

Practical New Strategies for Immobilising Ruthenium Alkylidene Complexes: Part II

IMMOBILISATION VIA SCHIFF BASES, ARENES, AND ANIONIC AND TAGGED LIGANDS

By Ileana Dragutan* and Valerian Dragutan**

Institute of Organic Chemistry "Costin D. Nenitescu", Romanian Academy, 202B Spl. Independentei, PO Box 35-108, 060023 Bucharest, Romania; E-mail: *idragutan@yahoo.com; **vdragutan@yahoo.com

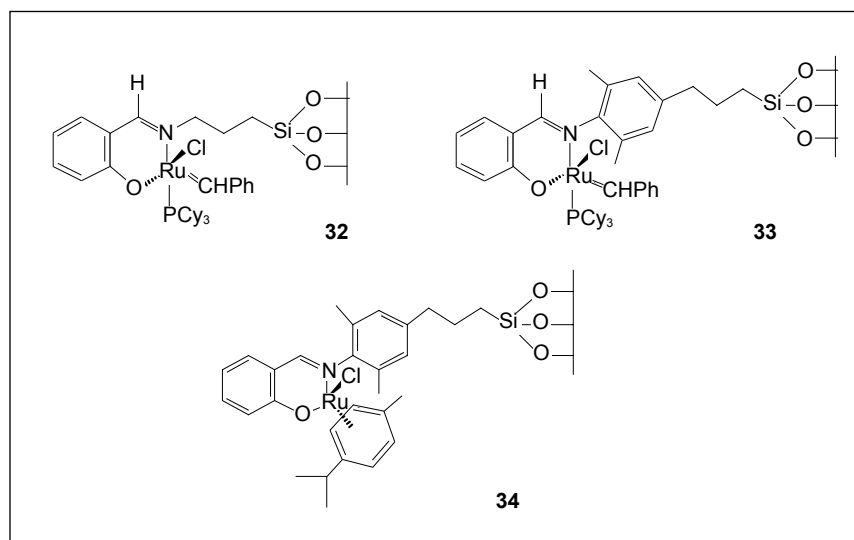
Following Part I, previously published in this Journal (1), the present paper discusses new routes for immobilisation of ruthenium alkylidene complexes through their ligands. Systematically addressed as suitable participants for immobilisation are Schiff bases, arenes, anionic ligands and specifically tagged (ionic liquid tag, fluoro tag) substituents.

1. Immobilisation *via* the Schiff Base Ligand

Detailed studies by Verpoort *et al.* (2–5) have been directed towards the design, synthesis and progressive development of homogeneous and immobilised *N,O*-bidentate ruthenium complexes bearing Schiff base ancillary ligands, as an attractive alternative to *N*-heterocyclic carbenes (NHCs) (6–15) for applications in ring-closing metathesis (RCM), Kharasch addition, ring-opening metathesis polymerisation (ROMP), atom transfer radical polymerisation (ATRP) and vinylation reactions (16, 17). Structurally robust and effective supported catalysts have been devised (for example,

32–34) in which the homogeneous Ru complex was anchored to the carrier by a non-labile tether, bound to the Schiff base ligand yet imposing little or no steric hindrance at the reactive site (18–20) (Scheme I). (Structures 1–31 are given in Part I (1).)

From all potential inorganic supports, the mesoporous silica gel MCM-41 (mobile crystalline material) was selected as most appropriate because of its advantages (21–24): (i) retention of a constant exposed surface area, in contrast to conventional polymer beads that typically swell and shrink variably in different media, resulting in unpredictable effects on the catalyst activity; (ii) the greater robustness of MCM-41 than organic

