DOI: 10.1002/chem.201001659

Ruthenium–Indenylidene Olefin Metathesis Catalyst with Enhanced Thermal Stability

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Abstract: Two new ruthenium complexes bearing a bidentate (κ^2O,C)-isopropoxy–indenylidene ligand and a PPh_3 (**9**) or PCy_3 (**10**, Cy = cyclohexyl) ligand have been synthesized and fully characterized by ^1H and ^{13}C NMR spectroscopy and X-ray crystallography. Complex **10** displays a very high thermal stability with a half life of six days at 110 °C in [D_8]toluene. Complex **10** was evaluated in various ring-closing metathesis reactions and ring-opening metathesis polymerization of dicyclopentadiene, in which it showed a latent behavior with low activity at room temperature and high activity upon thermal activation.

Keywords: indenylidene · latent catalysts · metathesis · olefins · ruthenium

Introduction

Olefin metathesis[1] is a powerful tool for the transformation of C=C bonds that has found many applications in organic synthesis[2] and polymer chemistry.[3] Since the first well-defined ruthenium-based catalyst isolated by Grubbs and co-workers in 1992,[4] the continuous development of new catalysts with enhanced performances[5] now offers new perspectives for the transformation of functionalized olefins that arise from renewable resources[6] and in enantioselective transformations.[7] Thus, over the last 15 years the portfolio of ruthenium catalysts has considerably increased, driven by several families of complexes. Since the neutral 16-electron complex [Ru(=CHPh)$Cl_2(PCy_3)_2$] (**1**; Cy = cyclohexyl) was discovered by Grubbs and co-workers in 1995,[8] the most noticeable modification came from the introduction of N-heterocyclic carbene (NHC) ligands[9] and the development of a series of new complexes based on the Grubbs benzylidene architecture (i.e., **1**–**3**; Scheme 1) and the more stable Hoveyda-type complexes (i.e., **4** and **5**; Scheme 1).[10]

Beside these catalysts, several structurally different complexes based on vinylidene,[11] allenylidene,[12] and indenylidene[13] compounds have been reported. Ruthenium–indenylidene complexes are particularly interesting because they can be easily prepared without the requirement of a diazo compound as the benzylidene source and also because of their better stability under harsh conditions.[13e] Prominent examples are **6**,[14] **7**,[15] and **8**,[16] which are now commercially available (Scheme 2).

To date, most transformations of ruthenium–indenylidene catalysts have focused on modification of the NHC ligand[17] and substitution of tricyclohexylphosphine by other ligands, such as pyridine[18] or Schiff bases.[19] So far, a complex that combines a (κ^2O,C)-isopropoxy-indenylidene bidentate ligand has never been reported. We anticipated that such a complex should display very high stability that results in some degree of latency, which is a feature of increasing interest in particular for the preparation of polymers.[20] Herein, we present the synthesis and characterization of a new family of olefin metathesis catalysts that feature a (κ^2O,C)-isopropoxy–indenylidene bidentate ligand. The first-generation complex **10** displays a very high thermal stability that surpasses those of the related complexes **4b** and **6**. This complex has been evaluated in various test reactions, such as ring-closing metathesis (RCM), cross-metathesis (CM), and ring-opening metathesis polymerization (ROMP) of dicyclopentadiene (DCPD), in which it showed a latent

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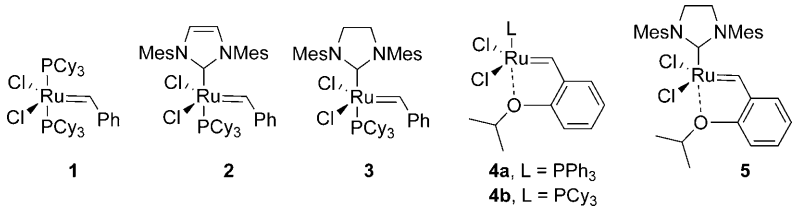
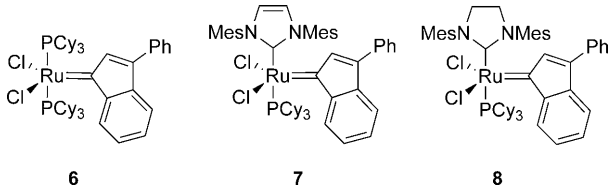
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201001659.



Scheme 1. Ruthenium-based olefin metathesis catalysts.

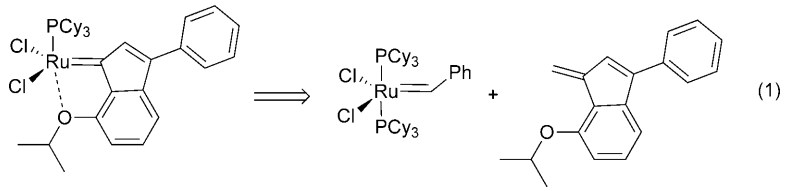


Scheme 2. Ruthenium–indenylidene complexes.

behavior with low activity at room temperature and higher activity upon thermal activation.

Results and Discussion

Synthesis of the catalyst: The most straightforward synthesis of the targeted complexes certainly involves the reaction of the Grubbs catalysts with an indenyl fragment [Eq. (1)]. However, because the synthesis of such an indenyl ligand did not look straightforward we turned our attention to the classical synthesis of ruthenium–indenylidene complexes that involves the thermal-[14] or acid-promoted[13b,21] rearrangement of a ruthenium–allenylidene transient complex synthesized from $[RuCl_2(PPh_3)_3]$ and a propargylic alcohol.

