DOI: 10.1002/adsc.200700149

Noels' *vs.* Grubbs' Catalysts: Evidence for One Unique Active Species for Two Different Systems!

Mathieu Ahr,[a] Chloé Thieuleux,[a,]* Christophe Copéret,[a] Bernard Fenet,[b,c] and Jean-Marie Basset[a,]*

[a] C2P2, UMR 5265 CNRS ESCPE Lyon, Laboratoire de Chimie Organométallique de Surface, ESCPE Lyon, 43 Bd du 11 Novembre 1918, 69616 Villeurbanne Cedex, France
Fax: (+33)- 4-7243-1795; e-mail: thieuleux@cpe.fr
[b] Centre de RMN, Université de Lyon, 69003 Lyon, France
[c] Université Lyon 1 Claude Bernard, ESCPE Lyon, 43, Bd du 11 Novembre 1918, 69616 Villeurbanne Cedex, France

Received: March 22, 2007

Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: The catalytically active propagating species involved in the self-metathesis of ethyl oleate obtained from the multi-component Noels' catalytic system {[RuCl$_2$(*p*-cymene)(PCy$_3$)]+Me$_3$SiCHN$_2$} are probably the same as those of the single-component well-defined Grubbs' 1st generation catalyst, [Cl$_2$Ru=CHPh(PCy$_3$)$_2$] (**1-Ph**). In the case of the Noels' catalyst, it involves the de-coordination of *p*-cymene, and the redistribution of PCy$_3$ ligands to generate only 5–10% of [Cl$_2$Ru=CHR(PCy$_3$)$_2$], where R=CH–(CH$_2$)$_6$–CH$_3$ (**1-Oct**) and R=CH–(CH$_2$)$_6$–COOEt (**1-E**), while **1-Ph** can generate 100% of these species.

Keywords: active species; ethyl oleate; Grubbs' catalyst; Noels' catalyst; olefin metathesis

Within the context of sustainable development, the use of fatty oils (obtained from the biomass) as raw materials appears to be an alternative to petroleum,[1] and metathesis can be used to produce key olefinic intermediates from fatty acid esters. Recent advances in olefin metathesis, based on the Chauvin mechanism,[2] have allowed numerous well-defined catalysts to be developed,[3] and today olefin metathesis can be used to construct complex molecular assemblies.[4] While the catalysts developed by Grubbs have been studied for the metathesis of oleate derivatives,[5] no data have been reported on the cheaper Noels' type catalyst,[6] which is generated *in situ* by reacting [RuCl$_2$(*p*-cymene)(PCy$_3$)] or a mixture of [RuCl$_2$(*p*-cymene)]$_2$ dimer and PCy$_3$ with a carbene initiator such as (trimethylsilyl)diazomethane (TMSD). Here, we have investigated in detail this catalytic system in the self-metathesis of ethyl oleate (EO) (ratio of Ru, initiatior and PCy$_3$, effect of temperature and solvents) and shown that [Cl$_2$Ru=CHR(PCy$_3$)$_2$], the Grubbs' 1st generation catalyst (**1-Ph**, Grubbs I),[7] is in fact generated *in situ*.

First, using the experimental conditions reported by Noels et al. for the ROMP of cycloolefins {[RuCl$_2$(*p*-cymene)(PCy$_3$)] 1 mol%, 60 °C, in chlorobenzene in the presence of an excess of TMSD (12 equivs.)}, only 10% of EO is converted after 24 h (Table 1, entry 1). Note that the use of [RuCl$_2$(*p*-cymene)]$_2$ in the absence of PCy$_3$ gives only poor conversion (*ca.* 1% after 24 h, entry 2) in contrast to what is observed in ROMP of norbornene and norbornadiene esters, which can be performed without PCy$_3$.[6e] In fact, increasing the amount of PCy$_3$ to 2 equivs. per Ru improves slightly the conversion of EO to 27% (entry 3). Second, the effect of the amount of initiator (TMSD), typically used in excess (2–7 equivs./Ru), was tested.[6b] Decreasing the amount from 12 to 4 to 1 equiv. increased the conversion at 24 h from 10 to 32 to 34%, respectively (entries 1 *vs.* 4 and 5). However, further decreasing the amount of TMSD is detrimental, and the conversions decreased from 25% to 3% when the amount of TMSD decreased from 0.5 to 0 equiv. (entries 5 *vs.* 6 and 7). Thus, the addition of a stoichiometric amount of TMSD per [RuCl$_2$(*p*-cymene)(PCy$_3$)] is better for good conversions. Third, the reaction can be run between 25 and 60 °C without major influence on the conversion (33–34%) after 24 h, while higher temperatures, e.g., 80 °C, destroy the catalyst (conversion of EO reaches 13% and stops after 2 h, in agreement with a deactivation of the catalyst; entries 5 *vs.* 8 and 9).

