

Ruthenium Indenylidene Complexes

METATHESIS CATALYSTS WITH ENHANCED ACTIVITY

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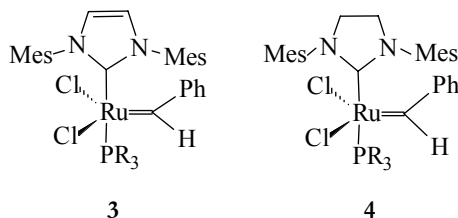
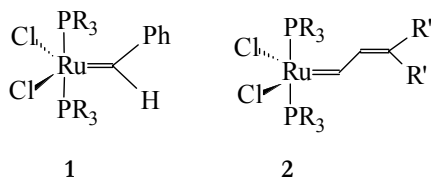
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This paper describes a class of ruthenium indenylidene complexes which constitute robust and efficient pre-catalysts for olefin metathesis reactions, specifically ring-closing metathesis of substituted linear dienes, acyclic diene metathesis of α,ω -dienes, enyne metathesis and ring-opening metathesis polymerisation of cycloolefins. They readily allow reactions not promoted by many prior ruthenium catalysts, such as the synthesis of tri- and tetrasubstituted cycloalkenes as well as ring-closing metathesis involving highly substituted dienes. The activity and stability of these pre-catalysts can be finely tuned by adjusting both steric and electronic effects in the metal coordination sphere through an appropriate selection of ancillary ligands. Due to their accessibility, enhanced activity and good stability, this class of ruthenium complexes gratifyingly extends the scope and utility of the currently used metathesis catalysts.

Nowadays the synthesis of single-site ruthenium (Ru) metathesis pre-catalysts (1) is emerging as an appealing challenge for a large number of research groups working in the area of organometallic chemistry (2–10). The 16-electron ruthenium benzylidene and vinyl carbene complexes 1 and 2 (R = Ph or Cy), developed by Grubbs and coworkers (11, 12), turned out to be versatile and reliable metathesis pre-catalysts enjoying a variety of applications in advanced organic synthesis and polymer chemistry (13, 14). They display a wide spectrum of activity while exhibiting good tolerance towards air, moisture and many organic functionalities. Despite this attractive application profile some drawbacks of the bisphosphane complexes 1 and 2 have to be taken into account. The drawbacks are:

- special precautions during their preparation involving diazoalkane derivatives and cyclopropane,
 - limited thermal stability upon heating, and
 - significant sensitivity towards substitution patterns in highly substituted olefinic substrates.
- In the last instance, the complexes allow synthesis

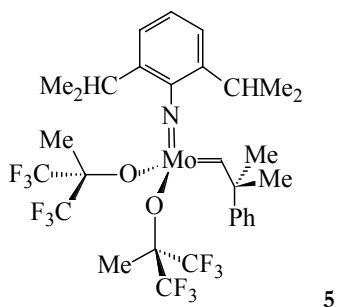
of trisubstituted olefins by ring-closing metathesis (RCM) only with a limited number of olefinic substrates and generally fail in the case of tetrasubstituted counterparts.



R is phenyl (Ph) or cyclohexyl (Cy), R' is methyl (Me) or phenyl (Ph) and Mes is 2,4,6-trimethylphenyl.

With the aim of improving their stability in solution and increasing their metathesis activity,

new ruthenium complexes were created, in the following years, by replacing one or two of the phosphane groups, mainly in the benzylidene complex 1, with sterically demanding 1,3-dimesitylimidazolin-2-ylidene ligands or their fully saturated analogues, (as in complexes 3 and 4) (15–20). Nonetheless, some applications in RCM reactions, not possible with these ruthenium pre-catalysts, are still restricted to the realm of the more active and selective, but quite sensitive, Schrock molybdenum imido alkylidene complex 5 (21, 22).



In addition to the above mentioned inconveniences, synthesis of complexes 1–4 requires rather expensive starting materials and implies caution during some of the preparation steps.

In order to eliminate these disadvantages, a series of new ruthenium complexes has recently been designed and prepared by further variations in the ligand sphere of complex 1. Thus, a novel class of ruthenium indenylidene pre-catalysts, displaying a wide application profile in metathesis

chemistry, has emerged. This type of ruthenium complex which is of special interest to organic and polymer catalysis will be discussed in this paper.

