

Ruthenium Vinylidene Complexes

SYNTHESES AND APPLICATIONS IN METATHESIS CATALYSIS

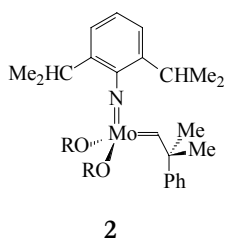
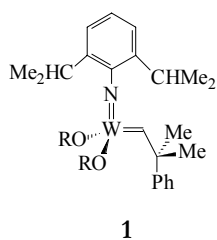
By Valerian Dragutan* and Ileana Dragutan

Institute of Organic Chemistry, Romanian Academy, 202B Spl. Independentei, PO Box 15-254, 060023 Bucharest, Romania;

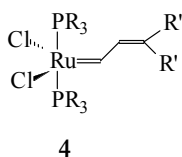
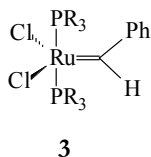
*E-mail: vdraguta@cco.ro

This paper surveys an attractive family of ruthenium complexes with great potential for applications in organic and polymer synthesis. When compared with traditional ruthenium alkylidene pre-catalysts, these alternative ruthenium vinylidene complexes are easily accessible from commercial starting materials. In addition, they display moderate to high metathesis activity and stability, and exhibit good tolerance towards an array of functional groups, air and moisture. Their synthesis, physical-chemical properties and catalytic attributes indicate they are quite promising initiators of efficient applications in ring-closing metathesis, cross metathesis and ring-opening metathesis polymerisation.

Previous papers recently published in this Journal have highlighted the role and scope of platinum group metals in the development of metathesis catalysts (1, 2). Following the seminal discovery of the highly active and stereoselective tungsten and molybdenum imido alkylidene metathesis catalysts, for example, 1 and 2 (R =



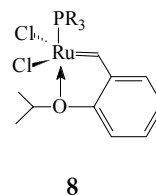
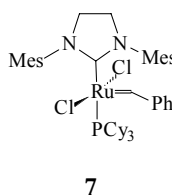
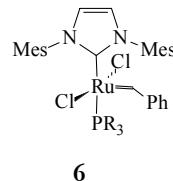
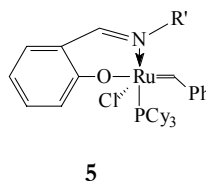
alkyl groups) by Schrock and coworkers (3, 4), an important class of ruthenium bisphosphane alkylidene catalysts, for example, 3 and 4, have been



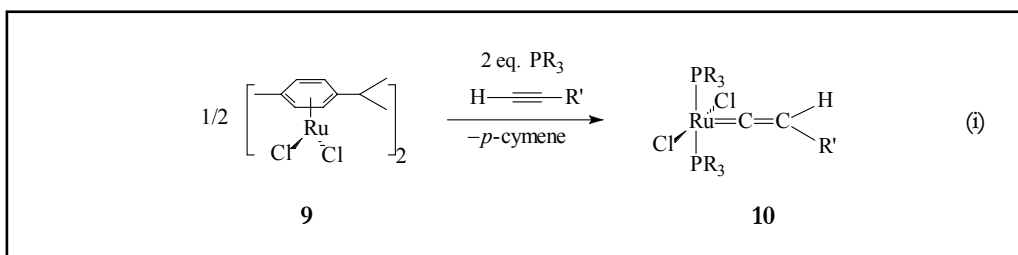
R = phenyl (Ph), isopropyl (iPr) or cyclohexyl (Cy)
R' = phenyl (Ph) or tert-butyl (tBu) groups

disclosed and successfully applied in metathesis reactions by Grubbs and coworkers (5, 6).

These ruthenium complexes enjoyed considerable popularity within the organic synthesis community, especially the neutral 16-electron ruthenium bisphosphane benzylidene complex 3, which combines good activity with high tolerance towards many organic functionalities, air and moisture. Many improvements in the preparation of classical Grubbs' catalysts have subsequently been performed (7, 8) and different variations of the ligand and sphere of complex 3 have been created. These include: Schiff base ligated complexes 5 (9–11), N-heterocyclic carbene complexes 6 and 7 (12–14), and isopropoxy tethered benzylidene complexes 8 (15). However, their synthesis *via* hazardous dia-



R = phenyl (Ph), isopropyl (iPr) or cyclohexyl (Cy)
R' = phenyl (Ph) or tert-butyl (tBu) groups
Mes = mesityl



zoalkane derivatives remains of considerable concern.