Finally, while the reaction cannot be run in neat EO, concentrations varying between 0.5 and 2.0 M can be used. It is also possible to replace chloroben-

Table 1. Metathesis of ethyl oleate (EO).[a]

Entry	Pre-catalyst	T [°C]	TMSD/Ru (equivs.)	Conversion [%][b] @ 2 h	Conversion [%][b] @ 24 h
1	$RuCl_2(cym)PCy_3$	60	12	7	10
2	$[RuCl_2(cym)]_2$	60	12	1	1
3	$RuCl_2(cym)PCy_3+PCy_3$	60	12	5	27
4	$RuCl_2(cym)PCy_3$	60	4	18	32
5	$RuCl_2(cym)PCy_3$	60	1	26	34
6	$RuCl_2(cym)PCy_3$	60	0.5	22	25
7	$RuCl_2(cym)PCy_3$	60	0	0	3
8	$RuCl_2(cym)PCy_3$	25	1	15	33
9	$RuCl_2(cym)PCy_3$	80	1	12	13

[a] Experimental conditions: 0.56M solution of EO in chlorobenzene and EO/Ru:100.
[b] Thermodynamic equilibrium at *ca.* 47% conversion.

zene by toluene with no significant effect, but conversions are significantly improved when dichloromethane is used (43% within 24 h), and in this case the thermodynamic equilibrium (47%) is reached after 48 h.

Using these optimized conditions {[$RuCl_2$(*p*-cymene)PCy_3], TMSD (1 equiv./Ru), 25°C, EO (*ca.* 0.6M), CH_2Cl_2}, the influence of the substrate/catalyst ratio was investigated. First, decreasing the amount of [$RuCl_2$(*p*-cymene)PCy_3] from 1 mol% to 0.2 mol%, the thermodynamic equilibrium is also reached within 24 h of reaction. Further decreasing the amount of [$RuCl_2$(*p*-cymene)PCy_3] to 0.05 mol% gives a maximum conversion of 26% after 48 h, which corresponds to 520 TON per total Ru. Noteworthy, when the metathesis reaction is monitored over time, the conversions of EO are similar whether using 1 or 0.2 mol% of catalyst precursor (see Fig. S1 in the Supporting Information), which clearly indicates that only a fraction of Ru active species is formed from [$RuCl_2$(*p*-cymene)PCy_3] and TMSD. It was therefore tempting to detect and characterize this active species.

This system has therefore been further investigated by monitoring the metathesis reaction by ^1H and ^{31}P NMR spectroscopies. After 20 min of reaction (Ru:TMSD:EO = 1:3:3), the ^1H NMR spectrum displays a new multiplet centered at *ca.* 19.72 ppm (Figure 1, trace a), while two signals appear in the ^{31}P NMR at 36.22 and 36.24 ppm, respectively (Figure 1, trace b). Based on chemical shifts, these species are tentatively attributed to propagating carbenic species (*vide infra*), and they correspond to about 5–10% of the total ruthenium based on ^1H NMR spectra {the major part of [$RuCl_2$(*p*-cymene)PCy_3] being untouched}. These species are still observed after 180 and 360 min of reaction, while a new signal appears at 30.8 ppm in the ^{31}P NMR, which is assigned to {[$RuCl_2$(toluene)PCy_3]} resulting from the *p*-cymene–toluene exchange.[8] Noteworthy, the ^1H and ^{31}P NMR signals of these putative propagating carbenic species generated from the multi-component Noels' catalytic system in the metathesis of EO have identical chemical shifts to those observed when **1-Ph** is used (Figure 1, traces c and d); in the latter case remaining unreacted **1-Ph** is still observed