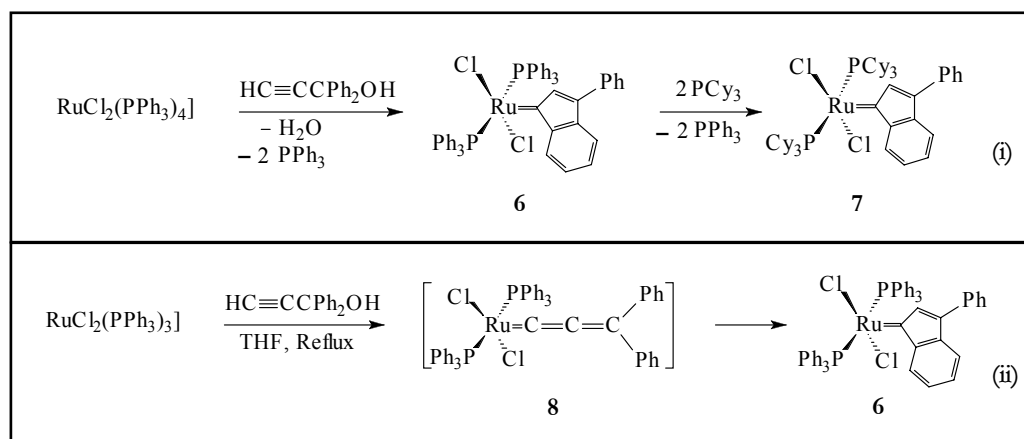
Bisphosphane Ruthenium Indenylidene Complexes

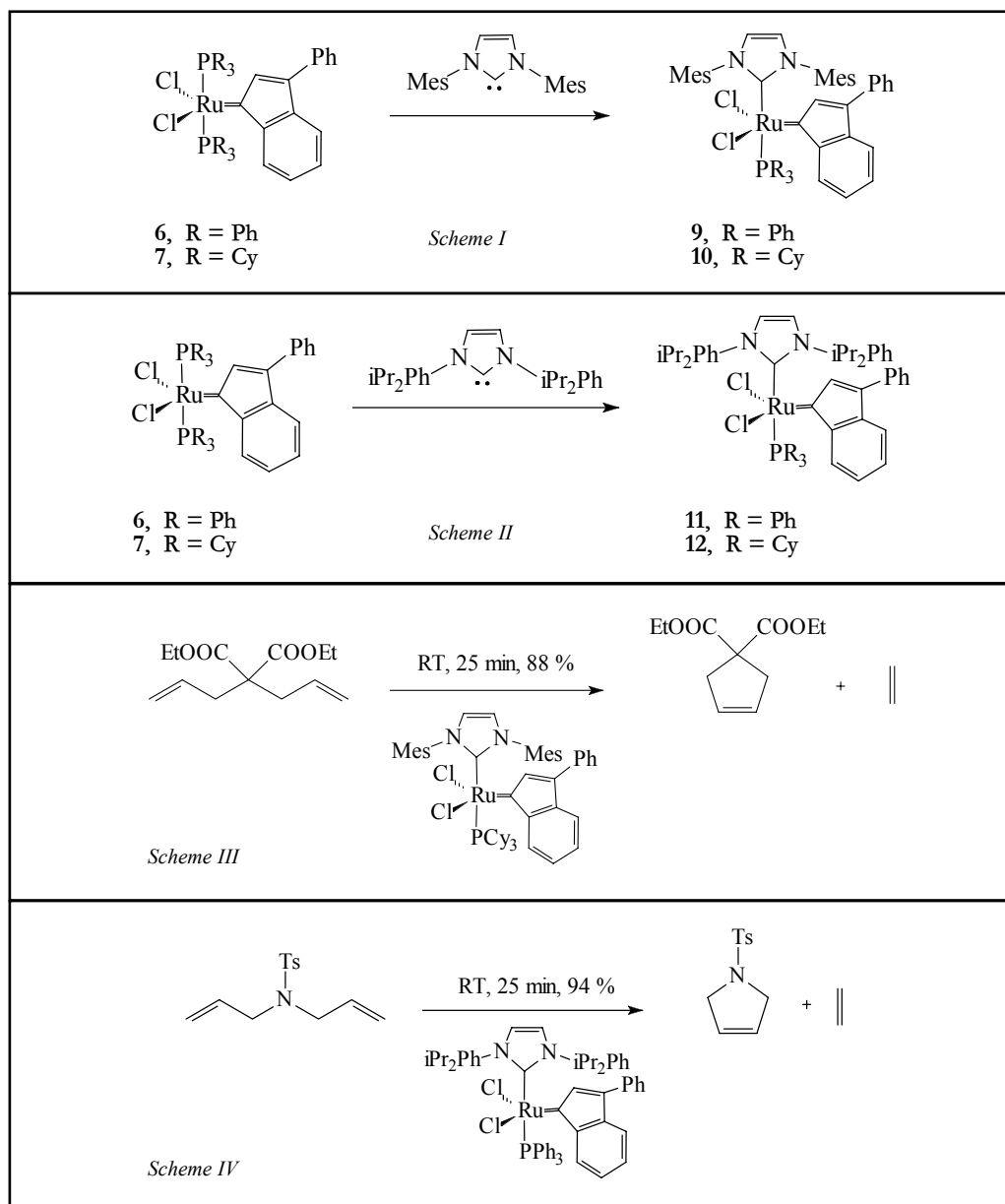
The 3-phenyl indenylidene complex 6 was conveniently obtained from $\text{RuCl}_2(\text{PPh}_3)_4$ and commercially available 3,3-diphenylpropyn-3-ol as the carbene precursor. Starting from complex 6, the PPh_3 ligands have been readily replaced by the better donating ligands PCy_3 , affording the parent indenylidene complex 7 (23, 24) (Equation (i)).