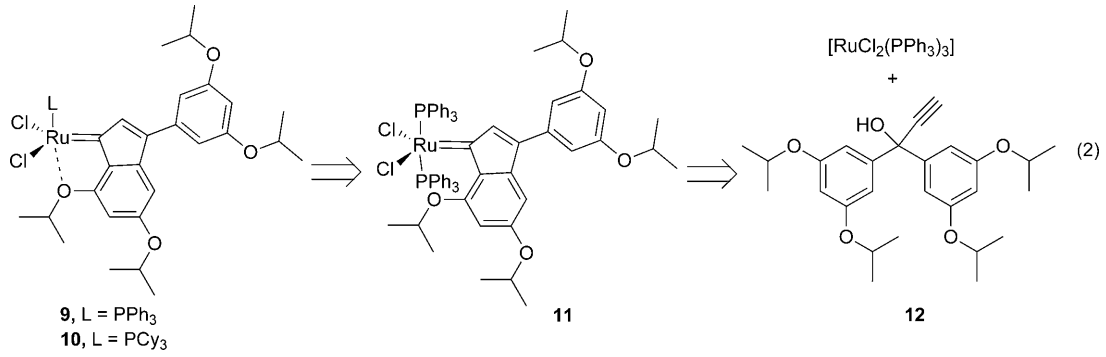


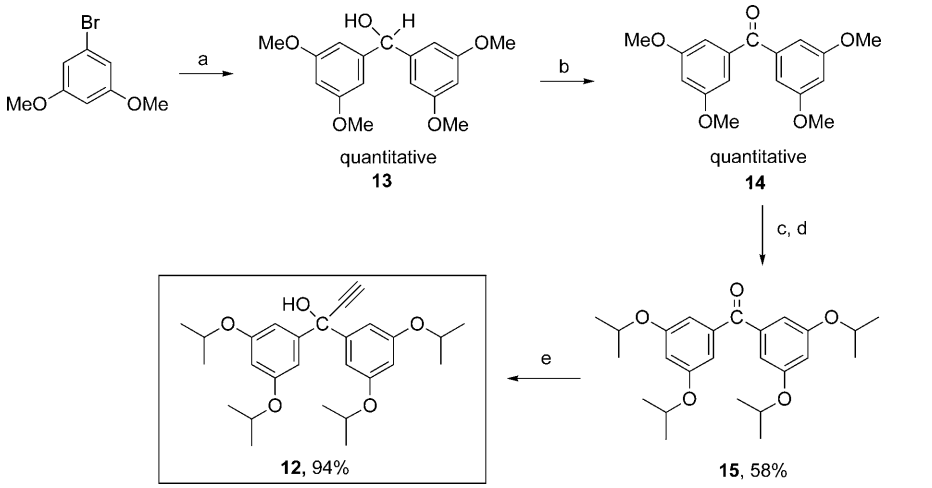
Thus, the synthesis of complexes **9** and **10** was envisioned via the intermediate complex **11**, which results from an initial reaction of the propargylic alcohol **12** with $[RuCl_2(PPh_3)_3]$ [Eq. (2)]. The symmetrical alcohol **12** was chosen to prevent any regioselectivity problems during the allenylidene-to-indenylidene rearrangement. Note that **11** is represented as a 16-electron complex but a 18-electron structure with a (κ^2O,C)-isopropoxy–indenylidene bidentate ligand could also be postulated at this stage.

With this synthetic pathway in mind, the synthesis of propargylic alcohol **12** was performed in five steps by modification of a reported protocol (Scheme 3).[22]

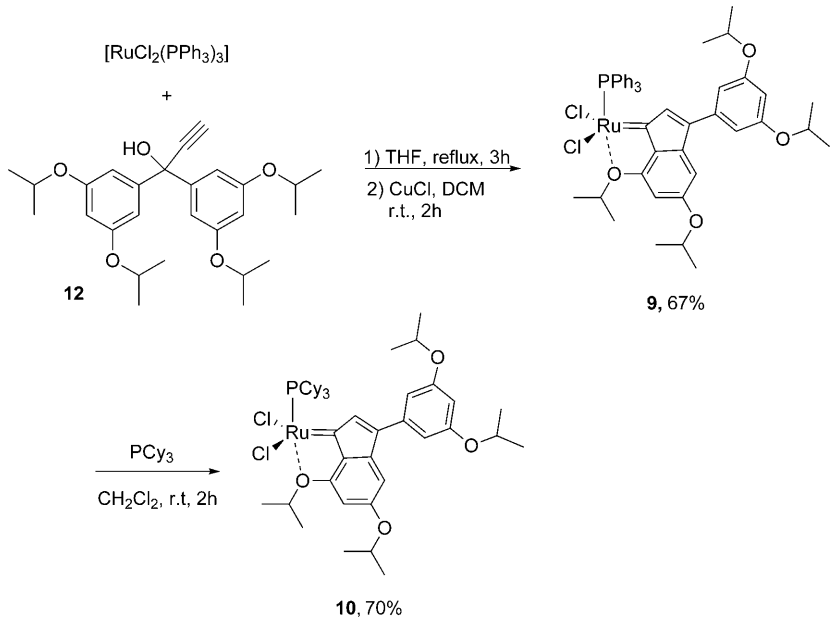
Next, the synthesis of the diphosphine–indenylidene complex **11** was attempted by reaction of the propargylic alcohol **12** with $[RuCl_2(PPh_3)_3]$ in THF heated to reflux. The reaction progress was monitored by ^{31}P NMR spectroscopy, which showed two signals at $\delta = 65$ and 55 ppm. Surprisingly, none of these signals corresponded to the chemical shift expected for a complex such as **11**,[23] but were close to the chemical shift of a Hoveyda-type architecture that comprises a bidentate ligand (i.e., $\delta = 61.1$ ppm for **4a**).[10b] The procedure was modified by using CuCl as a phosphine scavenger, thus resulting in a cleaner reaction mixture that consisted of a major and minor compound ($\delta = 65$ and 55 ppm, respectively). Purification by column chromatography on silica gel furnished the complex, which displayed a ^{31}P NMR chemical shift of $\delta = 65$ ppm and was isolated in 67% yield as a brown-red powder (Scheme 4). Crystallization of this compound by slow diffusion of hexane in THF provided crystals suitable for X-ray characterization. The molecular structure unambiguously revealed the expected (κ^2O,C)-isopropoxy-indenylidene bidentate complex **9** (Figure 1).