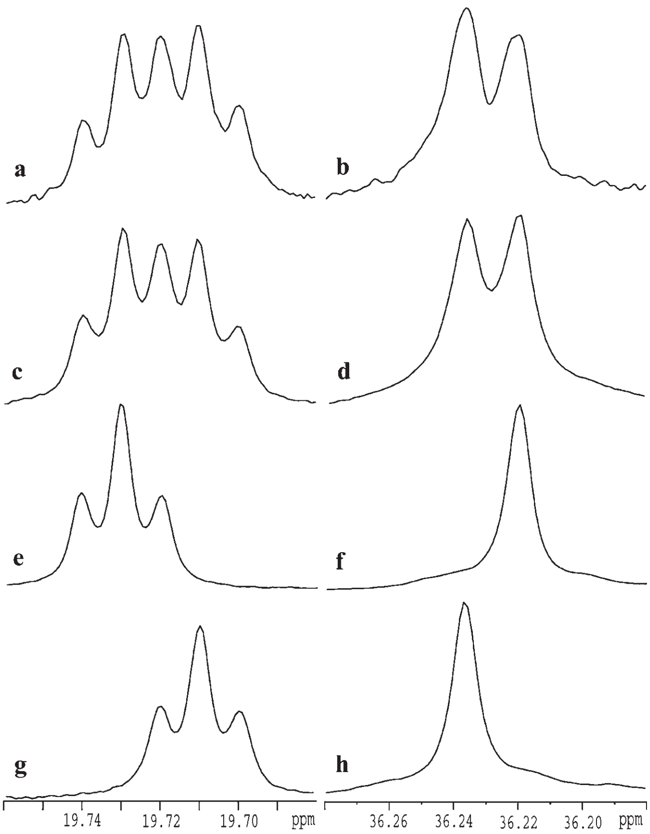
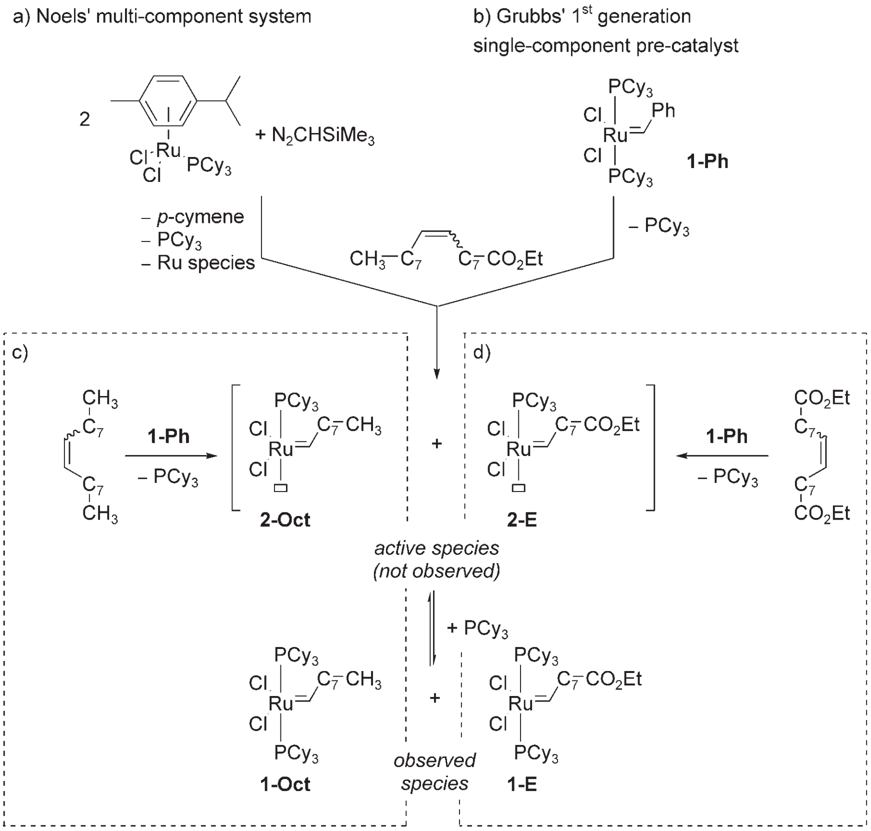