In order to circumvent this important drawback of ruthenium benzylidene complexes, research has been directed to produce alternative metathesis initiators of comparable performance but easier accessibility from commercial ruthenium sources (16, 17). The present paper reviews the class of ruthenium vinylidene complexes applied as efficient pre-catalysts in olefin metathesis reactions, such as cross metathesis (CM), ring-closing metathesis (RCM) and ring-opening metathesis polymerisation (ROMP).

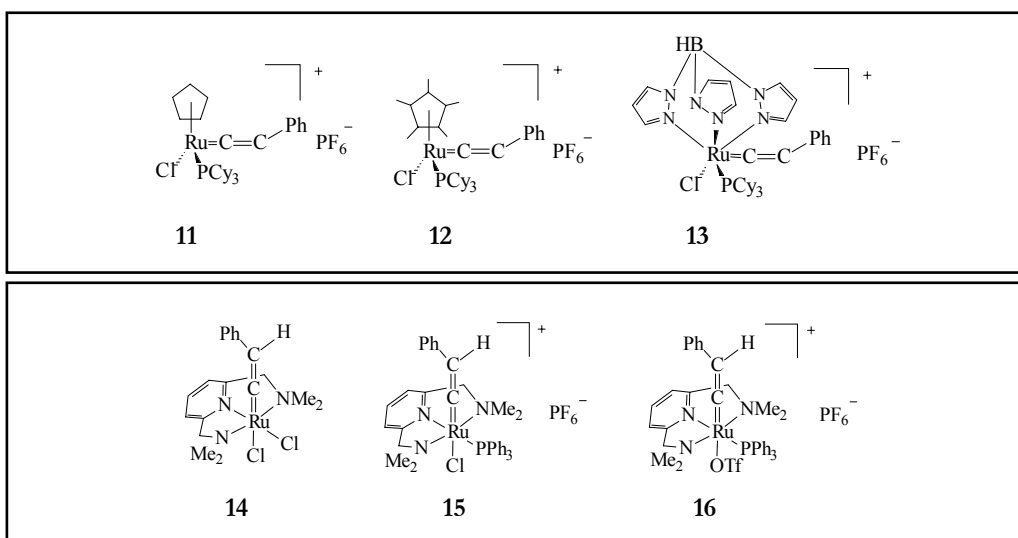
Ruthenium Vinylidene Complexes: Syntheses and Catalytic Properties

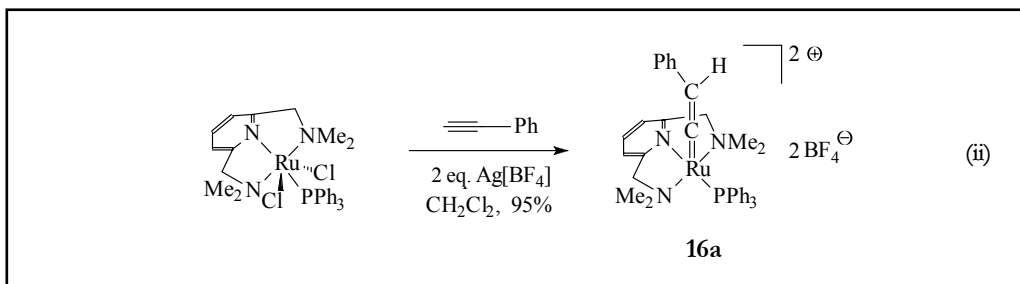
A first set of neutral 16-electron ruthenium vinylidene complexes **10** was easily prepared by Katayama and Ozawa (18) from common terminal alkynes and the arene ruthenium dimer **9**, $[\text{RuCl}_2(\text{p-}$

cymene) $_2$, see Equation (i). Unfortunately, these complexes showed only moderate metathesis activity in processes such as RCM of unsubstituted α,ω -dienes and ROMP of highly strained norbornenes (19).

New cationic 18-electron ruthenium vinylidene complexes, for example, **11**, **12** and **13**, were designed, prepared and screened for their metathesis activity by Grubbs and coworkers (20) but their applicability remained limited to a small range of olefinic substrates.