The structural data of **9** were compared to those of the Hoveyda complex **4a**.[10b] The main difference between the two





Scheme 3. Synthesis of propargylic alcohol **12**: a) *t*BuLi, −78 °C, Et_2O, 3,5-dimethoxybenzaldehyde; b) MnO_2, CH_2Cl_2, room temperature; c) BBr_3, CH_2Cl_2, room temperature; d) *i*PrBr, K_2CO_3, acetone, reflux; e) C_2H_2, *n*BuLi, −78 °C, THF.



Scheme 4. Synthesis of complexes **9** and **10**.

structures concerns the length of the Ru−O bond, which is longer in **9** than in **4a**, thus indicating a weaker bond in the newly prepared complex **9**. Other important structural data matched perfectly with complex **4a** (Table 1).

The PPh_3 ligand was efficiently substituted by the more electron-donating phosphine PCy_3 in dichloromethane at room temperature to furnish complex **10** as a brown powder in 70% yield (Scheme 4). This two-step procedure thus afforded **10** in about 50% yield. It must be noted that a one-pot procedure without isolating complex **9** could also be performed and furnished **10** in a better yield (70%).

Crystals suitable for X-ray analysis were obtained by slow diffusion of hexane in dichloromethane (Figure 2). The structural data of **10** were compared to a complex very similar to **4b** with an naphthalenylidene instead of a benzylidene ligand.[10b,24] As observed with the PPh_3 complexes, the main variation was the Ru−O bond length, which was again longer in **10** than in the naphthalenylidene Hoveyda-type complex (2.43 versus 2.26 Å, respectively). The Ru=C1 bond length (1.85 Å) falls into the range of bond lengths observed for benzylidene or indenylidene complexes.[10b,15] With this new complex in hand, we turned our attention to its stability in solution and catalytic activity in several RCM, CM, and ROMP reactions.

Thermal stability of complex 10: The thermal stability of a precatalyst is a key property of a latent catalyst. We studied the relative stability of the Hoveyda complex **4b**, indenylidene complex **6**, and new complex **10** in solution (23 mM in CD_2Cl_2 or [D_8]toluene) at room temperature, 80, and 110 °C, thereby monitoring their rate of decomposition by ^{1}H NMR spectroscopy with 1,3,5-trimethoxybenzene as an internal standard (12 mM).[20p, 25] The results reveal significant thermal stability of the new complex **10**, which only showed 50% decomposition after nearly 6 days at 80 and 110 °C (Figure 3). In contrast, **4b** had decomposed by 50% after 2 days at 80 °C and 1.5 days at 110 °C. Of the three complexes, **6** showed the lowest stability and had totally decomposed after 2 days at 80 °C.

Table 1. Selected bond lengths [Å] and angles [°] for complexes **9** and **4a**.

Structural feature	**9**	**4a**
Ru−C1	1.85	1.84
Ru−P	2.23	2.24
Ru−O	2.42	2.31
Ru−Cl1	2.32	2.31
Ru−Cl2	2.31	2.32
Cl-Ru-Cl	147.11	145.17
P-Ru-O	178.38	172.29

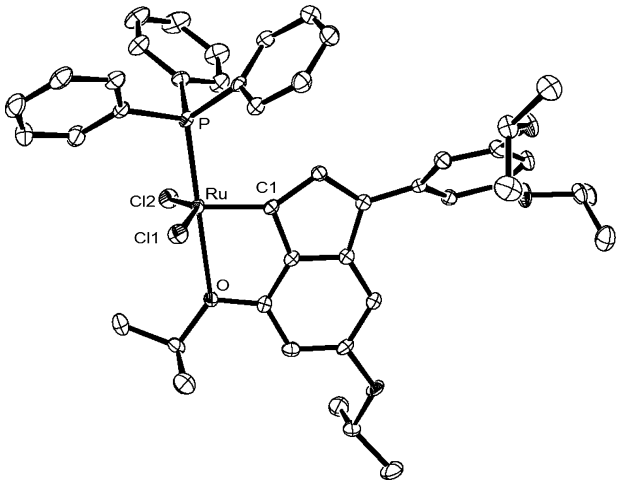


Figure 1. Molecular structure of complex **9** represented at 50% ellipsoid probability. The H atoms and solvent are omitted for clarity.

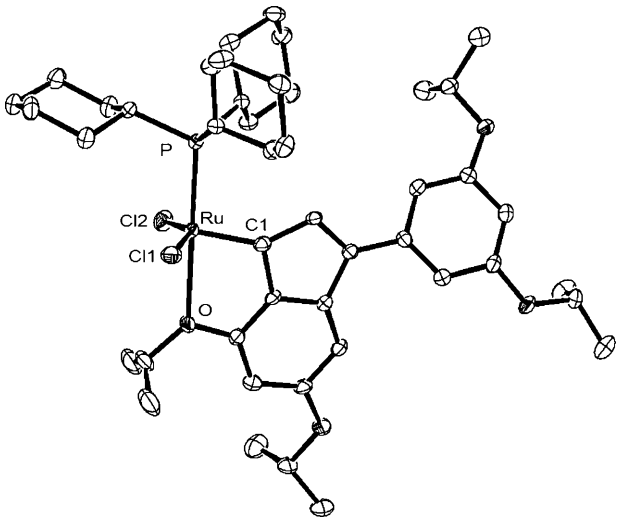


Figure 2. Molecular structure of complex **10** represented at 50% ellipsoid probability. The H atoms and solvent are omitted for clarity.