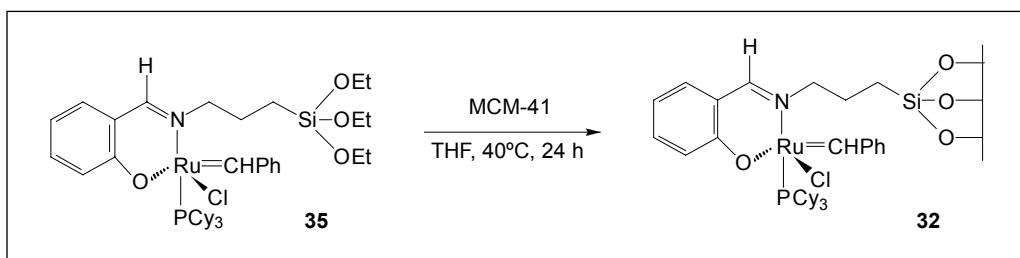


Scheme I
Immobilised
Schiff base
ruthenium
complexes 32–34

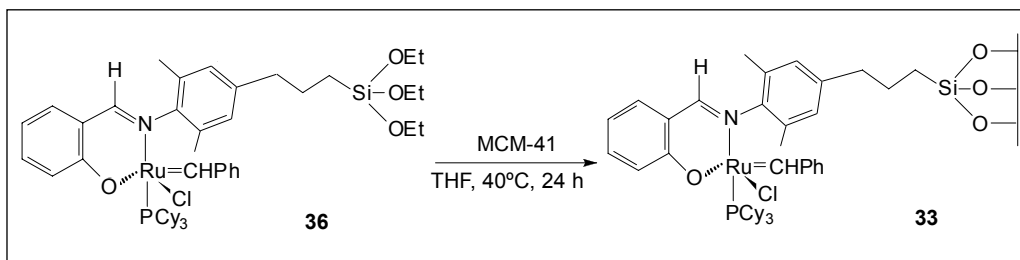
polymers and inorganic solids and, particularly for types with a structured surface, a considerably larger area; (iii) anchoring the active catalytic species on a larger surface area would help to overcome the activity loss (due to an inefficient interfacial mass transfer between the liquid phase and the solid), currently encountered in passing from homogeneous to heterogeneous catalysis; (iv) the MCM-41 solid support consists of an ordered array of hexagonal channels with the pore diameter in the mesoporous region, allowing lower resistance to diffusion of the reactant molecules accessing the metal active sites that are located within the channels (*vs.* nanoporous zeolite supports).

The methodology followed in preparing the MCM-41 supported catalyst systems 32–34 implies

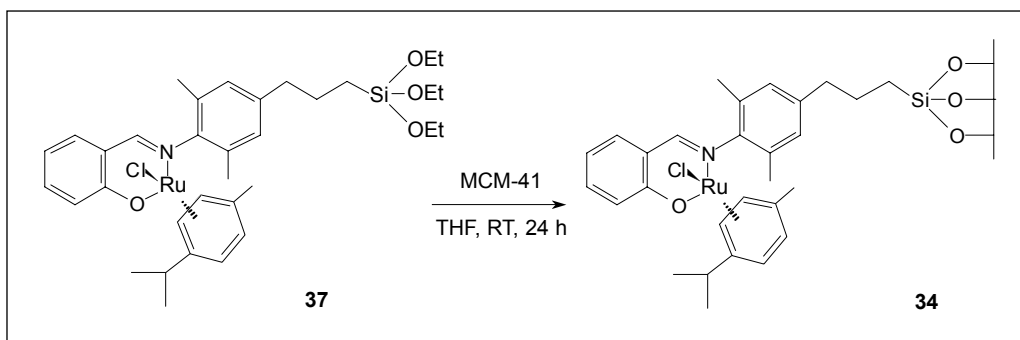
the prior synthesis of the immobilised Ru precursors 35–37 endowed with an anchorable tris(alkoxy)silyl functionality, followed by tethering onto the mesoporous silica surface (Schemes II–IV). Chemical tethering, as employed for 32–34, is one of the best strategies for anchoring a homogeneous catalyst to a solid support, in view of its minimising leaching behaviour. Structural measurements on the above immobilised complexes carried out by X-ray diffraction (XRD), N₂-adsorption analysis, Raman spectroscopy, X-ray fluorescence (XRF) spectroscopy and solid-state nuclear magnetic resonance (NMR) spectroscopy evidenced that in all cases, the homogeneous catalyst is anchored to MCM-41 *via* a spacer having two or three covalent bonds.