More effective neutral and cationic 16- and 18-electron ruthenium tridentate complexes, for example, **14**, **15** and **16**, were easily synthesised by van Koten and coworkers (21) by treating the ruthenium complex $[\text{RuCl}_2(\text{NN}'\text{N})(\text{PPh}_3)]$ (where $\text{NN}'\text{N}$ is 2,6-bis[(dimethylamino)methyl]pyridine ligand) with 2 equivalents of $\text{Ag}[\text{BF}_4]$, in CH_2Cl_2 , in the presence of an excess of phenylacetylene (isolated yield 95%), see Equation (ii).



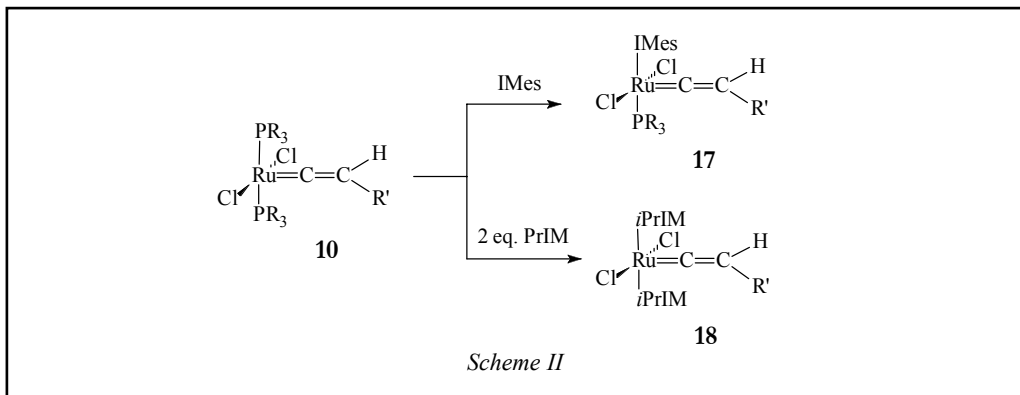
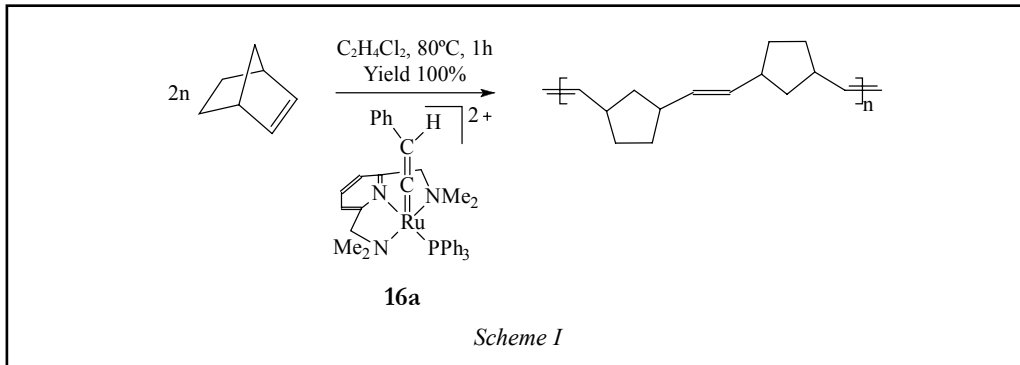