Figure 1. Monitoring the Ru carbenic species by NMR (toluene-d_8). $RuCl_2$(*p*-cymene)PCy_3 + TMSD (3 equivs.) + EO (3 equivs.): **a**) ^1H and **b**) ^{31}P. $RuCl_2(=CHPh)(PCy_3)_2$ (**1-Ph**) + EO (3 equivs.): **c**) ^1H and **d**) ^{31}P. **1-Ph** + 9-octadecene (3 equivs.): **e**) ^1H and **f**) ^{31}P. **1-Ph** + diethyl 9-octadecenedioate (3 equivs.): **g**) ^1H and **h**) ^{31}P.

(*ca.* 20% after 24 h of reaction). In fact, mixing these two reaction mixtures provides the identical NMR spectra (see Figs. S2a and S2b in the Supporting Information), confirming that the same species are observed in the metathesis of EO whether starting from **1-Ph** or [$RuCl_2$(*p*-cymene)PCy_3]/TMSD (Scheme 1). Furthermore, monitoring the reactions of **1-Ph** with each of the metathesis products of EO, namely 9-octadecene and diethyl 9-octadecenedioate, provides two discrete species : the NMR spectra obtained from the reaction of **1-Ph** with 9-octadecene giving **1-Oct** display a triplet at 19.73 ppm in ^{1}H NMR and a singlet at 36.22 in the ^{31}P NMR (Figure 1, traces e and f), while a triplet at 19.71 ppm and a singlet at 36.24 ppm are obtained in ^{1}H and ^{31}P NMR (Figure 1, traces g and h) from the reaction of **1-Ph** with diethyl 9-octadecenedioate giving **1-E** (see Fig. S3 in the Supporting Information for characterization of these species by HMBC NMR spectroscopy). Moreover, ERETIC NMR spectroscopy,[9] a quantitative NMR method applied for the first time to the ^{31}P nucleus, shows that the Ru species, obtained by the reaction of **1-Ph** with EO (3 equivs.), contain two PCy_3 per carbenic proton (see Fig. S4 in the Supporting Information), which is consistent with the presence of **1-Ph**. The active species **2**, having only one PCy_3 ligand, has not been observed under these conditions as previously reported.[10,11] Finally, the ^{1}H and ^{31}P NMR spectra of a mixture of these two complexes are identical (See Figs. S2c and S2d in the Supporting Information) to those obtained for the self-metathesis of EO with the Noels' catalyst and **1-Ph** (Figure 1, traces a–d).

Therefore, the two observed species are those expected in the metathesis of EO: [$Cl_2Ru{=}CHR(PCy_3)_2$], where $R = CH{-}(CH_2)_6{-}CH_3$ (**1-Oct**) and $R = CH{-}(CH_2)_6{-}COOEt$ (**1-E**). They correspond to the resting states (2 PCy_3/Ru, **1**) of the two active species (1 PCy_3/Ru, **2**) (Scheme 1). This shows that the same catalytic system is obtained whether using {[$RuCl_2$(*p*-cymene)PCy_3] + TMSD} or **1-Ph**! In fact, upon addition of TMSD to a solution of [$RuCl_2$(*p*-cymene)PCy_3] in toluene-d_8 or CD_2Cl_2 at room temperature, free *p*-cymene (variable amounts) appears in the reaction mixture as evidenced by ^{1}H NMR as previously reported by Noels.[6c]

Considering the structure of the species generated from [$RuCl_2$(*p*-cymene)PCy_3], TMSD, and ethyl oleate, the amount of these species was estimated (by integrating ^{1}H and ^{31}P NMR signals) to about 5–10 mol% of the total ruthenium, which is close to the amount of free *p*-cymene (*ca.* 5–10%) liberated during the formation of the carbenic species. Note the effective TON for the Noels' catalyst under optimized conditions is *ca.* 5000–10000 (considering mol 5–10%



Scheme 1.

of active species), which is close to that obtained (4400) with **1-Ph** under the same reaction conditions.