Scheme II Synthesis of immobilised ruthenium complex 32



Scheme III Synthesis of immobilised ruthenium complex 33



Scheme IV Synthesis of immobilised ruthenium complex 34

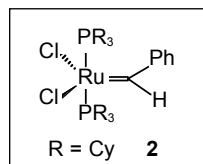
2. Immobilisation *via* the Arene Ligand

Arene ligands coordinated to Ru have also been employed to immobilise homogeneous complexes onto solid supports. This approach has been used by Akiyama and Kobayashi (25) to prepare the polystyrene-bound Ru-allenylidene complex **38** (Scheme V). Surprisingly, catalyst **38** showed wide-ranging activity, for example in RCM, hydrogenation and cyclisation reactions of olefins.

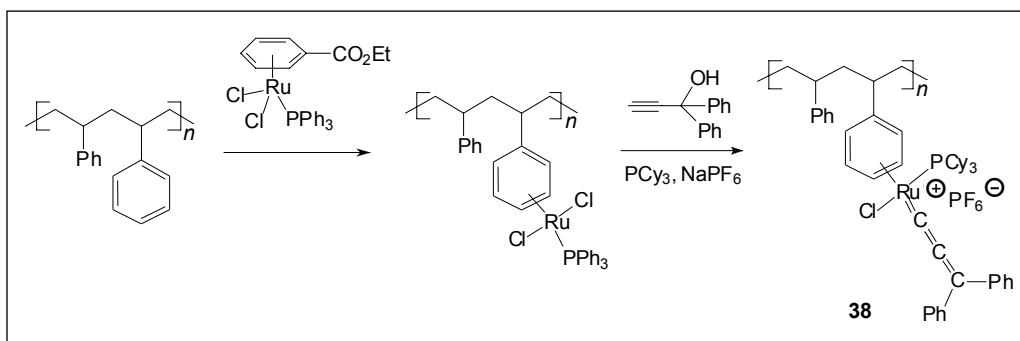
3. Immobilisation *via* Anionic Ligands

A totally different protocol for immobilisation of Ru complexes has been devised by Mol *et al.* (26). Taking advantage of the capacity of anionic ligands to create strong bonds with Ru which remain intact throughout the entire catalytic cycle, the authors used such ligands to generate a permanent covalent link between the Ru centre and the

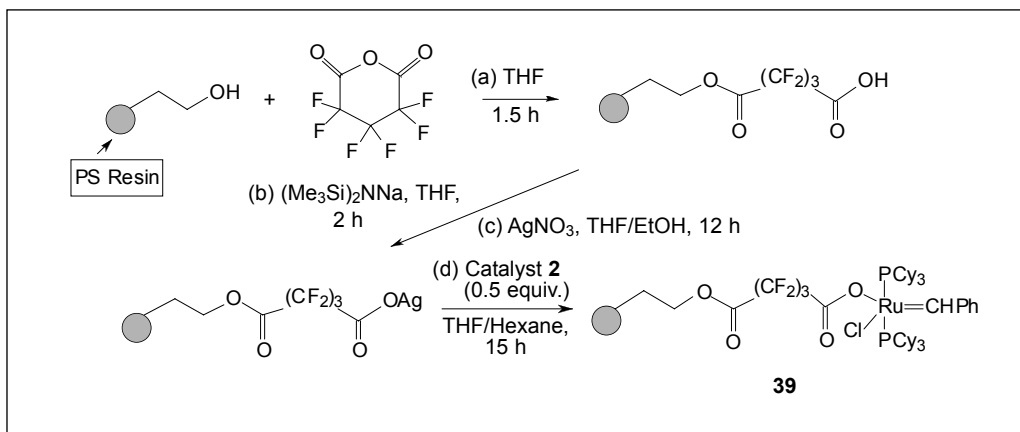
support. Using this method, they replaced the chloride ligand from the first-generation Grubbs catalyst $\text{Cl}_2(\text{PCy}_3)_2\text{Ru}(\text{=CHPh})$, **2**, with a carboxylate group attached to a polystyrene (PS) resin *via* a strongly electron-withdrawing tether, finally gaining access to the immobilised Ru complex **39** (Scheme VI).