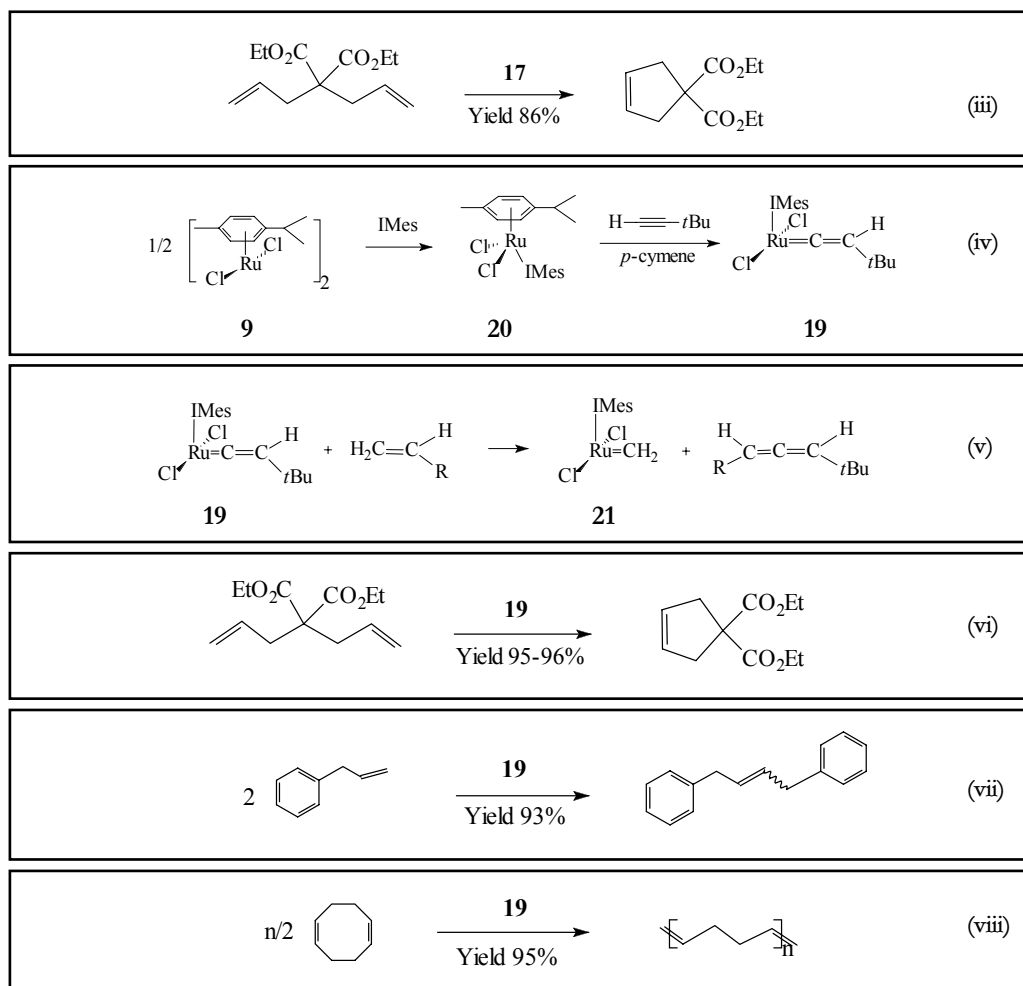
Significantly, a highly active and selective, coordinatively unsaturated, ruthenium 16-electron dicationic complex, **16a**, was found to quantitatively promote ROMP of norbornene to polynorbornene under mild conditions, in the absence of any cocatalyst (Scheme I). The IR, ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the polynorbornene obtained under the above conditions indicated 90–95% *trans* C=C, in accordance with similar results reported previously (12).

Substantial progress was made by Louie and Grubbs through the synthesis of ruthenium vinyl-

idene complexes coordinated with an imidazolyli-dene ligand (22). This class of ruthenium complexes, including complexes with formula **17** [IMes = 1,3-(2',4',6'-trimethylphenyl)imidazol-2-ylidene, R = Cy, R' = *t*Bu] and **18** (*i*PrIM = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene, R' = Ph) has been prepared directly from the bisphosphane ruthenium complex **10** (R = Cy) and free imidazoline carbenes or their salts (Scheme II).

Of these two complexes, **17** and **18**, the ruthenium compound **17**, possessing a mixed ligand system, displayed a substantial metathesis activity





in RCM of diethyl diallylmalonate to substituted cycloolefin (Equation (iii)), although the reaction rate was slower than that with the parent bisimidazolylidene ruthenium carbene complex.

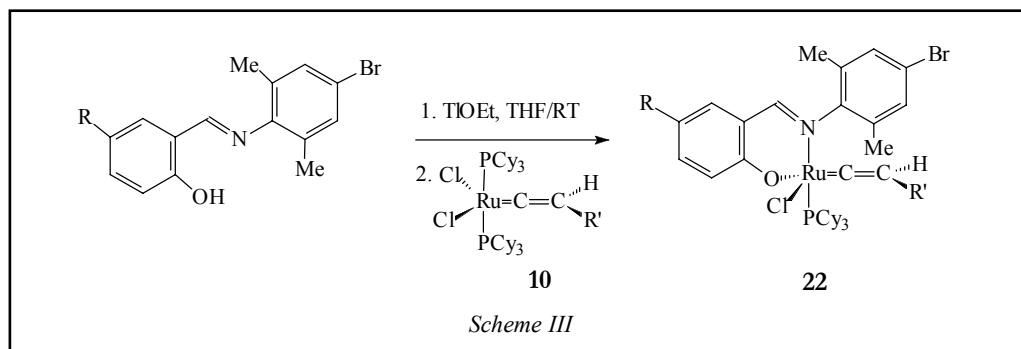
Detailed mechanistic investigations of the ruthenium-catalysed metathesis chemistry strongly indicated that increased ligand dissociation (that is of phosphane) is necessary to accelerate initiation and thereby enhance catalytic activity in this type of reaction. Thus, a phosphane-free coordinatively unsaturated ruthenium vinylidene complex 19 can be formed directly *in situ* from the commercial ruthenium dimer 9, *N*-heterocyclic carbene (IMes) as such or as its salts, and a terminal alkyne (Equation (iv)).