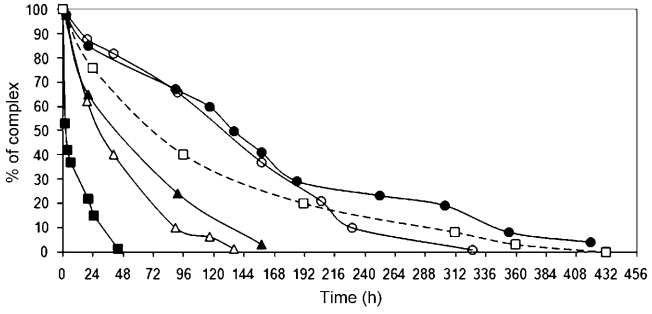
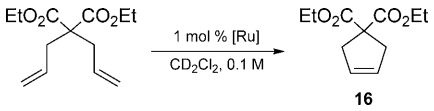


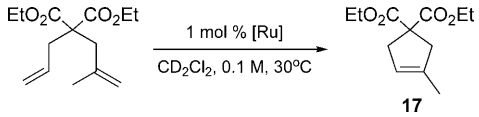
Figure 3. Decomposition of complexes **4b**, **6**, and **10** as a function of time and temperature. **4b**: (▲) 80°C, (△) 110°C; **6**: (□) RT, (■) 80°C; **10**: (●) 80°C, (○) 110°C.

Of note, **10** showed only 20% decomposition at room temperature in CD_2Cl_2 after 1 month, whereas **4b** had decomposed by 32% in the same amount of time and **6** had fully decomposed after 18 days. These results all together show that, as anticipated, **10** bearing a chelating indenylidene–isopropoxy ligand is extremely stable in solution, even after long periods at high temperature.

Catalytic performance of 10: Ideally, a latent catalyst should be inactive at room temperature and switched on by external stimuli, such as temperature, light, or chemical activation. So far most of the reported latent catalysts for olefin metathesis showed very low activity at room temperature, and the catalyst efficiency increased with temperature. First, we focused on testing the catalytic activity of **10** in the RCM reaction of diethyl diallylmalonate (DEDAM; Scheme 5) and diethyl allyl(2-methylallyl)malonate (Scheme 6).[26]



Scheme 5. RCM of diethyl diallylmalonate.



Scheme 6. RCM of diethyl allyl(2-methylallyl)malonate.

Catalyst **10** was evaluated at room temperature for the RCM of DEDAM. Complex **10** showed a very low activity at this temperature, which allowed less than 10% conversion after 2 h and reached almost complete conversion after 10 h (Figure 4).

The reaction was repeated at 30°C with **4b**, **6**, and **10** and the conversions were monitored by ^{1}H NMR spectroscopy. All three complexes allowed complete conversion within 1 h, but with very different reaction profiles (Figure 5).

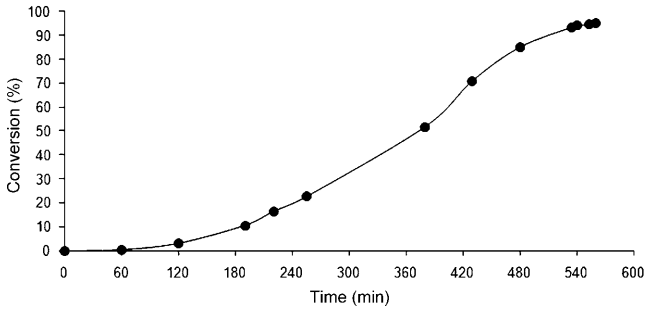


Figure 4. RCM conversion of DEDAM with complex **10** at room temperature. The conversion was determined by ^{1}H NMR spectroscopy.

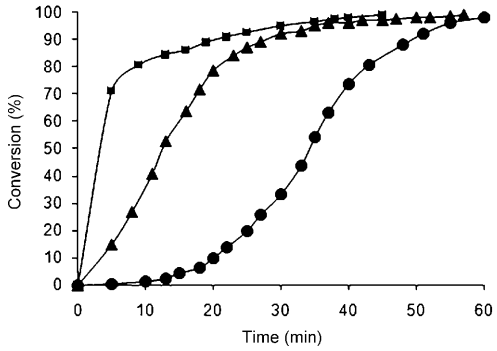


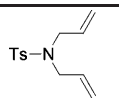
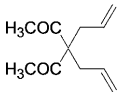
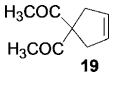
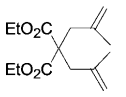
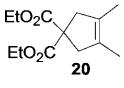
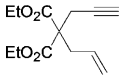
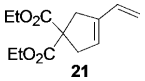
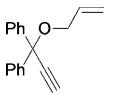
Figure 5. RCM conversion of DEDAM into **16** with complexes **4b** (▲), **6** (■), and **10** (●) at 30 °C.

Whereas **6** showed high initial efficiency with 80% conversion reached after 10 min, **4b** and especially **10** displayed a much different behavior that allowed only 40 and 1% conversion, respectively, after 10 min. The reaction profile obtained with **4b** and **10** can be attributed to the higher stability provided by the chelating ligands, which resulted in a slower initiation step. This result contrasts with the structural data obtained for **10**, which showed a weaker Ru–O bond than in a related Hoveyda catalyst.[27] It can be postulated that the extra stability brought by the indenyl fragment in **10** counterbalances this weaker metal-oxygen bond.

