Pergamon

Tetrahedron Letters 44 (2003) 8421–8425

TETRAHEDRON LETTERS

Kharasch addition catalysed by half-sandwich ruthenium complexes. Enhanced activity of ruthenacarboranes

Oscar Tutusaus,[a,†] Sébastien Delfosse,[b] Albert Demonceau,[b,]* Alfred F. Noels,[b] Clara Viñas[a,]* and Francesc Teixidor[a]

[a]*Institut de Ciència de Materials de Barcelona, CSIC, Campus de la U.A.B., 08193 Bellaterra, Spain*

[b]*Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart-Tilman (B.6a), B-4000 Liège, Belgium*

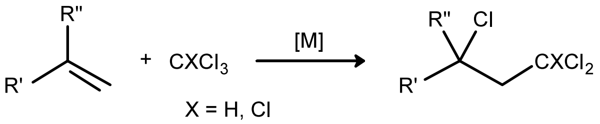
Received 5 August 2003; revised 30 August 2003; accepted 12 September 2003

Abstract—Ruthenium complexes of the type $[RuH(\eta^5\text{-}CB)(PPh_3)_2]$ {CB is a monoanionic charge-compensated carborane ligand such as $[9\text{-}SR_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$ and $[9\text{-}SR_2\text{-}7\text{-}CH_3\text{-}7,8\text{-}C_2B_9H_9]^-$} efficiently catalyse the Kharasch addition of CCl_4 across olefins and, with maximum total turnover numbers of 9000 and initial turnover frequencies of 1900 h^{-1} at 40°C, highly surpass their Ru–Cp$^{\#}$ analogues in these reactions.

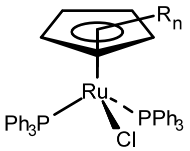
Cyclopentadienyl and derivatives are ubiquitous ligands in organometallic chemistry. In the period between the discovery of ferrocene in 1951[1] and the development of metallocene catalysts for the polymerisation of olefins,[2] a wide variety of useful transition–metal complexes has been discovered. Besides the classic cyclopentadienyl $[(\eta^5\text{-}C_5H_5)^-$, $Cp^-]$ and pentamethylcyclopentadienyl $[(\eta^5\text{-}C_5Me_5)^-$, $Cp^{*-}]$ ligands, a great number of suitably tailored indenyl and fluorenyl derivatives have been synthesised with the aim of designing more efficient catalyst systems.

In the last 30 years, Hawthorne has developed the coordination chemistry of dicarbollide ligands $[(7,8\text{-}C_2B_9H_{11})^{2-}$ and $(7,9\text{-}C_2B_9H_{11})^{2-}]$, which are isolobal to cyclopentadienyl and derivatives $(Cp^{\#-})$.[3] However, apart from olefin hydrogenation,[4] metallacarboranes have scarcely been employed as catalysts. In our ongoing efforts to investigate the potential of metallacarboranes in homogeneous catalysis,[4,5] we turned our attention to the addition of alkyl halides to olefins (the so-called Kharasch reaction or atom transfer radical addition (ATRA), Scheme 1),[6] which has seen an incredible renaissance in the last few years as the result of the development of atom transfer radical polymerisation (ATRP).[7,8]

To this end, ruthenium–carborane complexes **1**–**6** (see Scheme 3) were synthesised, in which the uninegative carborane ligands, $[9\text{-}SR_2\text{-}7,8\text{-}C_2B_9H_{10}]^-$, were obtained upon substitution of one terminal open face hydrogen of the dicarbollide dianion $[(C_2B_9H_{11})^{2-}]$ by an SR_2 group.[9] Contrary to the dicarbollide dianions, the monoanionic carborane ligands (also known as charge-compensated carborane ligands) allow for proper comparisons with their $(C_5H_{5-n}R_n)^-$ analogues in terms of steric and electronic effects, when they are investigated in organometallic chemistry and in homogeneous catalysis.



Scheme 1. Kharasch addition of polyhalogenated compounds to olefins.



Scheme 2. Structure of $[RuCl(Cp^{\#})(PPh_3)_2]$ complexes.

Keywords: catalysis; olefins; radicals and radical reactions; ruthenium and compounds.