Indeed, the catalytic activity of complex 19

proved to be superior to that of the ruthenium complex 17, supporting the concept of a higher degree of unsaturation in the coordination sphere of the metal promoting catalysis. The pathway for generation of the true catalyst 21 from the catalyst precursor 19, by reaction with an olefin substrate, can be seen in Equation (v).

The particular catalytic behaviour of the pre-catalyst 19 in the RCM of diethyl diallylmalonate, metathesis homodimerisation CM of allyl benzene and ROMP of 1,5-cyclooctadiene is compared in Equations (vi), (vii) and (viii). It is worth noting that the solvent (hexane or tetrahydrofuran) plays an important role in the *in situ* generation of the ruthenium catalyst from these starting materials.

Another interesting array of ruthenium vinyli-



dene complexes, **22**, containing Schiff bases as chelating ligands, was prepared by Verpoort and coworkers (23–26) from ruthenium vinylidene complex **10** and various aromatic salicylaldimines, see Scheme III in which R = H or NO₂ and R' = Ph, *t*Bu or Me₃Si. This class of ruthenium complexes, easily accessible from [RuCl₂(*p*-cymene)]₂, **9**, terminal alkynes and salicylalimine salts, showed good activity in olefin metathesis and enol ester synthesis due to the “one-arm” de-coordination ability of the bidentate Schiff base ligand creating unsaturation in the coordination sphere of the metal. These complexes, **22**, have also been found to serve as excellent pre-catalysts in the RCM of α,ω -dienes and the ROMP of norbornene, substituted norbornene, cyclooctene and polycyclic olefins. Moreover, the related ruthenium vinylidene complexes that contain imidazolin-2-ylidene ligands displayed considerable stability, even for several days at high temperature (24).

Conclusions

Applying ruthenium vinylidene complexes in olefin metathesis reactions (RCM, CM, ROMP) seems to be a convenient alternative to the classical ruthenium bisphosphane catalysts largely employed in organic synthesis and polymer chemistry. Due to the particular steric and electronic environment provided by the ligands, some of the vinylidene ruthenium complexes exhibit remarkable activity and selectivity. They are readily accessible, only requiring commercially available starting materials for their synthesis. Importantly, when generated *in situ*, coordinatively unsaturated

complexes displayed considerably high RCM activity. Combining vinylidene ligands with other specific ligands (such as imidazolyidene, Schiff bases, etc.), in the coordination sphere of the ruthenium core, allows further access to highly efficient ruthenium metathesis pre-catalysts.

References

- 1 V. Dragutan, I. Dragutan and A. T. Balaban, *Platinum Metals Rev.*, 2001, 45, (4), 155
- 2 (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
- 3 (a) R. R. Schrock and A. H. Hoveyda, *Angew. Chem. Int. Ed.*, 2003, 42, 4592; (b) C. J. Schaverien, R. R. Schrock and J. C. Dewan, *J. Am. Chem. Soc.*, 1986, 108, 2771; (c) R. R. Schrock, D. T. DePue, J. Feldman, C. J. Schaverien, J. C. Dewan and A. H. Liu, *J. Am. Chem. Soc.*, 1987, 109, 1423
- 4 (a) R. O'Dell, D. H. McConville, G. H. Hofmeister and R. R. Schrock, *J. Am. Chem. Soc.*, 1994, 116, 3414; (b) D. H. McConville, J. R. Wolf and R. R. Schrock, *J. Am. Chem. Soc.*, 1993, 115, 4413
- 5 (a) R. H. Grubbs (ed.), “Handbook of Metathesis”, Wiley-VCH, Weinheim, 2003; (b) P. Schwab, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1996, 118, 100; (c) B. M. Novak and R. H. Grubbs, *J. Am. Chem. Soc.*, 1988, 110, 7542
- 6 (a) S. T. Nguyen, L. K. Johnson, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1992, 114, 3974; (b) S. T. Nguyen, R. H. Grubbs and J. W. Ziller, *J. Am. Chem. Soc.*, 1993, 115, 9858
- 7 (a) T. R. Belderrain and R. H. Grubbs, *Organometallics*, 1997, 16, 4001; (b) T. E. Wilhelm, T. R. Belderrain, S. N. Brown and R. H. Grubbs, *Organometallics*, 1997, 16, 3867
- 8 J. Wolf, W. Stuer, C. Grunwald, H. Werner, P. Schwab and M. Schulz, *Angew. Chem. Int. Ed.*, 1998, 37, 1124