Next, the RCM reaction of the more sterically demanding diethyl allyl(2-methylallyl)malonate was investigated (Scheme 6). As observed with DEDAM, **6** showed the highest initial activity, but failed to reach high conversion (Figure 6). In the same manner, **4b** provided little improvement and reached 72% conversion within 6 h. In contrast, **10** showed again the lowest initial activity, but almost complete conversion was obtained within 6 h. This important improvement is likely because of the combined high thermal stability and low initiation rate, which resulted in the capability of **10** to deliver active catalytic species throughout the extended reaction time.

We extended the scope of **10** to various RCM and enyne metathesis reactions. Complex **10** showed very good catalytic activity for the RCM of *N*,*N*-diallyltosylamide and 3,3-diallyl-2,4-pentanedione by providing very high conversions in both cases (Table 2, entries 1 and 2). However, **10** failed to promote the RCM reaction of the sterically demanding di(2-methylallyl)malonate, even at a temperature as high as 110 °C. These results are in good agreement with those reported for other first-generation complexes, and to the best of our knowledge only a few second-generation catalysts can promote the formation of tetrasubstituted olefins with moderate-to-good efficiency.[28] Two enyne metathesis reactions were also realized with moderate-to good efficiency still in the range of reactivity of other first-generation catalysts (Table 2, entries 4 and 5).[13d,29]

Table 2. RCM and enyne metathesis catalyzed by **10**.

Entry	Substrate	Product[a]	Solvent	*T* [°C]	Time	Conv. [%][b]
1		 **18**	CD_2Cl_2	RT	15 min	100
2		 **19**	CD_2Cl_2	40 °C	11 h	96
3[c]		 **20**	C_6D_6 $[D_8]$toluene	80 °C 110 °C	72 h 5 h	0 0
4		 **21**	CD_2Cl_2	40 °C	72 h	68
5		 **22**	CD_2Cl_2 C_6D_6 C_6D_6	RT 60 °C 80 °C	16 days 24 h 8 h	64 64 85

[a] Catalyst loading: 1 mol%. [b] Determined by ^{1}H NMR spectroscopy. [c] Catalyst loading: 5 mol%.

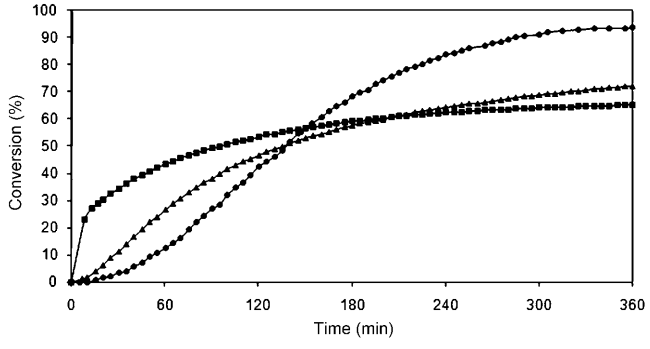


Figure 6. RCM conversion of diethyl allyl(2-methylallyl)malonate into **17** with complexes **4b** (▲), **6** (■), and **10** (●). The conversion was determined by ^{1}H NMR spectroscopy.

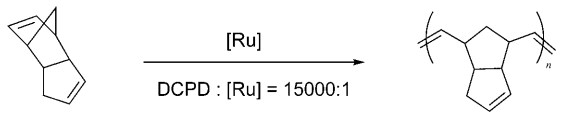
The activity of **10** was evaluated for the transformation of methyl oleate by CM with ethylene (ethenolysis) and compared to our previous results obtained with **4b** (Table 3).[6b] Under our standard conditions (i.e., toluene, room temperature, 3.5 h, 1 bar of ethylene, 2.5 mol% **10**), similar results were displayed relative to **4b** with 90% conversion and 1-decene and methyl 9-decenoate were provided in 89 and 90% yields, shown by GC analysis, without double-bond migration. Of note: the performance of **10** was slightly improved by using dimethyl carbonate (DMC) as the solvent.[6d,30]

Finally, **10** was evaluated in the ROMP of dicyclopentadiene (DCPD) (Scheme 7). Bulk polymerization with a mo-

Table 3. Ethenolysis of methyl oleate with catalysts **4b** and **10**.[a]

Catalyst	Solvent	Conv. [%][b]	Yield [%]	
			1-decene[b]	methyl 9-decenoate[b]
4b	toluene	93	93	93
10	toluene	90	89	90
	DMC	93	91	92

[a] Room temperature, 2.5 mol% catalyst, 3.5 h, ethylene (1 bar). [b] Determined by GC analysis with hexadecane as an internal standard.



Scheme 7. Bulk polymerization of DCPD.

nomer/catalyst ratio of 15000:1 was performed at various temperatures from room temperature to 120 °C.[31]

As previously observed, **10** showed very low activity for the ROMP of DCPD at room temperature. The reaction mixture was only slightly viscous after five days at room temperature, and the polymer was isolated in 7% yield after precipitation in methanol. Polymerization was repeated at 80, 110, and 120 °C, which lead to gels in 100, 20, and 10 min, respectively, and to polymer yields of 40%. Fast gelification of the reaction media is certainly the cause of the low yields observed due to mass transport limitation Further optimization of the polymerization is necessary to improve the polymer yields. However, **10** once again displayed the main features of a latent catalyst for polymerization, that is, a very low activity at room temperature that is restored upon thermal activation.