This methodology can also use $\text{RuCl}_2(\text{PPh}_3)_3$, (tris(triphenylphosphine) complex) as the ruthenium source, resulting in the same indenylidene complex 6. The rationalisation behind this finding, that the initially formed ruthenium allenylidene complex 8 leads by intramolecular rearrangement to the more stable indenylidene complex 6, has been proved unequivocally (25) (Equation (ii)). The above indenylidene ruthenium complexes showed higher thermal stability than the related alkylidene complexes 1 and 2 and performed well in various ring-closing metathesis reactions.

N-Heterocyclic Carbene (NHC) Indenylidene Ruthenium Complexes

Substitution of phosphane ligands in the ruthenium complexes 6 and 7 by imidazolin-2-ylidene ligands containing bulky groups in the 1 and 3 positions of the five-membered ring allowed the



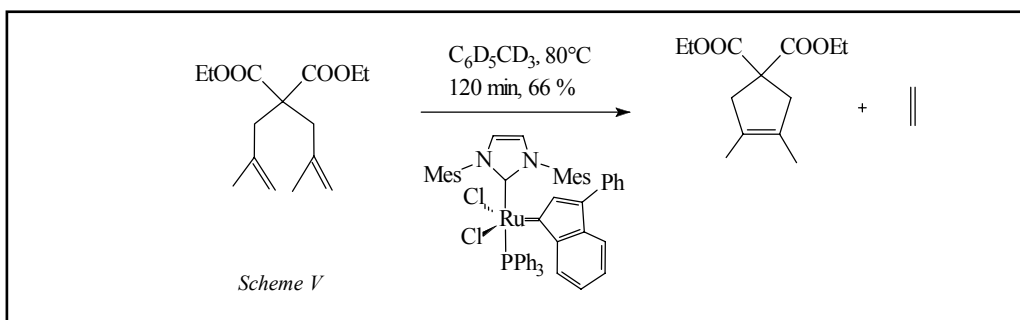


synthesis of further 16-electron ruthenium indenylidene complexes of improved activity and stability. Thus, the addition of 1,3-dimesitylimidazol-2-ylidene to 3-phenylindenylidene complexes 6 and 7, in toluene at room temperature, leads to the high yield of complexes 9 and 10, respectively (26) (Scheme I).