Complex **39** was very active and versatile in self-metathesis of internal olefins (*trans*-decene and methyl oleate) and RCM of α,ω -dienes (diethyl diallylmalonate); it could easily be separated from the reaction products, resulting in virtual freedom from Ru contamination. Additionally, catalyst **39** could be recycled for at least six reaction cycles and



Scheme V Synthesis of immobilised ruthenium arene complex **38**



Scheme VI Synthesis of immobilised ruthenium benzylidene complex **39** ($(\text{Me}_3\text{Si})_2\text{NNa}$ = sodium bis(trimethylsilyl)amide)

be stored for more than six months, under nitrogen, retaining its initial activity intact. Functionalised, partially fluorinated Hoveyda and Grubbs-Hoveyda catalysts supported on silica gel (SG 60), were obtained by Blechert *et al.* (27) from their homogeneous counterparts; these catalysts performed conventional RCM with activity comparable to that of similar heterogeneous systems (28–31).

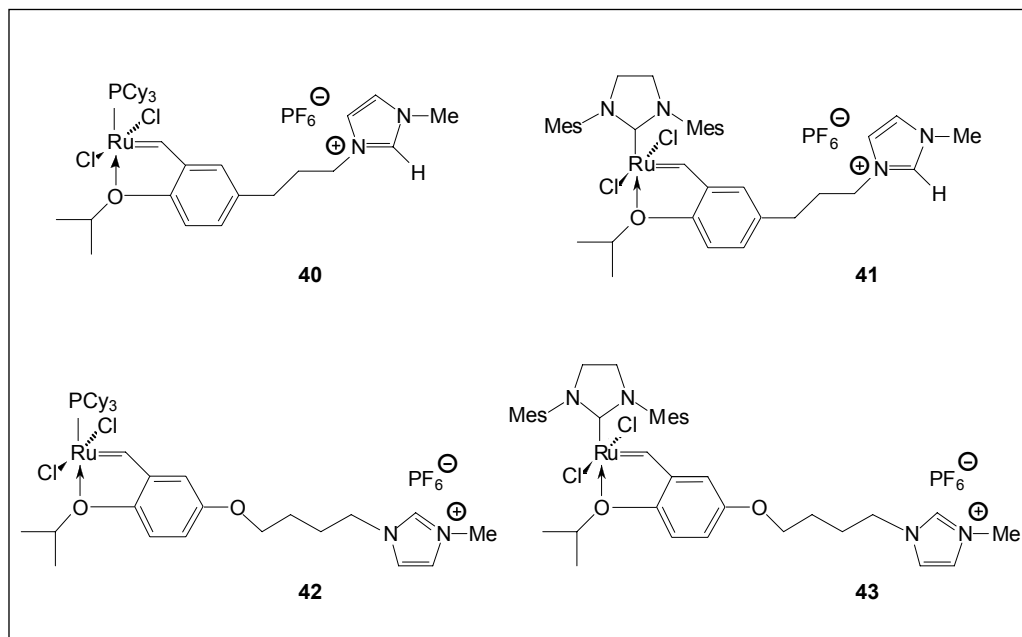
4. Tagged Ruthenium Alkylidene Complexes

A fairly recent technique for non-covalent immobilisation of homogeneous Ru metathesis catalysts onto liquid supports focuses on the advantages provided by room temperature ionic liquids (RTILs). Applied first in reactions involving RTILs merely as reaction media, in particular in earlier work by Dixneuf *et al.* using allenylidene-Ru precatalysts (32–34), the technique was further extended to ionic liquid-tagged catalyst precursors. Thus, several NHC-Ru complexes, in particular the IL-tagged counterparts of the Hoveyda or Hoveyda-Grubbs catalysts, such as 40 (35), 41 (36, 37) and 42 (38) or 43 (39), have been used with improved results in various metathesis reactions