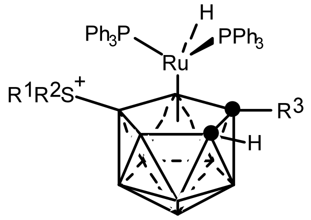
* Corresponding authors. Fax: +32/(0)4366 3497 (A.D.); fax: +34/(0)93 580 5729 (C.V.); e-mail: A.Demonceau@ulg.ac.be; clara@icmab.es

[†] O. Tutusaus is enrolled in the U.A.B. PhD Program.

0040-4039/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2003.09.100

Herein, we wish to report that complexes **1**–**6** display remarkable activity in Kharasch chemistry,[10] and surpass $[RuCl(Cp^{\#})(PPh_3)_2]$ ($Cp^{\#}$ = Cp* and indenyl, Scheme 2) which have so far set the standard in the field.[11]

First, we explored the addition of carbon tetrachloride to methyl methacrylate (MMA) at 40°C, under standardised conditions,[8b,11] and found that ruthenacarboranes **1**–**4** were equipotent catalysts. MMA conversion was complete and adduct formation was almost quantitative within a few hours (Table 1). However, analysis of the kinetics of the reactions revealed that complexes **1** and **2** were more active than their derivatives, **5** and **6**, in which the carborane moiety possesses a methyl group bonded *exo*-cluster to a carbon atom (Fig. 1). Under the same conditions, a quantitative conversion of styrene into (1,3,3,3-tetrachloropropyl)benzene was also obtained in the presence of complexes **1**–**6** (Table 1).



	R^1, R^2	R^3
1	CH_3	H
2	C_2H_5	H
3	C_2H_5, C_6H_5	H
4	$(CH_2)_4$	H
5	CH_3	CH_3
6	C_2H_5	CH_3

Scheme 3. Complexes **1**–**6**.

Table 1. Kharasch addition of carbon tetrachloride to representative olefins catalysed by ruthenacarboranes **1**–**6**[a]

Complex	Substrate conversion (%)/Kharasch addition (%)[b]			
	n-Butyl acrylate	Methyl methacrylate	Styrene	1-Decene
1	70/47	99/95	100/99	55/52
2	70/46	99/95	100/99	52/48
3	72/58	99/99	100/99	66/58
4	76/47	99/99	100/99	57/51
5	75/25	97/89	100/99	50/43
6	75/23	96/89	100/99	41/37

[a] *Reaction conditions*. Prior to use, the reagents, the solvent (toluene) and the internal standard (dodecane) were dried using well established procedures, distilled and kept under nitrogen at −20°C. The catalyst (0.03 mmol) was dissolved in toluene (1 mL) and subsequently added through a septum to the solution of alkene (9 mmol), CCl_4 (13 mmol), dodecane (0.25 mL) in toluene (3 mL). Temperature, 40°C. Reaction time, 16 h.

[b] Conversion and yield are based on the alkene, and determined by GC using dodecane as internal standard.

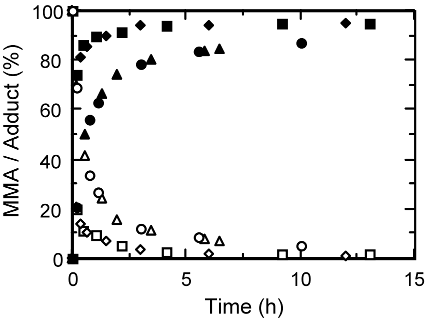


Figure 1. Methyl methacrylate (□, ◇, △, ○) and adduct (■, ◆, ▲, ●) versus time for the Kharasch addition of carbon tetrachloride to MMA catalysed by complexes **1** (□, ■), **2** (◇, ◆), **5** (△, ▲), and **6** (○, ●), at 40°C. Reaction conditions are the same as in Table 1.

n-Butyl acrylate, on the other hand, was less prone to undergo Kharasch addition of carbon tetrachloride than methyl methacrylate and styrene (Table 1). Indeed, a 70–75% conversion and a 25–60% yield (depending on the catalyst used) of the Kharasch adduct were obtained after 16 h at 40°C. In all cases, higher oligomers also formed and accounted for the mass balance. As expected, 1-decene was the least reactive substrate among those under study (Fig. 2), and only moderate yields (35–60%) were obtained after 16 h. Prolonged reaction times (up to 80–100 h), however, gave around 75–80% conversion and 70–75% yield. With 1-decene, complex **3** showed the highest catalytic activity, giving the desired adduct (1,1,1,3-tetrachloroundecane) in 58% yield after 16 h. Notably, all reactions catalysed by complexes **1** and **2** were faster than those catalysed by their methyl-substituted derivatives, **5** and **6**.