Most conveniently, complex 10 can be prepared in hot hexane when easier isolation of the product

by simple filtration (vs. evaporation of the solvent previously), followed by washing with hexane and drying, becomes possible. A similar procedure starting from 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene and 3-phenylindenylidene, 6 and 7, yielded imidazol-2-ylidene ruthenium complexes 11 and 12, respectively (Scheme II).

Thermal stability investigations showed compounds 10 and 12 incorporating a PCy₃ ligand are



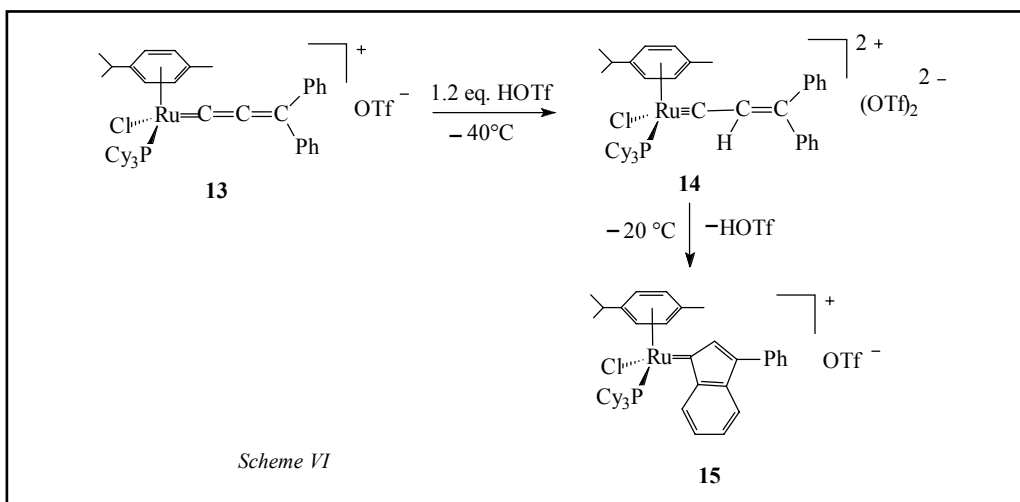
very stable and do not decompose even after heating at 80°C for several days. RCM studies using diethyl diallylmalonate and diallyltosylamide as the substrates showed good catalytic activity and selectivity for ruthenium indenylidene complexes of this pre-catalyst family (yield 88% and 94% of cyclic products, respectively) (Schemes III and IV). Remarkably, these types of complexes even allow the synthesis of tetrasubstituted cycloalkenes by RCM of the corresponding dienes, a process that meets severe restrictions or is not possible with common diphosphane ruthenium alkylidene complexes (Scheme V).

