = 93.7 equiv/h) compared to additive-free catalyst **2** ($N_t$ = 44.1 equiv/h).

Catalysis inhibition takes place when the donor ligand concentration is increased. The competition between the better donating ligand and the olefin leads to significantly lower conversion rates even with small amounts of added ligand. The addition of 0.06 equiv of PCy$_3$/equiv of catalyst **2** to the reaction results in the loss of activity greater than 75% ($N_t$ = 10.8 equiv/h). A complete deactivation of catalyst **2** is achieved by addition of 0.25 equiv of IMes, a more basic ligand. This fact is interesting, since the isolation of a complex bearing two IMes ligands has been impossible to date. This catalysis inhibition study result indicates that the complex may not be stable enough to be isolated but in virtue of the increased base strength of IMes it can inhibit substrate binding during the course of the catalysis. All catalytic results are summarized in Table 3.

**Cross Metathesis of *cis*-2-Pentene.** From reaction 7 are obtained products in an equilibrium mixture.



(7)

Products other than *trans*-2-pentene are observed: *cis*-/*trans*-2-butene and *cis*-/*trans*-3-hexene. $^1$H NMR allows us to quantify the distribution between the cis isomers of 2-butene and 2-pentene and the trans isomers of 2-butene and 2-pentene. The equilibrium mixture contains 85% trans and 15% cis products. The kinetics show first-order behavior. The activity difference between the catalyst pairs **1**, **2** and **5**, **6** for this reaction is as significant as for the RCM of diethyl diallylmalonate. However, IMes ligation clearly enhances the reaction rate. Compound **2** ($9.2 \times 10^2$ equiv/h) performs more than twice as well as catalyst **1** ($4.2 \times 10^2$ equiv/h) in this conversion. The vinylmethylene complex **6** converts $2.3 \times 10^2$ equiv/h, whereas its precursor **5** shows a very low activity with 15 equiv/h. Here again the more electron-rich metal center behaves more efficiently in this conversion.

## Conclusions

Significant enhancements in the properties of the novel catalysts **2** and **6** have been obtained by replacing one phosphine ligand of the catalysts **1** and **5** by the sterically more demanding and strongly donating carbene ligand IMes. These compounds are easily available from substitution reactions in high yields. Kinetic studies show acceleration in all investigated catalytic reactions for these complexes. The exception to this trend is observed when the vinylmethylene compounds **5** and **6** catalyze the RCM of diethyl dialkylmalonate. Moreover, the higher thermal stability observed for **2** and **6** allows applications at elevated temperatures without loss of reactivity, as illustrated by the RCM of diethyl bis(2-methylallyl)malonate by catalyst **2** at 80 °C. Carbene ligation other than IMes (ITol, IpCl) affording complexes **3** and **4** display lower catalytic activity when compared with **2**. X-ray data for complexes **2** and **6** reveal a significantly shorter metal–vinylmethylene bond distance compared to the metal–benzylidene distance. It has also been shown that the catalytic activity of compound **2** for RCM of diethyl diallylmalonate can be regulated by additives. Strong acids accelerate and basic ligands such as PCy$_3$ or IMes slow or shut down the reactivity. Electron-donating ligands that also afford steric protection of the 14-electron intermediate lead to higher catalytic activities in a number of processes. The search for even better donors of this type for olefin metathesis and other applications is ongoing.

## Experimental Section

**General Considerations**. All syntheses and kinetic studies were performed under inert atmospheres of argon using standard high-vacuum or Schlenk tube techniques or in an MBraun glovebox containing less than 1 ppm of oxygen and water. Solvents including deuterated solvents for NMR analysis were dried and distilled under nitrogen before use, employ-

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[14] (a) Sanford, M. S.; Henling, L. M.; Grubbs, R. H. *Organometallics* **1998**, *17*, 5384–5389. (b) Lynn, D. M.; Mohr, B., Grubbs, R. H. *J. Am. Chem. Soc.* **1998**, *120*, 1627–1628.

ing standard drying agents.[15] Catalysts **1** and **5** were purchased from Strem and used as received. The carbene ligand IMes was prepared according to the literature procedure.[10] The synthesis of compound **2** was carried out as previously described.[12] NMR spectra were recorded using a Varian Gemini 300 MHz or Oxford 400 MHz spectrometer. Elemental analyses were performed by Desert Analysis, Tucson, AZ.