Conclusion

We have prepared the first member of a new family of olefinmetathesis catalysts bearing a (κ^2*O*,*C*)-isopropoxy–indenylidene bidentate ligand. The latency of this complex was demonstrated by very high thermal stability combined with low activity at room temperature and high activity upon thermal activation. Further development and fine-tuning of the catalyst activity and stability can be envisaged by the introduction of NHC ligands. The flexibility of the synthetic route starting from propargylic alcohols should also allow the synthesis a variety of complexes with various steric and electronic demands.

Experimental Section

Full experimental details and the structural data for complexes **9** and **10** are given in the Supporting Information.[32]

Acknowledgements

The authors are grateful to the French Agence Nationale de la Recherche (ANR) for financial support and a post-doctoral grant for A.K. (ANR-08-EFC-03–01 BIOTANDEM) and to Prof. W. Leitner and Dr. J. Klankermayer (RWTH Aachen) for a fruitful ANR–Deutsche Forschungsgemeinschaft (DFG) collaboration.

[1] a) Y. Chauvin, *Angew. Chem.* **2006**, *118*, 3824–3831; *Angew. Chem. Int. Ed.* **2006**, *45*, 3740–3747; b) R. R. Schrock, *Angew. Chem.* **2006**, *118*, 3832–3844; *Angew. Chem. Int. Ed.* **2006**, *45*, 3748–3759; c) R. H. Grubbs, *Angew. Chem.* **2006**, *118*, 3845–3850; *Angew. Chem. Int. Ed.* **2006**, *45*, 3760–3765; d) R. H. Grubbs. *Handbook of Metathesis, Vols. 1–3*, Wiley-VCH, Weinheim, **2003**; e) S. J. Connon, S. Blechert in *Ruthenium Catalysts and Fine Chemistry, Vol. 11* (Eds.: P. H. Dixneuf, C. Bruneau), Springer, Heidelberg, **2004**, 93; f) A. Fürstner, *Angew. Chem.* **2000**, *112*, 3140–3172; *Angew. Chem. Int. Ed.* **2000**, *39*, 3012–3043; g) A. H. Hoveyda, A. R. Zhugralin, *Nature* **2007**, *450*, 243–251; h) P. H. Deshmukh, S. Blechert, *Dalton Trans.* **2007**, 2479–2491.

[2] a) T. J. Donohoe, L. P. Fishlock, P. A. Procopiou, *Chem. Eur. J.* **2008**, *14*, 5716–5726; b) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem.* **2005**, *117*, 4564–4601; *Angew. Chem. Int. Ed.* **2005**, *44*, 4490–4527; c) W. A. L. van Otterlo, C. B. de Koning, *Chem. Rev.* **2009**, *109*, 3743–3782; d) A. Gradillas, J. Perez-Castells, *Angew. Chem.* **2006**, *118*, 6232–6247; *Angew. Chem. Int. Ed.* **2006**, *45*, 6086–6101.

[3] a) M. R. Buchmeiser, *Chem. Rev.* **2000**, *100*, 1565–1604; b) J. E. Schwendeman, A. C. Church, K. B. Wagener, *Adv. Synth. Catal.* **2002**, *344*, 597–613.

[4] S. T. Nguyen, L. K. Johnson, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1992**, *114*, 3974–3975.

[5] For Ru-based catalysts, see: a) G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2010**, *110*, 1746–1787; b) C. E. Diesendruck, E. Tzur, N. G. Lemcoff, *Eur. J. Inorg. Chem.* **2009**, 4185–4203; c) C. Samojłowicz, M. Bieniek, K. Grela, *Chem. Rev.* **2009**, *109*, 3708–3742. For molybdenum- and tungsten-based catalysts, see: d) R. R. Schrock, A. H. Hoveyda, *Angew. Chem.* **2003**, *115*, 4740–4782; *Angew. Chem. Int. Ed.* **2003**, *42*, 4592–4633; e) R. R. Schrock, *J. Mol. Catal. A* **2004**, *213*, 21–30.

[6] a) C. Bruneau, C. Fischmeister, X. Miao, R. Malacea, P. H. Dixneuf, *Eur. J. Lipid Sci. Technol.* **2010**, *112*, 3–9; b) C. Thurier, C. Fischmeister, C. Bruneau, H. Olivier-Bourbigou, P. H. Dixneuf, *ChemSusChem* **2008**, *1*, 118–122; c) R. Malacea, C. Fischmeister, C. Bruneau, J.-L. Dubois, J.-L. Couturier, P. H. Dixneuf, *Green Chem.* **2009**, *11*, 152–155; d) V. Le Ravalec, C. Fischmeister, C. Bruneau, *Adv. Synth. Catal.* **2009**, *351*, 1115–1122 ; e) X. Miao, C. Fischmeister, C. Bruneau, P. H. Dixneuf, *ChemSusChem* **2009**, *2*, 542–545; f) M. A. R. Meier, J. O. Metzger, U. S. Schubert, *Chem. Soc. Rev.* **2007**, *36*, 1788–1802; g) A. Rybak, P. A. Fokou, M. A. R. Meier, *Eur. J. Lipid Sci. Technol.* **2008**, *110*, 797–804; h) B. M. Marvey, *Int. J. Mol. Sci.* **2008**, *9*, 1393–1406; i) J. C. Mol, *Green Chem.* **2002**, *4*, 5–13.

[7] a) A. H. Hoveyda, S. J. Malcolmson, S. J. Meek, A. R. Zhugralin, *Angew. Chem.* **2010**, *122*, 38–49; *Angew. Chem. Int. Ed.* **2010**, *49*, 34–44; b) T. J. Seiders, D. W. Ward, R. H. Grubbs, *Org. Lett.* **2001**, *3*, 3225–3228.