In light of these results, it became of interest to compare the activity of complexes **1**–**6** with those of $[RuCl(Cp^{\#})(PPh_3)_2]$ ($Cp^{\#}$ = Cp* and indenyl), the most efficient ATRA ruthenium-based catalysts reported so

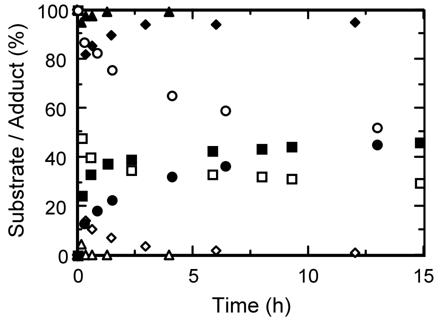


Figure 2. Substrate (□, ◇, △, ○) and adduct (■, ◆, ▲, ●) versus time for the Kharasch addition of carbon tetrachloride to *n*-butyl acrylate (□, ■), methyl methacrylate (◇, ◆), styrene (△, ▲), and 1-decene (○, ●), catalysed by complex **2** at 40°C. Reaction conditions are the same as in Table 1.

far (Fig. 3).[11] Interestingly, **1**–**6** exhibited reaction rates that were much faster than the rates determined in our earlier investigation using [RuCl(Cp$^{\#}$)(PPh$_3$)$_2$] as the catalysts.[11] With these encouraging results in hand, we then aimed to decrease the catalyst loading in order to determine the limitations of catalysts **1**–**6**. To this end, complex **3** was selected from among those investigated. The rate profiles corresponding to the addition of CCl$_4$ to methyl methacrylate for representative catalyst loadings are shown in Figure 4. They revealed that the Kharasch addition remained quantitative for MMA/catalyst molar ratios up to 3000. Beyond this value, the addition was no longer quantitative, and oligomerisation became competitive with monoaddition. The kinetic data also allowed us to estimate the maximum (unoptimised) turnovers. Thus, with methyl methacrylate, the maximum total turnover number (TTN) and initial turnover frequency (TOF) reached 4200 and 1900 h^{-1}, respectively. Likewise, with styrene, a maximum TTN of 9000 and TOF of 1500 h^{-1} were measured, as opposed to a maximum TTN of 1600–1700 and TOF of 400 h^{-1} obtained with [RuCl(Cp$^{\#}$)(PPh$_3$)$_2$] (Cp$^{\#}$ = Cp* or indenyl).[11] In addition, the TTN for **3** was also higher than that obtained with the pincer N,C,N-chelating aryldiaminonickel complex, the most efficient ATRA catalyst hitherto reported, with a TTN of 1730 and a TOF of 400 h^{-1} for MMA.[6a,12]

Encouraged by these findings, we then investigated the reaction of chloroform, a much less reactive halocarbon than carbon tetrachloride, with methyl methacrylate and styrene. Preliminary results of these experiments are outlined in Table 2. Unfortunately, the Kharasch addition of CHCl$_3$ to MMA at 80°C was unsuccessful, whereas with styrene moderate yields were obtained. Interestingly enough, with styrene, complex **3** was once again the most efficient catalyst among those investigated, since most of the styrene consumed during the reaction (35%) was converted into the Kharasch addition product (33%).

Ruthenium complexes **1**–**6** are 18-electron species, and it is generally agreed that the catalytic activity of half-sandwich ruthenium complexes of the general structure [RuX(Cp$^{\#}$)(PPh$_3$)$_2$] depends on the relative facility of dissociation of one phosphine ligand.[11,13] It is therefore reasonable to assume that, in the present case, the initial stage of the catalytic process implies the release of one triphenylphosphine ligand from complexes **1**–**6** to yield the corresponding 16-electron [RuH(CB)(PPh$_3$)] species. In order to test this hypothesis, Kharasch reactions were performed in the presence of free PPh$_3$, reasoning that addition of phosphine would decrease the rate significantly. Figure 5 does conform to our expectations. Addition of free PPh$_3$ slowed down the Kharasch reaction rate, and the effects were more pronounced as the amount of PPh$_3$ increased.