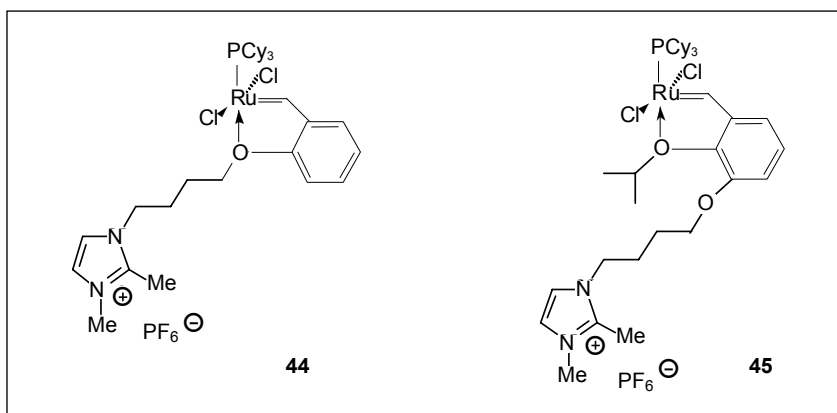
conducted in ILs or IL/organic solvent mixtures (biphasic catalysis) (Scheme VII). Complexes 40–43 demonstrated convenient recyclability, combined with high reactivity and extremely low residual Ru levels in the products.

Two new Hoveyda-type catalysts, containing an IL-tag linked either to the *ortho*-oxygen substituent (44) or to the *meta*-position (45) of the styrenylidene ligand have recently been reported (40). In catalyst 44, the IL-tag is innovatively attached through the Ru-chelated oxygen atom. The catalysts were evaluated for RCM of *N,N*-diallyltosylamide and dimethyldiallylmalonate, conducted in an IL medium, showing moderate recyclability, yet good activity for the first cycle (Scheme VIII).

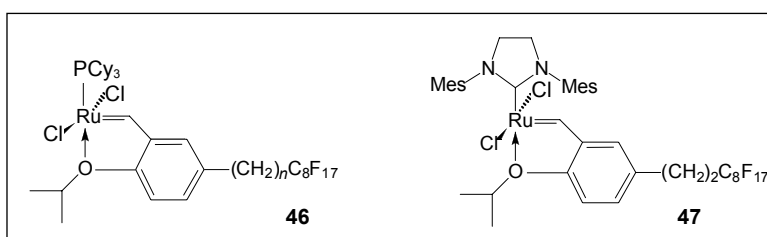
As an alternative for tagging Ru complexes, the 'light fluoruous' versions, 46 and 47, of the first- and second-generation Grubbs-Hoveyda metathesis catalysts have also been proposed (41) (Scheme IX). Catalysts 46 and 47 exhibit the expected reactivity profile, are readily recovered from reaction mixtures by fluoruous solid-phase extraction, and can routinely be recycled five or more times. They can be used in a stand-alone fashion, or supported on fluoruous silica gel.



Scheme VII Representative ionic liquid-tagged PCy₃- and NHC-ruthenium complexes 40–43



Scheme VIII
Representative
ionic liquid-tagged
PCy₃-ruthenium
complexes 44
and 45



Scheme IX Fluoro-tagged
first- and second-
generation Grubbs-
Hoveyda catalysts
46 and 47

5. Conclusion

As described here and in Part I (1), immobilisation of well defined homogeneous Ru alkylidene complexes by means of their anionic and coordinative ligands is now a readily accessible, efficient technique, providing active catalysts for metathesis reactions. Immobilisation is achieved on a broad range of solid supports ranging from organic polymers (polystyrene, vinyl polystyrene) to inorganic matrices (silica, mesoporous silica gel, zeolites) and the fashionable ionic liquids. So far immobilisation through NHCs appears to be the most popular approach. Synthetic applications of immobilised catalysts in the metathesis field

provide important advantages, among which the most valued are a high catalytic activity and stereoselectivity, simpler, clean and recyclable processes, and low impurity content in the reaction products. Future scale-up to industrial exploitation of the immobilised Ru catalysts is to be envisaged, allowing promotion of sustainable technologies within the framework of ‘green’ chemistry protocols. An attractive aspect of immobilisation is that it holds great promise for elaborate syntheses of fine chemicals, pharmaceuticals, nutraceuticals and speciality polymers, where a very low residual metal content from the catalyst is a requirement.