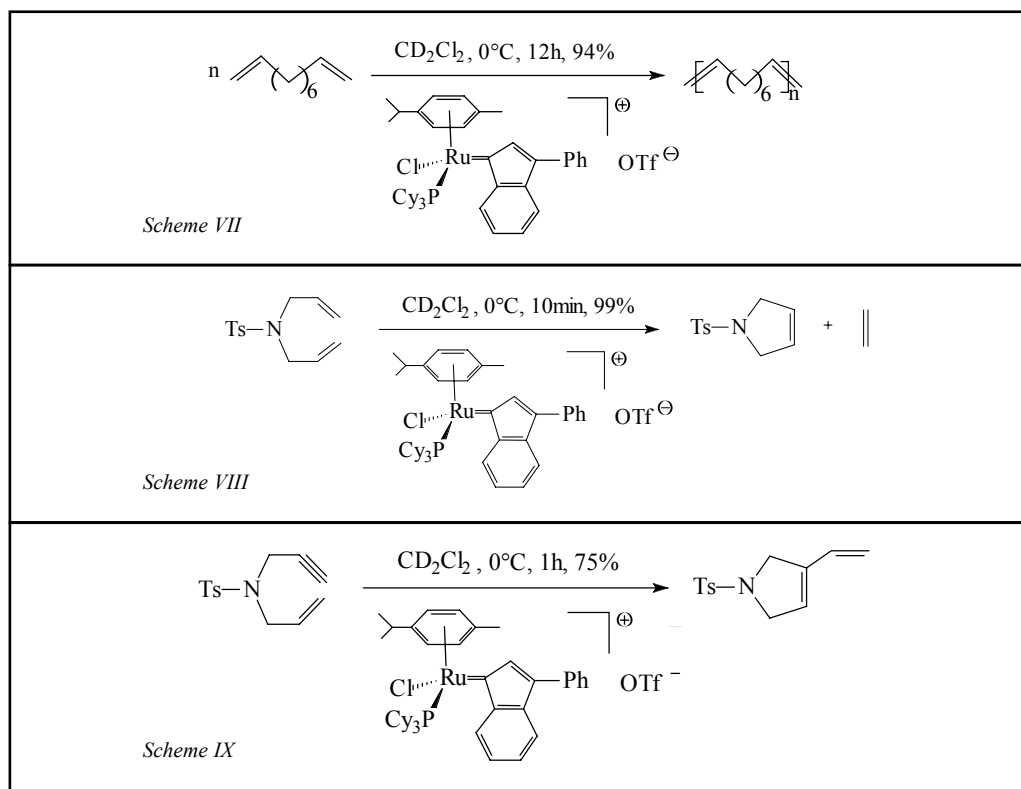
Arene Ruthenium Indenylidene Complexes

Low temperature NMR studies of protonated 18-electron ruthenium allenylidene complex **13**, undertaken by Dixneuf *et al.* (27), gave evidence of

the formation of an alkenylcarbyne ruthenium derivative **14** at -40°C which, upon heating at -20°C, readily converted to the ruthenium indenylidene complex **15** (Scheme VI).

It has been suggested that the alkenylcarbyne derivative **14** arises by protonation at the C β atom of the allenylidene ligand in complex **13** while the indenylidene derivative **15** is formed by further electrophilic substitution of the phenyl group with the rearranged C α atom. Complex **15**, generated *in situ* from **13** upon treatment with strong acids (HOTf, HBF $_4$), exhibited high activity in acyclic diene metathesis (ADMET) of 1,9-decadiene, RCM of diallyltosylamide, enyne metathesis of allylpropargyltosylamide and the ring-opening metathesis polymerisation (ROMP) of cyclopentene and cyclooctene. For instance, the ADMET reaction of 1,9-decadiene, carried out in CD $_2$ Cl $_2$ at 0°C, using the precursors HOSO $_2$ CF $_3$ and [RuCl(*p*-





cymene)(=C=C=CPh₂)(PCy₃)] [CF₃SO₃] of the *in situ* generated complex 15, gave a 94% yield of polymeric compound after 12 hours (Scheme VII).

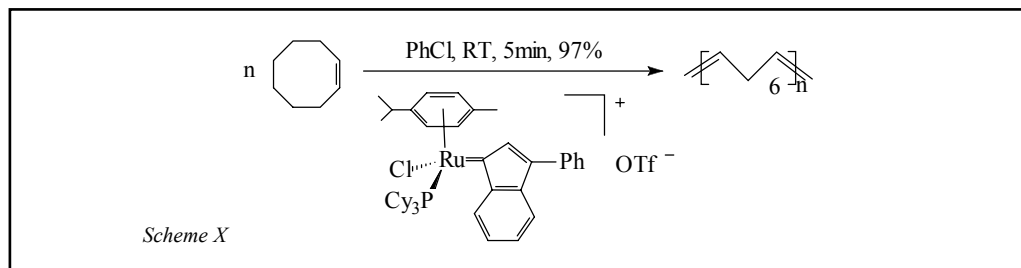
Similarly, in RCM of diallyltosylamide with the same catalytic system, 99% pyrrolidine N-tosylamide has been produced after a 10 min reaction time (Scheme VIII) whereas in enyne metathesis of allylpropargyltosylamide, only 75% yield of 3-allylpyrrolidine N-tosylamide resulted (Scheme IX).