In conclusion, the catalytically active propagating species involved in the self-metathesis of EO obtained from the multi-component Noels' catalytic system are probably the same as these of single-component well-defined Grubbs' 1st generation catalyst {both generated from [$Cl_2Ru{=}CHR(PCy_3)_2$] species}. In the case of the Noels' catalyst, it involves the de-coordination of *p*-cymene (thus avoiding the formation of a 20 e^- complex!), and the redistribution of PCy_3 ligands to generate only 5–10% of active species, while **1-Ph** can generate 100% of active species. This illustrates the difference of multi-[12] and single-component Ru-based catalysts.[3]

Experimental Section

Representative Procedure for Catalytic Tests

A dried Schlenk tube was loaded in a glovebox with [$RuCl_2$(*p*-cymene)PCy_3] (17 mg, 0.028 mmol, 1 equiv.), the solvent (4.0 mL) and ethyl oleate (1.0 mL, 2.8 mmol, 100 equivs.). Then, TMSD (0–0.15 mL, 0–0.33 mmol, 0–12 equivs.) was added, and the reaction mixture was stirred at the given temperature. Aliquots were regularly taken and analyzed by GC.

Representative Procedure for Catalytic Tests with the Noels' Catalyst Monitored by NMR Spectroscopy

An NMR tube equipped with a Young valve was loaded in a glovebox with the catalyst [$RuCl_2$(*p*-cymene)PCy_3] (9 mg, 15 μmol, 1 equiv.), toluene-d_8 (0.5 mL) and ethyl oleate (20 μL, 45 μmol, 3 equivs.). Then TMSD (25 μL, 45 μmol, 3 equivs.) was added, and ^1H and ^{31}P NMR spectra were recorded.

Representative Procedure for Catalytic Tests with the Grubbs' 1st Generation Catalyst Monitored by NMR Spectroscopy

An NMR tube equipped with a Young valve was loaded in a glovebox with the Grubbs' 1st generation catalyst (20 mg, 24 μmol, 1 equiv.), toluene-d_8 (0.5 mL) and 9-octadecene (50 mg, 200 μmol, 8 equivs.) or diethyl 9-octadecenedioate (75 mg, 200 μmol, 8 equivs.). After 24 h at room temperature, ^1H and ^{31}P NMR spectra were recorded.

Acknowledgements

This work has been sponsored by The Dow Chemical Company, and we would like to thank Drs. K. Geissler, J.-L. Guillaume and M. Schenk for helpful discussions.

References

[1] J. C. Mol, *Top. Catal.* **2004**, *27*, 97.

[2] a) J. L. Herisson, Y. Chauvin, *Makromol. Chem.* **1971**, *141*, 161; b) Y. Chauvin, *Angew. Chem. Int. Ed.* **2006**, *45*, 3741.

[3] a) T. M. Trnka, R. H. Grubbs, *Acc. Chem. Res.* **2001**, *34*, 18; b) T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem. Int. Ed.* **1998**, *37*, 2490; c) R. R. Schrock, *Angew. Chem. Int. Ed.* **2006**, *45*, 3748; d) R. H. Grubbs, *Angew. Chem. Int. Ed.* **2006**, *45*, 3760; e) A. H. Hoveyda, D. G. Gillingham, J. J. Van Veldhuizen, O. Kataoka, S. B. Garber, J. S. Kingsbury, J. P. A. Harrity, *Organic & Biomolecular Chemistry* **2004**, *2*, 8; f) C. Copéret, J.-M. Basset *Adv. Synth. Catal.* **2007**, *349*, 78.