- 9 S. Chang, L. R. Jones, C. Wang, L. M. Henling and R. H. Grubbs, *Organometallics*, 1998, 17, 3460
- 10 (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
- 11 (a) B. De Clercq and F. Verpoort, *J. Mol. Catal. A: Chem.*, 2002, 180, 67; (b) T. Opstal and F. Verpoort, *Angew. Chem. Int. Ed.*, 2003, 42, 2876
- 12 T. Weskamp, W. C. Schattenmann, M. Spiegler and W. A. Herrmann, *Angew. Chem. Int. Ed.*, 1998, 37, 2490
- 13 J. K. Huang, E. D. Stevens, S. P. Nolan and J. L. Petersen, *J. Am. Chem. Soc.*, 1999, 121, 2674
- 14 (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
- 15 (a) J. P. A. Harrity, D. S. La, M. S. Visser and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1998, 120, 2343; (b) J. S. Kingsbury, J. P. A. Harrity, P. J. Bonetatebus and A. H. Hoveyda, *J. Am. Chem. Soc.*, 1999, 121, 791
- 16 (a) A. Demonceau, A. W. Stumpf, E. Saive and A. F. Noels, *Macromolecules*, 1997, 30, 3127; (b) A. W. Stumpf, E. Saive, A. Demonceau and A. F. Noels, *J. Chem. Soc., Chem. Commun.*, 1995, 1127
- 17 (a) A. Hafner, A. Muhlebach and P. A. Van der Schaaf, *Angew. Chem. Int. Ed.*, 1997, 36, 2121; (b) A. Furstner and L. Ackermann, *Chem. Commun.*, 1999, (1), 95; (c) M. Picquet, C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 1998, (20), 2249
- 18 (a) H. Katayama and F. Ozawa, *Organometallics*, 1998, 17, 5190; (b) H. Katayama and F. Ozawa, *Chem. Lett.*, 1998, 27, (1), 67
- 19 C. Bruneau and P. H. Dixneuf, *Acc. Chem. Res.*, 1999, 32, 311
- 20 M. S. Sanford, L. M. Henling and R. H. Grubbs, *Organometallics*, 1998, 17, 5384
- 21 I. del Río and G. van Koten, *Tetrahedron Lett.*, 1999, 40, 1401
- 22 J. Louie and R. H. Grubbs, *Angew. Chem. Int. Ed.*, 2001, 40, 247
- 23 T. Opstal and F. Verpoort, *J. Mol. Catal. A: Chem.*, 2003, 200, 49
- 24 T. Opstal and F. Verpoort, *Synlett*, 2002, 935
- 25 T. Opstal and F. Verpoort, *Tetrahedron Lett.*, 2002, 43, 9259
- 26 T. Opstal and F. Verpoort, *Synlett*, 2003, 314

The Authors

Valerian Dragutan is a Senior Researcher at the Institute of Organic Chemistry of the Romanian Academy. His research interests are homogeneous catalysis by transition metals and Lewis acids; olefin metathesis and ROMP of cycloolefins; bioactive organometallic compounds; and mechanisms and stereochemistry of reactions in organic and polymer chemistry.



Ileana Dragutan is a Senior Researcher at the Institute of Organic Chemistry of the Romanian Academy. Her interests are in sterically hindered amines, syntheses of olefinic monomers via olefin metathesis, stable organic free radicals as spin probes for ESR of organised systems and membrane bioenergetics. She is also interested in transition metal complexes with free radical ligands.