Having thus generated a coordinatively unsaturated 16-electron ruthenium centre, the electron-transfer (halide assisted) from a carbon–chlorine bond of CCl$_4$ could then occur, yielding both the corresponding 17-electron ruthenium(III) species, [RuHCl(CB)(PPh$_3$)], and the $^{\bullet}$CCl$_3$ radical. The latter could then add to the olefin, therefore initiating the catalytic cycle (Scheme 4),

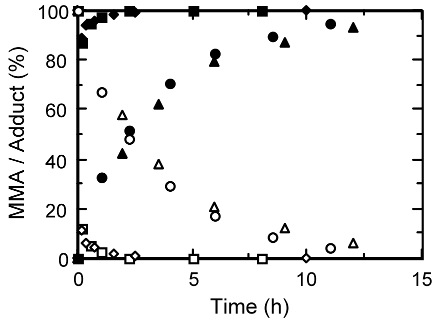


Figure 3. Methyl methacrylate (□, ◇, △, ○) and adduct (■, ◆, ▲, ●) versus time for the Kharasch addition of carbon tetrachloride to MMA catalysed by complexes **3** (□, ■), **4** (◇, ◆), [RuCl(Cp*)(PPh$_3$)$_2$] (△, ▲), and [RuCl(Ind)(PPh$_3$)$_2$] (○, ●), at 40°C. Reaction conditions are the same as in Table 1.

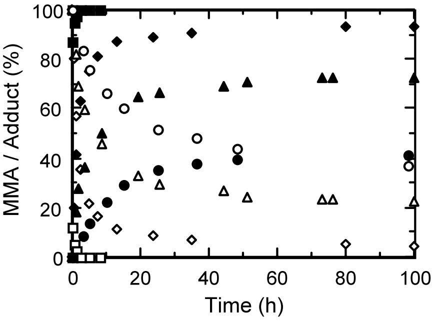


Figure 4. Methyl methacrylate (□, ◇, △, ○) and adduct (■, ◆, ▲, ●) versus time for the Kharasch addition at 40°C of carbon tetrachloride to MMA catalysed by complex **3**. Influence of catalyst loading: MMA/**3** = 300 (□, ■), 4500 (◇, ◆), 6000 (△, ▲), and 9000 (○, ●). Reaction conditions are the same as in Table 1.

Table 2. Kharasch addition of chloroform to methyl methacrylate and styrene catalysed by ruthenacarboranes **1**–**6**[a]

Complex	Substrate conversion (%)/Kharasch addition (%)[b]	
	Methyl methacrylate	Styrene
1	44/3	46/17
2	40/4	38/21
3	42/7	35/33
4	40/4	36/10
5	46/2	39/20
6	48/2	36/18

[a] Reaction conditions are the same as in Table 1, except the temperature (80°C) and the reaction time (24 h).

[b] Conversion and yield are based on the alkene, and determined by GC using dodecane as internal standard.

or react with the Ru^{III} species just formed. On this point, two pathways seem viable: either $^{\bullet}CCl_3$ recombines with the halogen according to the equilibrium indicated in Scheme 4, or abstracts the hydrogen atom from the Ru^{III} species to yield chloroform. Studies along this line are underway. On the other hand, the radical nature of the mechanism has been confirmed by adding galvinoxyl (a radical scavenger) to the reaction medium. Indeed, the Kharasch addition of CCl_4 to methyl methacrylate was retarded in the presence of one equivalent of galvinoxyl, and almost completely inhibited when 5 equivalents of galvinoxyl were added to complex **1** (Fig. 6).[11]