[8] P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs, *Angew. Chem.* **1995**, *107*, 2179–2181; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2039–2041.

[9] a) T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem.* **1998**, *110*, 2631–2633; *Angew. Chem. Int. Ed.* **1998**, *37*, 2490–2493; b) J. Huang, E. D. Stevens, S. P. Nolan, L. J. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678; c) M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.* **1999**, *40*, 2247–2250; d) T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem.* **1999**, *111*, 2573–2576; *Angew. Chem. Int. Ed.* **1999**, *38*, 2416–2419; e) M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.

[10] a) J. P. A. Harrity, D. S. La, D. R. Cefalo, M. S. Visser, A. H. Hoveyda, *J. Am. Chem. Soc.* **1998**, *120*, 2343–2351; b) J. S. Kingsbury, J. P. A. Harrity, P. J. Bonitatebus, A. H. Hoveyda, *J. Am. Chem. Soc.* **1999**, *121*, 791–799; c) S. B. Garber, J. S. Kingsbury, B. L. Gray, A. H. Hoveyda, *J. Am. Chem. Soc.* **2000**, *122*, 8168–8179; d) S. Gessler, S. Randl, S. Blechert, *Tetrahedron Lett.* **2000**, *41*, 9973–9976; e) H. Wakamatsu, S. Blechert, *Angew. Chem.* **2002**, *114*, 2509–2511; *Angew. Chem. Int. Ed.* **2002**, *41*, 2403–2405; f) K. Grela, S. Harutyunyan, A. Michrowska, *Angew. Chem.* **2002**, *114*, 4210–4212; *Angew. Chem. Int. Ed.* **2002**, *41*, 4038–4040; g) A. H. Hoveyda, D. G. Gillingham, J. J. Van Veldhuizen, O. Kataoka, S. B. Garber, J. S. Kingsbury, J. P. A. Harrity, *Org. Biomol. Chem.* **2004**, *2*, 8–23.

[11] a) V. Dragutan, I. Dragutan, *Platinum Met. Rev.* **2004**, *48*, 148–153; b) T. Opstal, F. Verpoort, *J. Mol. Catal. A* **2003**, *200*, 49–61; c) H. Katayama, H. Urushima, F. Ozawa, *J. Organomet. Chem.* **2000**, *606*, 16–25; d) J. Louie, R. H. Grubbs, *Angew. Chem.* **2001**, *113*, 253–255; *Angew. Chem. Int. Ed.* **2001**, *40*, 247–249.

[12] a) A. Fürstner, M. Picquet, C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1998**, 1315–1316 ; b) A. Fürstner, M. Liebl, C. W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard, P. H. Dixneuf, *Chem. Eur. J.* **2000**, *6*, 1847–1857; c) R. Castarlenas, C. Fischmeister, C. Bruneau, P. H. Dixneuf, *J. Mol. Catal. A* **2004**, *213*, 31–37; d) N. Ledoux, R. Drozdzak, B. Allaert, A. Linden, P. Van Der Voort, F. Verpoort, *Dalton Trans.* **2007**, 5201–5210.

[13] a) R. Castarlenas, P. H. Dixneuf, *Angew. Chem.* **2003**, *115*, 4662–4665; *Angew. Chem. Int. Ed.* **2003**, *42*, 4524–4527; b) R. Castarlenas, C. Vovard, C. Fischmeister, P. H. Dixneuf, *J. Am. Chem. Soc.* **2006**, *128*, 4079–4089; c) T. Opstal, F. Verpoort, *Angew. Chem.* **2003**, *115*, 2982–2985; *Angew. Chem. Int. Ed.* **2003**, *42*, 2876–2879. For recent reviews, see: d) V. Dragutan, I. Dragutan, F. Verpoort, *Platinum Met. Rev.* **2005**, *49*, 33–40; e) F. Boeda, H. Clavier, S. P. Nolan, *Chem. Commun.* **2008**, 2726–2740.

[14] A. Fürstner, O. Guth, A. Düffels, G. Seidel, M. Liebl, B. Gabor, R. Mynott, *Chem. Eur. J.* **2001**, *7*, 4811–4820.

[15] L. Jafarpour, H.-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 5416–5419.

[16] K. Puentener, M. Scalone, PCT Int. Appl., WO 2006111491, **2006**.

[17] a) H. Clavier, C. A. Urbina-Blanco, S. P. Nolan, *Organometallics* **2009**, *28*, 2848–2854; b) S. Monsaert, E. De Canck, R. Drozdzak, P. Van Der Voort, F. Verpoort, J. C. Martins, P. M. S. Hendrickx, *Eur. J. Org. Chem.* **2009**, 655–665; c) H. Clavier, F. Caijo, E. Borré, D. Rix, F. Boeda, S. P. Nolan, M. Mauduit, *Eur. J. Org. Chem.* **2009**, 4254–4265.

[18] H. Clavier, J. L. Petersen, S. P. Nolan, *J. Organomet. Chem.* **2006**, *691*, 5444–5477.

[19] A. M. Lozano Vila, S. Monsaert, R. Drozdzak, S. Wolowiec, F. Verpoort, *Adv. Synth. Catal.* **2009**, *351*, 2689–2701.