References

- 1 I. Dragutan and V. Dragutan, *Platinum Metals Rev.*, 2008, 52, (2), 71
- 2 R. Drozdak, B. Allaert, N. Ledoux, I. Dragutan, V. Dragutan and F. Verpoort, *Coord. Chem. Rev.*, 2005, 249, (24), 3055
- 3 B. Allaert, N. Dieltiens, C. Stevens, R. Drozdak, I. Dragutan, V. Dragutan and F. Verpoort, in “Metathesis Chemistry: From Nanostructure Design to Synthesis of Advanced Materials”, eds. Y. Imamoglu and V. Dragutan, NATO Science Series II: Mathematics, Physics and Chemistry, Vol. 243, Springer Verlag, Berlin, Heidelberg, 2007, pp. 39–78
- 4 R. Drozdak, N. Ledoux, B. Allaert, I. Dragutan, V. Dragutan and F. Verpoort, *Cent. Eur. J. Chem.*, 2005, 3, (3), 404
- 5 R. Drozdak, B. Allaert, N. Ledoux, I. Dragutan, V. Dragutan and F. Verpoort, *Adv. Synth. Catal.*, 2005, 347, (14), 1721
- 6 W. A. Herrmann, *Angew. Chem. Int. Ed.*, 2002, 41, (8), 1290
- 7 “Handbook of Metathesis”, ed. R. H. Grubbs, in 3 vols., Wiley-VCH, Weinheim, Germany, 2003, Vol. I
- 8 V. Dragutan, I. Dragutan and A. Demonceau, *Platinum Metals Rev.*, 2005, 49, (3), 123
- 9 I. Dragutan, V. Dragutan, L. Delaude and A. Demonceau, *ARKIVOC*, 2005, (x), 206