**Synthesis. (ITol)(PCy$_3$)Cl$_2$Ru(=CHPh) (3).** A 50 mL flask was charged with 0.290 g (0.352 mmol) of complex **1**, 0.096 g (0.386 mmol) of ITol, and 20 mL of benzene. The brown solution was stirred at room temperature for 1 h; then the solvent was removed under vacuum. The residue was washed with pentane (3 × 5 mL) and filtered, and the resulting green solid was dried under vacuum. Yield: 0.222 g, 80%. $^1$H NMR (500.1 MHz, 25 °C, C$_6$D$_6$): $\delta$ 19.93 (d [$^3J(^{31}P^1H) = 8.4$ Hz], 1 H, Ru−CH), 8.02 (d, 4 H), 7.12 (d, 4 H), 2.13 (s, 6 H, C$_6$H$_4$-CH$_3$), 6.86 (m, 2 H), 6.50 (m, 2 H), 6.43 (m, 1 H, C$_6$H$_5$), 6.38 (s, 2 H, NCHCHN), 2.38 (m, 3 H), 1.86 (m, 6 H), 1.63 (m, 6 H), 1.53−1.47 m, 12 H), 1.13 (m, 6 H, PCy$_3$). $^{31}$P NMR (121.4 MHz, 25 °C, C$_6$D$_6$): $\delta$ 22.6. Anal. Calcd for $C_{42}H_{55}Cl_2N_2PRu$: C, 63.79; H, 7.01; N, 3.54. Found: C, 63.91; H, 7.09; N, 3.92.

**(IpCl)(PCy$_3$)Cl$_2$Ru (=CHPh) (4).** A 50 mL flask was charged with 0.218 g (0.265 mmol) of complex **1**, 0.077 g (0.266 mmol) of IpCl, and 20 mL of toluene. The brown solution was stirred at room temperature for 1 h; then the solvent was removed under vacuum. The residue was washed with pentane (3 × 5 mL) and filtered, and the resulting green solid was dried under vacuum. Yield: 0.192 g, 87%. $^1$H NMR (500.1 MHz, 25 °C, C$_6$D$_6$): $\delta$ 19.78 (d [$^2J(^{31}P^1H) = 8.6$ Hz], 1 H, Ru−CH), 7.87 (d, 2 H), 7.27 (d, 2 H, *p*-C$_6$H$_4$Cl), 6.92 (m, 2 H), 6.60 (m, 2 H), 6.34 (m, 1 H, C$_6$H$_5$), 6.19 (s, 2 H, NCHCHN), 2.35 (m, 3 H), 1.86 (m, 6 H), 1.68 (m, 6 H), 1.58−1.48 (m, 12 H), 1.15 (m, 6 H, PCy$_3$). $^{31}$P NMR (121.4 MHz, 25 °C, C$_6$D$_6$): $\delta$ 24.0. Anal. Calcd for $C_{40}H_{49}Cl_4N_2PRu$: C, 61.16; H, 6.23; N, 3.04. Found: C, 61.20; H, 6.32; N, 3.04.

**Cl$_2$Ru(IMes)(PCyp$_3$)(=CHCH=CMe$_2$) (6).** IMes (2.199 g/7.221 mmol) was suspended in 250 mL of hexanes before compound **2** (5.072 g/7.092 mmol) was added in one portion to the suspension. The mixture was heated at 60 °C for 2.5 h with magnetic stirring. During this time, the formation of an orange-brown precipitate was observed. The suspension was cooled to −78 °C and filtered at this temperature. The residue was washed with 2 × 20 mL of pentane (−78 °C), and 3.968 g (5.074 mmol/72%) of pure compound **6** was obtained after drying for 30 min in vacuo. $^1$H NMR (400.1 MHz, 25 °C, C$_6$D$_6$): $\delta$ 19.39 (d, 1H), 7.77 (d, 1H), 1.07 (s, 3 H), 0.87 (s, 3 H, =CHCH=CMe$_2$), 2.38 (m, 3 H), 1.64 (m, 6 H), 1.62 (m, 6 H), 1.57 (m, 6 H), 1.34 (m, 6 H, PCyp$_3$), 6.85 (s, 2 H), 6.58 (s, 2 H), 6.17 (s, 1H), 6.15 (s, 1 H), 2.60 (s, 6 H), 2.33 (s, 6 H), 2.20 (s, 3 H), 1.99 (s, 3H, IMes). $^{31}$P NMR (121.4 MHz, 25 °C, C$_6$D$_6$): $\delta$ 31.6. Anal. Calcd for $C_{41}H_{59}Cl_2N_2PRu$: C, 62.90; H, 7.60; N, 3.58. Found: C, 62.49; H, 7.50; N, 3.83.

When the same procedure is used for the preparation of (IMes)(PCy$_3$)RuCl$_2$(=CHPh) (**2**), a yield of 83% is obtained. NMR data have previously been reported.[12]

**Structure Determination of Cl$_2$Ru(IMes)(PCyp$_3$)(=CHCH=CMe$_2$) (6).** Orange crystals of **6** were obtained by slow evaporation of solvent from a saturated CH$_2$Cl$_2$/hexane solution. A single crystal was placed in a capillary tube and mounted on a Bruker SMART CCD X-ray diffractometer. Data were collected using Mo K$\alpha$ radiation at a temperature of 150 K. Cell dimensions were determined by least-squares refinements of the measured setting angles of 49 422 reflections with $4.4° < 2\theta < 60.0°$. The structure was solved using direct methods (SHELXS-86) and refined by full-matrix least-squares techniques. Crystallographic data are given in Table 1.