[20] a) S. Monsaert, A. M. Lozano Vila, R. Drozdzak, P. Van Der Voort, F. Verpoort, *Chem. Soc. Rev.* **2009**, *38*, 3360–3372; b) S. Monsaert, N. Ledoux, R. Drozdzak, F. Verpoort, *J. Polym. Sci. Polym. Chem. Ed.* **2010**, *48*, 302–310; c) C. E. Diesendruck, Y. Vidavsky, A. Ben-Asuly, N. G. Lemcoff, *J. Polym. Sci. Polym. Chem. Ed.* **2009**, *47*, 4209–4213; d) A. Ben-Asuly, A. Aharoni, C. E. Diesendruck, Y. Vidavsky, I. Goldberg, B. N. Straub, N. G. Lemcoff, *Organometallics* **2009**, *28*, 4652–4655; e) T. Kost, M. Sigalov, I. Goldberg, A. Ben-Asuly, N. G. Lemcoff, *J. Organomet. Chem.* **2008**, *693*, 2200–2203; f) A. Ben-Asuly, E. Tzur, C. E. Diesendruck, M. Sigalov, I. Goldberg, N. G. Lemcoff, *Organometallics* **2008**, *27*, 811–813; g) A. Szadkowska, X. Gstrein, D. Burtscher, K. Jarzembska, K. Wozniak, C. Slugovc, K. Grela, *Organometallics* **2010**, *29*, 117–124; h) M. Barbasiewicz, A. Szadkowska, R. Bujok, K. Grela, *Organometallics* **2006**, *25*, 3599–3604; i) C. Slugovc, D. Burtscher, F. Stelzer, K. Mereiter, *Organometallics* **2005**, *24*, 2255–2258; j) A. Hejl, M. W. Day, R. H. Grubbs, *Organometallics* **2006**, *25*, 6149–6154; k) T. Ung, A. Hejl, R. H. Grubbs, Y. Schrodi, *Organometallics* **2004**, *23*, 5399–5401; l) T. C. Mauldin, M. R. Kessler, *J. Therm. Anal. Calorim.* **2009**, *96*, 705–713; m) N. Ledoux, B. Allaert, D. Schaubroeck, S. Monsaert, R. Drozdzak, P. Van Der Voort, F. Verpoort, *J. Organomet. Chem.* **2006**, *691*, 5482–5486; n) P. A. van der Schaaf, A. Kolly, H.-J. Kirner, F. Rime, A. Muhlebach, A. Hafner, *J. Organomet. Chem.* **2000**, *606*, 65; o) H. Kunkely, A. Vogler, *Inorg. Chim. Acta* **2001**, *325*, 179; p) J. Louie, R. H. Grubbs, *Organometallics* **2002**, *21*, 2153; q) B. De Clercq, F. Verpoort, *Tetrahedron Lett.* **2002**, *43*, 9101.

[21] For a mechanistic study on indenylidene synthesis, see: a) E. A. Shaffer, C.-L. Chen, A. M. Beatty, E. J. Valente, H.-J. Schanz, *J. Organomet. Chem.* **2007**, *692*, 5221–5233; b) M. Bassetti, F. Centola, D. Sémeril, C. Bruneau, P. H. Dixneuf, *Organometallics* **2003**, *22*, 4459–4466.

[22] T. Akita, N. Koga, *Polyhedron* **2005**, *24*, 2321–2325.

[23] ^{31}P NMR spectra of [Ru(3-phenylindenylid-1-ene)$Cl_2(PPh_3)_2$] gave a signal at $\delta = 28.7$ ppm (see ref. [14]).

[24] Structural data of complex **4b** could not be found.

[25] M. Ulman, R. H. Grubbs, *J. Org. Chem.* **1999**, *64*, 7202–7207.

[26] T. Ritter, A. Hejl, A. G. Wenzel, T. W. Funk, R. H. Grubbs, *Organometallics* **2006**, *25*, 5740–5745.

[27] Weakening the Ru–O bond by steric or electronic effects resulted in faster initiation reactions, see ref [10e] and [10f].

[28] a) C. Lo, C. Fischmeister, C. Bruneau, P. H. Dixneuf, *Adv. Synth. Catal.* **2007**, *349*, 546–550; b) I. C. Stewart, T. Ung, A. A. Pletnev, J. M. BerlinR. H. Grubbs, Y. Schrodi, *Org. Lett.* **2007**, *9*, 1589–1592; c) H. Clavier, S. Nolan, *Chem. Eur. J.* **2007**, *13*, 8029–8036; d) C. Samłojowicz, M. Bieniek, A. Zarecki, R. Kadyrov, K. Grela, *Chem. Commun.* **2008**, 6282–6284; e) D. Rost, M. Porta, S. Gessler, S. Blechert, *Tetrahedron Lett.* **2008**, *49*, 5968–5971; f) T. Vorfalt, S. Leuthußer, H. Plenio, *Angew. Chem.* **2009**, *121*, 5293–5296; *Angew. Chem. Int. Ed.* **2009**, *48*, 5191–5193; g) V. Sashuk, L. H. Peeck, H. Plenio, *Chem. Eur. J.* **2010**, *16*, 3983–3993.

[29] M. Mori, N. Sakakibora, A. Kinoshita, *J. Org. Chem.* **1998**, *63*, 6082–6083.

[30] DMC was recently shown to be a greener solvent for olefin-metathesis transformations: a) X. Miao, C. Fischmeister, C. Bruneau, P. H. Dixneuf, *ChemSusChem* **2008**, *1*, 813–816; b) A. Keraani, T. Renouard, C. Fischmeister, C. Bruneau, M. Rabiller-Baudry, *ChemSusChem* **2008**, *1*, 927–933.

[31] Complex **10** was fully soluble in DCPD and did not require preliminary dissolution in a solvent like dichloromethane.

[32] CCDC-791241 (**9**) and CCDC-791240 (**10**) contain the supplementary crystallographic data for 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.

Received: June 11, 2010
Published online: September 13, 2010