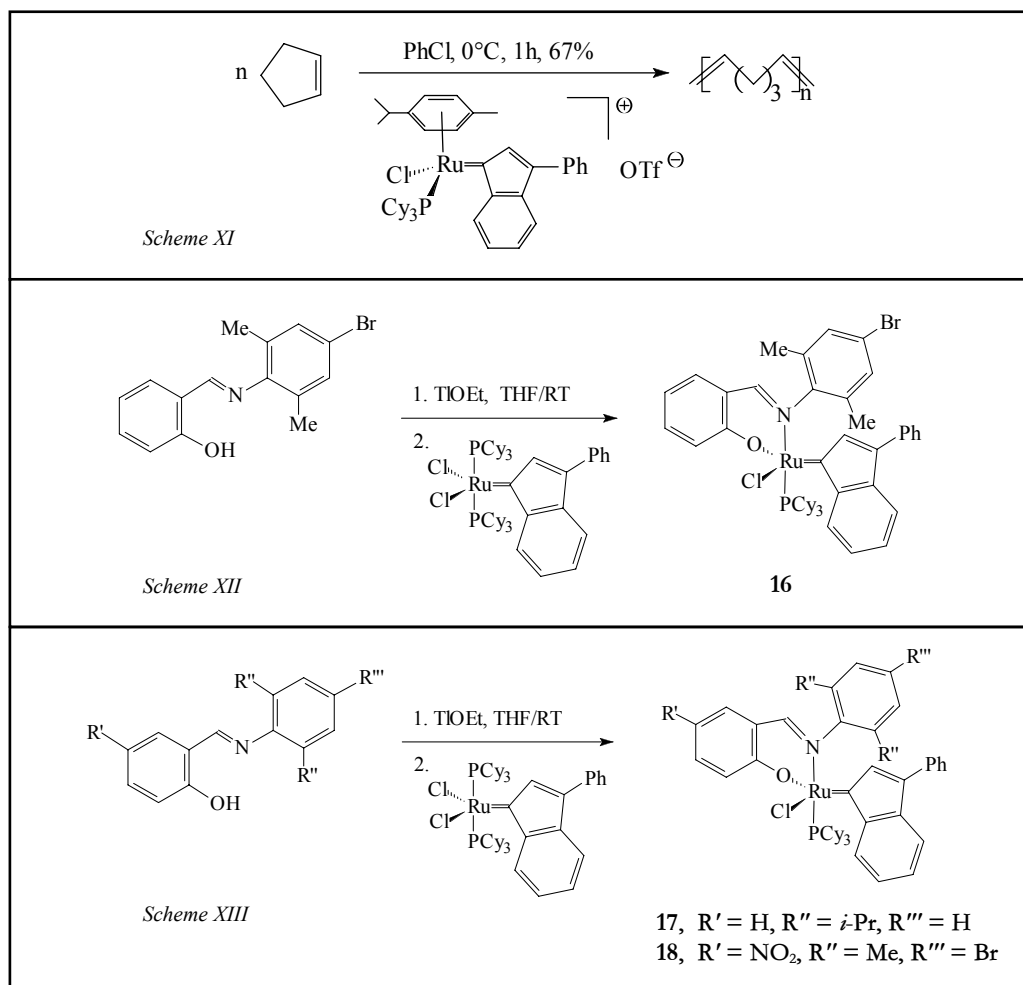
It is important to point out that in the ROMP of cyclooctene using the system [RuCl(*p*-cymene)(=C=C=CPh₂)(PCy₃)] [CF₃SO₃] / HOSO₂CF₃,

in chlorobenzene, an unexpectedly high yield of polyoctenamer was obtained, even after a short reaction time at room temperature (Scheme X). In contrast, starting from a less reactive monomer like cyclopentene, a maximum yield of 67% could be obtained after 1 hour at 0°C (Scheme XI).

Schiff Base Ruthenium Indenyldene Complexes

Starting from the diphosphane indenylidene complex 7 and an aromatic salicylaldehyde, the Schiff base containing ruthenium indenylidene





complex 16 has been obtained in high yield (28) (Scheme XII). Complex 16 was characterised by ¹H, ¹³C, ³¹P-NMR spectroscopies and elemental analysis, and successfully applied to the synthesis of enol-esters implying nucleophilic addition of carboxylic acids to terminal alkynes. Importantly, the results obtained with catalyst 16 are comparable with previously reported data for the best metathesis ruthenium catalysts (29). Related Schiff base ligated ruthenium indenylidene complexes 17 and 18 have been prepared by this procedure, characterised by ¹H, ¹³C, ³¹P-NMR spectroscopy and elemental analysis, and tested for their activity in ROMP of cycloolefins and atom transfer radical polymerisation (ATRP) of vinyl monomers (30–32) (Scheme XIII).