[4] a) S. J. Connon, S. Blechert, *Angew. Chem. Int. Ed.* **2003**, *42*, 1900; b) K. C. Nicolaou, P. G. Bulger, D. Sarlah, *Angew. Chem. Int. Ed.* **2005**, *44*, 4490; c) A. Gradillas, J. Pérez-Castells, *Angew. Chem. Int. Ed.* **2006**, *45*, 6086; d) P. Van de Weghe, P. Bisseret, N. Blanchard, J. Eustache, *J. Organomet. Chem.* **2006**, *691*, 5078.

[5] a) C. Braendli, T. R. Ward, *Helv. Chim. Acta* **1998**, *81*, 1616; b) M. B. Dinger, J. C. Mol, *Adv. Synth. Catal.* **2002**, *344*, 671; c) K. A. Burdett, L. D. Harris, P. Margl, B. R. Maughon, T. Mokhtar-Zadeh, P. C. Saucier, E. P. Wasserman, *Organometallics* **2004**, *23*, 2027.

[6] a) A. Demonceau, A. F. Noels, E. Saive, A. J. Hubert, *J. Mol. Cat.* **1992**, *76*, 123; b) A. Strumph, E. Saive, A. Demonceau, A. F. Noels, *J. Chem. Soc., Chem. Commun.* **1995**, 1127; c) A. Demonceau, A. W. Stumpf, E. Saive, A. F. Noels, *Macromolecules* **1997**, *30*, 3127; d) L. Delaude, A. Demonceau, A. F. Noels, *Macromolecules* **1999**, *32*, 2091; e) D. Jan, L. Delaude, F. Simal, A. Demonceau, A. F. Noels, *J. Organomet. Chem.* **2000**, *606*, 55; f) L. Delaude, A. Demonceau, A. F. Noels, *Macromolecules* **2003**, *36*, 1446; g) A. Furstner, L. Ackermann, *Chem. Commun.* **1999**, 95.

[7] S. T. Nguyen, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1993**, *115*, 9858.

[8] M. A. Bennett, A. K. Smith, *J. Chem. Soc., Dalton Trans.* **1974**, 233.

[9] a) S. Akoka, L. Barantin, M. Trierweiler, *Analytical Chemistry* **1999**, *71*, 2554; b) V. Molinier, B. Fenet, J. Fitremann, A. Bouchu, Y. Queneau, *Carbo. Res.* **2006**, *341*, 1890.

[10] a) M. S. Sanford, J. A. Love, R. H. Grubbs, *J. Am. Chem. Soc.* **2001**, *123*, 6543; b) J. A. Love, M. S. Sanford, M. W. Day, R. H. Grubbs, *J. Am. Chem. Soc.* **2003**, *125*, 10103.

[11] Metallacyclobutane intermediates have been observed at low temperatures: a) P. E. Romero, W. E. Piers, *J. Am. Chem. Soc.* **2005**, *127*, 5032; b) A. G. Wenzel, R. H. Grubbs, *J. Am. Chem. Soc.* **2006**, *128*, 16048; c) for metallocarbene intermediates, see: D. R. Anderson, D. D. Hickstein, D. J. O'Leary, R. H. Grubbs, *J. Am. Chem. Soc.* **2006**, *128*, 8387.

[12] a) A. Furstner, M. Picquet, C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1998**, 1315; b) D. Semeril, C. Bruneau, P. H. Dixneuf, *Adv. Synth. Catal.* **2002**, *344*, 585; c) A. Fürstner, M. Liebl, C. W. Lehmann, M. Picquet,

R. Kunz, C. Bruneau, D. Touchard, P. H. Dixneuf, *Chem. Eur. J.* **2000**, *6*, 1847; d) R. Castarlenas, C. Vovard, C. Fischmeister, P. H. Dixneuf, *J. Am. Chem. Soc.* **2006**, *128*, 4079; e) L. Jafarpour, J. Huang, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 5735; f) L. Delaude, M. Szypa, A. Demonceau, A. F. Noels, *Adv. Synth. Catal.* **2002**, *344*, 749; g) R. Castarlenas, D. Semeril, A. F. Noels, A. Demonceau, P. H. Dixneuf, *J. Organomet. Chem.* **2002**, *663*, 235; h) L. Delaude, A. Demonceau, A. F. Noels, *Chem. Commun.* **2001**, 986.