**Thermal Stability**. In an NMR tube, 5 $\mu$mol of the compounds **1**, **2**, **5**, and **6** was dissolved in 0.5 mL of solvent (toluene-$d_8$) and the solution placed into an oil bath maintained at constant temperatures (60 and 100 °C). NMR data were recorded at 30 min intervals. The progression of decomposition was determined by integration of all $^{31}$P NMR signals.

**ROMP of Cyclooctene.** In an NMR tube, 50 $\mu$L of a 6.0 mM stock solution of catalysts **1**, **2**, **5**, and **6** (0.30 $\mu$mol) in CD$_2$Cl$_2$ was added to 0.45 mL of a 13 mM stock solution of COE (6.0 mmol/2 × 10$^3$ equiv) in CD$_2$Cl$_2$. After the addition, $^1$H NMR spectra were recorded. The progress of the polymerization was monitored by integrating the multiplets in the range $\delta$ 5.58−5.70 ppm (CH of COE monomer) and $\delta$ 5.30−5.50 ppm (CH of COE polymer).

**RCM of Diethyl Diallylmalonate**. In an NMR tube, 0.400 mL of a 12.5 mM stock solution of catalysts **1**−**6** (5.00 $\mu$mol) in CD$_2$Cl$_2$ was added to 0.100 mL of a 1.00 M stock solution of diethyl diallylmalonate (100 $\mu$mol/20 equiv) in CD$_2$Cl$_2$. After the addition, $^1$H NMR spectra were recorded, integrating the signals at $\delta$ 2.99 ppm (CH$_2$, 4,4-dicarbethoxycyclopent-1-ene, virtual singlet) and $\delta$ 2.62 (CH$_2$, diethyl diallylmalonate, doublet), respectively.

**RCM of Diethyl Diallylmalonate with 2 and HCl.** An HCl solution in dioxane (4 M, 1.25 $\mu$L, 5 $\mu$mol) and diethyl diallylmalonate (72.1 mg/300 $\mu$mol/60 equiv) were added to 0.400 mL of a 12.5 mM stock solution of complex **2** (5.0 $\mu$mol) in an NMR tube. The conversion rate was determined as described above.

**RCM of Diethyl Diallylmalonate with Complex 3 and PCy$_3$.** PCy$_3$ (6 mol %) and 0.100 mL of a 1.00 M stock solution of diethyl diallylmalonate (100 $\mu$mol/20 equiv) in CD$_2$Cl$_2$ were added to 0.400 mL of a 12.5 mM stock solution of complex **2** (5.0 $\mu$mol) in an NMR tube. The conversion rate was determined as described above.

**RCM of Diethyl Diallylmalonate with 2 and IMes.** IMes (0.4 mg, 1.3 $\mu$mol) and 0.100 mL of a 1.00 M stock solution of diethyl diallylmalonate (100 $\mu$mol/20 equiv) in CD$_2$Cl$_2$ were added to 0.400 mL of a 12.5 mM stock solution of complex **3** (5.0 $\mu$mol) in an NMR tube. The conversion rate was determined as described above.

**RCM of Diethyl Bis(2-methylallyl)malonate**. In a 10 mL Schlenk tube, 33.1 mg of diethyl bis(2-methylallyl)malonate (120 $\mu$mol/20 equiv) and 5.1 mg (6 $\mu$mol) of compound **3** were dissolved in 1 mL of toluene-$d_8$ and heated with stirring to 80 °C. Then the pressure was reduced until the solvent was boiling under reflux. The formed ethylene was removed in vacuo five more times at 10 min intervals. After 60 min the solution was cooled to room temperature and was poured into an NMR tube.

**Cross Metathesis of *cis*-2-Pentene**. In an NMR tube, 50 $\mu$L portions of 0.02 M stock solutions of catalysts **1**, **2**, **5**, and **6** (1.0 $\mu$mol) in CD$_2$Cl$_2$ were added to 0.50 mL of a 1.0 M stock solution of *cis*-2-pentene (500 $\mu$mol/500 equiv) in CD$_2$Cl$_2$. After the addition, $^1$H NMR spectra were recorded, integrating the C(1)H$_3$ signals (doublet) in the ranges $\delta$ 1.41−1.50 ppm (*cis*-2-butene/*cis*-2-pentene) and $\delta$ 1.50−1.57 (*trans*-2-butene/*trans*-2-pentene).

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**Supporting Information Available:** Details of the crystal structure determination for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

OM990788Y

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