It should be emphasised that the bidentate Schiff base ligands incorporated in this type of complex exert, due to their “dangling” propensity, a pronounced effect on both their activity and stability (32).

Conclusions

Ruthenium indenylidene complexes bearing different ancillary ligands in the metal coordination sphere emerge as quite efficient and versatile metathesis pre-catalysts. They proved to be rather robust and are stable even upon heating. These features are very promising for various metathetic applications. As a special bonus they allow reactions not promoted by many previous Ru catalysts, in particular the convenient synthesis of tri- and

tetrasubstituted cycloalkenes, as well as RCM involving highly substituted dienes. Due to easy accessibility, enhanced activity, increased stability, and wide area of application they successfully com-

plement conventional ruthenium complexes currently employed in the RCM of linear dienes, ADMET of α,ω -dienes, enyne metathesis and ROMP of cycloolefins.

References

- (a) V. Dragutan, I. Dragutan and A. T. Balaban, *Platinum Metals Rev.*, 2000, 44, (2), 58; (b) V. Dragutan, I. Dragutan and A. T. Balaban, *Platinum Metals Rev.*, 2000, 44, (3), 112; (c) V. Dragutan, I. Dragutan and A. T. Balaban, *Platinum Metals Rev.*, 2000, 44, (4), 168; (d) V. Dragutan, I. Dragutan and A. T. Balaban, *Platinum Metals Rev.*, 2001, 45, (4), 155; (e) V. Dragutan and I. Dragutan, *Platinum Metals Rev.*, 2004, 48, (4), 148
- (a) A. Demonceau, F. Simal, S. Delfosse and A. F. Noels, "Ring-Opening Metathesis Polymerization and Related Chemistry", eds. E. Khosravi and T. Szymanska-Buzar, NATO Science Series, Kluwer Academic Publishers, Dordrecht, 2002, pp. 91-104; (b) A. Demonceau, A. W. Stumpf, E. Saive and A. F. Noels, *Macromolecules*, 1997, 30, 3127
- (a) P. Dixneuf and C. Bruneau, *Acc. Chem. Res.*, 1999, 32, 311; (b) I. del Rio and G. van Koten, *Tetrahedron Lett.*, 1999, 40, 1401
- (a) A. Fürstner, *Angew. Chem., Int. Ed.*, 2000, 39, 3012; (b) A. Fürstner, *Top. Organomet. Chem.*, 1999, 1, 1
- (a) R. H. Grubbs and S. Chang, *Tetrahedron*, 1998, 54, 4413; (b) "Handbook of Metathesis", ed. R. H. Grubbs, Wiley-VCH, Weinheim, 2003
- (a) A. Hafner, A. Mühlebach and P. A. van der Schaaf, *Angew. Chem. Int. Ed.*, 1997, 36, 2121; (b) J. P. A. Harrity, D. S. La, D. R. Cefalo, M. S. Visser and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1998, 120, 2343; (c) J. S. Kingsbury, J. P. A. Harrity, P. J. Bonetatebus and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1999, 121, 791
- (a) W. Herrmann and C. Kocher, *Angew. Chem., Int. Ed.*, 1997, 36, 2162; (b) T. Weskamp, F. J. Kohl and W. A. Herrmann, *J. Organomet. Chem.*, 1999, 582, 362
- J. Huang, H. J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, 18, 2370
- (a) B. De Clercq and F. Verpoort, *Tetrahedron Lett.*, 2001, 42, 8959; (b) B. De Clercq and F. Verpoort, *Adv. Synth. Catal.*, 2002, 344, 639; (c) B. De Clercq and F. Verpoort, *J. Mol. Catal. A: Chem.*, 2002, 180, 67