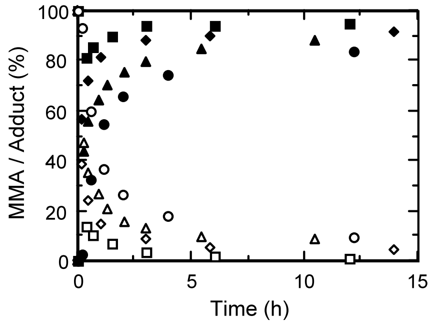
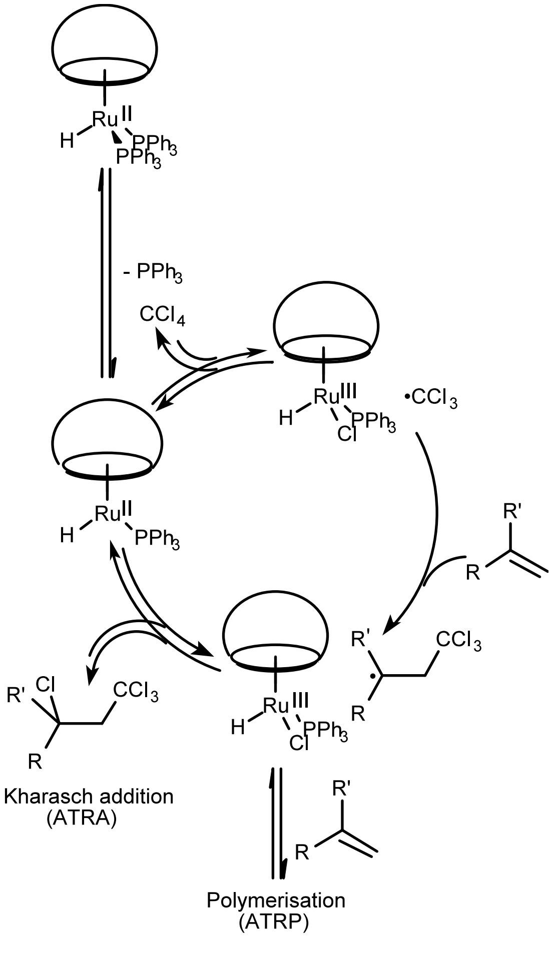


Figure 5. Methyl methacrylate (□, ◇, △, ○) and adduct (■, ◆, ▲, ●) versus time for the Kharasch addition of carbon tetrachloride to MMA catalysed by complex **2**, without added PPh_3 (□, ■) and in the presence of PPh_3, 1.02 equiv. (◇, ◆), 1.88 equiv. (△, ▲), and 3.24 equiv. (○, ●), at 40°C. Reaction conditions are the same as in Table 1.



Scheme 4. Tentative mechanism for the Kharasch addition catalysed by ruthenacarboranes **1**–**6**.

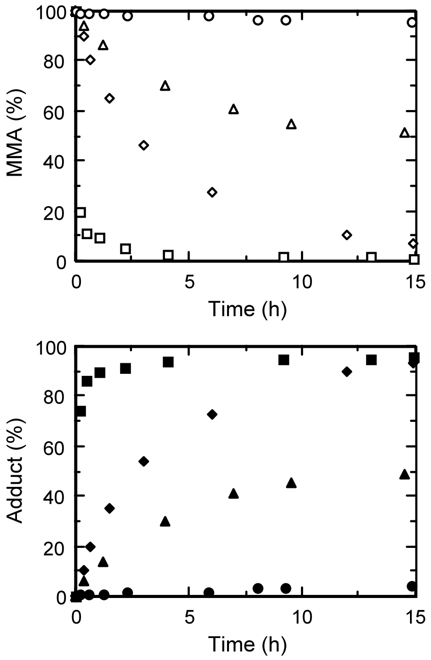


Figure 6. Methyl methacrylate (□, ◇, △, ○) and adduct (■, ◆, ▲, ●) versus time for the Kharasch addition of carbon tetrachloride to MMA catalysed by complex **1**, without galvinoxyl (□, ■) and in the presence of galvinoxyl, 1.05 equiv. (◇, ◆), 2.85 equiv. (△, ▲), and 5.35 equiv. (○, ●), at 40°C. Reaction conditions are the same as in Table 1.

In conclusion, ruthenium complexes **1**–**6** bearing charge-compensated carborane ligands have proven to be highly efficient catalyst precursors for the Kharasch addition of carbon tetrachloride to methyl methacrylate and styrene under mild reaction conditions (40°C). In addition, they surpass the most efficient ATRA catalysts reported so far. However, the precise role of the charge-compensated carborane ligand, of the phosphines, and of the hydride as well, makes detailed mechanistic analysis a challenging endeavour at this time. Further studies of this chemistry are in progress.