- 10 "N-Heterocyclic Carbenes in Synthesis", ed. S. P. Nolan, Wiley-VCH, Weinheim, 2006
- 11 "N-Heterocyclic Carbenes in Transition Metal Catalysis", ed. F. Glorius, Topics in Organometallic Chemistry, Vol. 21, Springer-Verlag, Berlin, 2007
- 12 S. Díez-González and S. P. Nolan, *Coord. Chem. Rev.*, 2007, 251, (5–6), 874
- 13 "Metathesis Chemistry: From Nanostructure Design to Synthesis of Advanced Materials", eds. Y. Imamoglu and V. Dragutan, NATO Science Series II: Mathematics, Physics and Chemistry, Vol. 243, Springer Verlag, Berlin, Heidelberg, 2007
- 14 V. Dragutan, I. Dragutan, L. Delaude and A. Demonceau, *Coord. Chem. Rev.*, 2007, 251, (5–6), 765
- 15 I. Dragutan, V. Dragutan, L. Delaude, A. Demonceau and A. F. Noels, *Rev. Roumaine Chim.*, 2007, 52, (11), 1013
- 16 V. Dragutan and I. Dragutan, *J. Organomet. Chem.*, 2006, 691, (24–25), 5129
- 17 V. Dragutan and F. Verpoort, *Rev. Roumaine Chim.*, 2007, 52, (8–9), 905
- 18 K. Melis, D. De Vos, P. Jacobs and F. Verpoort, *J. Mol. Catal. A: Chem.*, 2001, 169, (1–2), 47
- 19 H. I. Beerens, W. Wang, L. Verdonck and F. Verpoort, *J. Mol. Catal. A: Chem.*, 2002, 190, (1–2), 1
- 20 B. De Clercq, T. Opstal, K. Melis and F. Verpoort, in "Ring Opening Metathesis Polymerisation and Related Chemistry: State of the Art and Visions for the New Century", eds. E. Khosravi and T. Szymanska-Buzar, NATO Science Series II: Mathematics, Physics and Chemistry, Vol. 56, Kluwer Academic Publishers, Dordrecht, The Netherlands, 2002, p. 451
- 21 "Heterogeneous Catalysis and Fine Chemicals IV", eds. H. U. Blaser, A. Baiker and R. Prins, Studies in Surface Science and Catalysis, Vol. 108, Elsevier, Amsterdam, 1997
- 22 S. Ernst, R. Gläser and M. Selle, in "Progress in Zeolite and Microporous Materials, Proceedings of the 11th International Zeolite Conference", eds. H. Chon, S. Kilhm and Y. S. Uh, Studies in Surface Science and Catalysis, Vol. 105, Part 2, Elsevier, Amsterdam, 1997, pp. 1021–1028
- 23 B. De Clercq, F. Lefebvre and F. Verpoort, *New J. Chem.*, 2002, 26, (9), 1201
- 24 B. De Clercq, F. Lefebvre and F. Verpoort, *Appl. Catal. A: Gen.*, 2003, 247, (2), 345
- 25 R. Akiyama and S. Kobayashi, *Angew. Chem. Int. Ed.*, 2002, 41, (14), 2602
- 26 P. Nieczypor, W. Buchowicz, W. J. N. Meester, F. P. J. T. Rutjes and J. C. Mol, *Tetrahedron Lett.*, 2001, 42, (40), 7103
- 27 K. Vehlou, S. Maechling, K. Köhler and S. Blechert, *J. Organomet. Chem.*, 2006, 691, (24–25), 5267
- 28 D. Fischer and S. Blechert, *Adv. Synth. Catal.*, 2005, 347, (10), 1329
- 29 L. Li and J.-I. Shi, *Adv. Synth. Catal.*, 2005, 347, (14), 1745
- 30 X. Elias, R. Pleixats, M. Wong Chi Man and J. J. E. Moreau, *Adv. Synth. Catal.*, 2006, 348, (6), 751
- 31 M. R. Buchmeiser, *New J. Chem.*, 2004, 28, (5), 549
- 32 D. Sémeril, H. Olivier-Bourbigou, C. Bruneau and P. H. Dixneuf, *Chem. Commun.*, 2002, (2), 146
- 33 S. Csíhony, C. Fischmeister, C. Bruneau, I. T. Horváth and P. H. Dixneuf, *New J. Chem.*, 2002, 26, (11), 1667
- 34 R. Castarlenas, C. Fischmeister, C. Bruneau and P. H. Dixneuf, *J. Mol. Catal. A: Chem.*, 2004, 213, (1), 31
- 35 N. Audic, H. Clavier, M. Mauduit and J.-C. Guillemin, *J. Am. Chem. Soc.*, 2003, 125, (31), 9248
- 36 H. Clavier, N. Audic, M. Mauduit and J.-C. Guillemin, *Chem. Commun.*, 2004, (20), 2282
- 37 H. Clavier, N. Audic, J.-C. Guillemin and M. Mauduit, *J. Organomet. Chem.*, 2005, 690, (15), 3585
- 38 Q. Yao and Y. Zhang, *Angew. Chem. Int. Ed.*, 2003, 42, (29), 3395
- 39 Q. Yao and M. Sheets, *J. Organomet. Chem.*, 2005, 690, (15), 3577
- 40 C. Thurier, C. Fischmeister, C. Bruneau, H. Olivier-Bourbigou and P. H. Dixneuf, *J. Mol. Catal. A: Chem.*, 2007, 268, (1–2), 127
- 41 M. Matsugi and D. P. Curran, *J. Org. Chem.*, 2005, 70, (5), 1636

The Authors



Ileana Dragutan is a Senior Researcher at the Institute of Organic Chemistry "Costin D. Nenitescu" of the Romanian Academy. Her interests lie in the synthesis of stable organic radicals, EPR spin probe applications in organised systems and biological environments, late transition metal complexes with radical ligands, ruthenium catalysis in organic and polymer chemistry, iminocyclitols and prostaglandin-related prodrugs.



Valerian Dragutan is a Senior Researcher at the Institute of Organic Chemistry "Costin D. Nenitescu" 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. He is a member of several national and international chemical societies, and has contributed significant books, book chapters, patents and papers to the scientific literature.