- (a) M. Schuster and S. Blechert, *Angew. Chem. Int. Ed.*, 1997, 36, 2036; (b) M. Zaja, S. J. Connon, A. M. Dunne, M. Rivard, N. Buschmann, J. Jiricek and S. Blechert, *Tetrahedron*, 2003, 59, 6545
- (a) P. Schwab, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1996, 118, 100; (b) B. M. Novak and R. H. Grubbs, *J. Am. Chem. Soc.*, 1988, 110, 7542
- (a) S. T. Nuygen, L. K. Johnson, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1992, 114, 3974; (b) S. T. Nuygen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, 115, 9858; (c) S. T. Nuygen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1995, 117, 5503
- A. K. Chatterjee, J. P. Morgan, M. Scholl and R. H. Grubbs, *J. Am. Chem. Soc.*, 2000, 122, 3783
- V. Dragutan and R. Streck, "Catalytic Polymerization of Cycloolefins", Elsevier, Amsterdam, 2000
- (a) J. Huang, E. D. Stevens, S. P. Nolan and J. L. Pedersen, *J. Am. Chem. Soc.*, 1999, 121, 2674; (b) J. Huang, H.-J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, 18, 5375
- (a) L. Ackermann, A. Fürstner, T. Weskamp, F. J. Kohl and W. A. Herrmann, *Tetrahedron Lett.*, 1999, 40, 4787; (b) T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich and W. A. Herrmann, *Angew. Chem. Int. Ed.*, 1999, 38, 2416
- (a) M. Scholl, T. M. Trnka, J. P. Morgan and R. H. Grubbs, *Tetrahedron Lett.*, 1999, 40, 2247; (b) M. Scholl, S. Ding, C. W. Lee and R. H. Grubbs, *Org. Lett.*, 1999, 1, 953
- U. Frenzel, T. Weskamp, F. J. Kohl, W. C. Schattenmann, O. Nuyken and W. A. Herrmann, *J. Organomet. Chem.*, 1999, 586, 263
- (a) C. W. Bielawski, O. A. Sherman and R. H. Grubbs, *Polymer*, 2001, 42, 4939; (b) R. H. Grubbs, Paper presented at the 221st ACS National Meeting, San Diego, CA, 1-5 April, 2001; (c) M. S. Sanford, M. Ulman and R. H. Grubbs, *J. Am. Chem. Soc.*, 2001, 123, 749
- A. Fürstner, L. Ackermann, B. Gabor, R. Goddard, C. W. Lehmann, R. Mynott, F. Stelzer and O. R. Thiel, *Chem. Eur. J.*, 2001, 7, 3236
- R. R. Schrock, J. S. Murzdek, G. C. Bazan, J. Robbins, M. DiMare and M. O'Regan, *J. Am. Chem. Soc.*, 1990, 112, 3815
- (a) R. R. Schrock and A. H. Hoveyda, *Angew. Chem. Int. Ed.*, 2003, 42, 4592; (b) R. R. Schrock, *Top. Organomet. Chem.*, 1998, 1, 1
- A. Fürstner, A. F. Hill, M. Liebl and J. D. E. T. Wilton-Ely, *J. Chem. Soc., Chem. Commun.*, 1999, 601
- H.-J. Schanz, L. Jafarpour, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, 18, 5187
- A. Fürstner, O. R. Thiel, L. Ackermann, H.-J. Schanz and S. P. Nolan, *J. Org. Chem.*, 2000, 65, 2204
- L. Jafarpour, H.-J. Schanz, E. D. Stevens and S. P. Nolan, *Organometallics*, 1999, 18, 5416
- R. Castarlenas and P. Dixneuf, *Angew. Chem. Int. Ed.*, 2003, 42, 4524
- T. Opstal and F. Verpoort, *Synlett*, 2002, 935
- A. Fürstner, J. Grabowski and C. W. Lehmann, *J. Org. Chem.*, 1999, 64, 8275
- T. Opstal and F. Verpoort, *New J. Chem.*, 2003, 27, 257
- R. Drozdak, B. Allaert, N. Ledoux, I. Dragutan, V. Dragutan and F. Verpoort, submitted to *Adv. Synth. Catal.*
- T. Opstal and F. Verpoort, *Angew. Chem. Int. Ed.*, 2003, 42, 2876

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