Acknowledgements

This work was financially supported by a grant-in-aid (O.T.) joined to the project MAT2001-1575 from CICYT (Spain) and a Scientific Cooperation Project between Spain and Belgium (2000BE0003). Part of this work has also been carried out in the framework of the COST D17/0006/00 and TMR-HPRN CT 2000-10 'Polycat' programmes. The Belgian team is also grateful to the 'Fonds National de la Recherche Scientifique' (F.N.R.S.), Brussels, for the purchase of major instrumentation.

References

1. (a) Kealy, T. J.; Pauson, P. L. *Nature* **1951**, *168*, 1039–1040; (b) Wilkinson, G.; Rosenblum, M.; Whiting, M. C.; Woodward, R. B. *J. Am. Chem. Soc.* **1952**, *74*, 2125–2126.
2. (a) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 143–187; (b) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413–1418; (c) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587–2598; (d) Alt, H. G.; Peifer, B.; Jung, M. In *Education in Advanced Chemistry, Mechanistic Aspects of Molecular Catalysis*; Marciniec, B., Ed.; Wydawnictwo Poznanskie: Poznan–Wroclaw, 1999; Vol. 6, pp. 9–20.
3. (a) Hawthorne, M. F. *Acc. Chem. Res.* **1968**, *1*, 281–288; (b) Salentine, C. G.; Hawthorne, M. F. *Inorg. Chem.* **1976**, *15*, 2872–2882; (c) Fronczek, F. R.; Halstead, G. W.; Raymond, K. N. *J. Am. Chem. Soc.* **1977**, *99*, 1769–1775; (d) Hanusa, T. P. *Polyhedron* **1982**, *1*, 663–665; (e) Manning, M. J.; Knobler, C. B.; Hawthorne, M. F. *J. Am. Chem. Soc.* **1988**, *110*, 4458–4459; (f) Schubert, D. M.; Bandman, M. A.; Rees, W. S., Jr.; Knobler, C. B.; Lu, P.; Nam, W.; Hawthorne, M. F. *Organometallics* **1990**, *9*, 2046–2061; (g) Crowther, D. J.; Baenziger, N. C.; Jordan, R. F. *J. Am. Chem. Soc.* **1991**, *113*, 1455–1457.
4. (a) Teixidor, F.; Flores, M. A.; Viñas, C.; Kivekäs, R.; Sillanpää, R. *Angew. Chem.* **1996**, *108*, 2388–2391; *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2251–2253; (b) Teixidor, F.; Flores, M. A.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *J. Am. Chem. Soc.* **2000**, *122*, 1963–1973 and references cited therein.
5. (a) Demonceau, A.; Saive, E.; de Froidmont, Y.; Noels, A. F.; Hubert, A. J.; Chizhevsky, I. T.; Lobanova, I. A.; Bregadze, V. I. *Tetrahedron Lett.* **1992**, *33*, 2009–2012; (b) Pirotte, B.; Felekidis, A.; Fontaine, M.; Demonceau, A.; Noels, A. F.; Delarge, J.; Chizhevsky, I. T.; Zinevich, T. V.; Pisareva, I. V.; Bregadze, V. I. *Tetrahedron Lett.* **1993**, *34*, 1471–1474; (c) Felekidis, A.; Goblet–Stachow, M.; Liégeois, J. F.; Pirotte, B.; Delarge, J.; Fontaine, M.; Demonceau, A.; Noels, A. F.; Chizhevsky, I. T.; Zinevich, T. V.; Bregadze, V. I. *J. Pharm. Belg.* **1995**, *50*, 232; (d) Fontaine, M. A.; Messere, R.; Demonceau, A.; Noels, A. F.; Chizhevsky, I. T.; Zinevich, T. V.; Bregadze, V. I. *Rhodium Express* **1995**, *12*, 32–39; (e) Demonceau, A.; Simal, F.; Noels, A. F.; Viñas, C.; Nuñez, R.; Teixidor, F. *Tetrahedron Lett.* **1997**, *38*, 4079–4082; (f) Demonceau, A.; Simal, F.; Noels, A. F.; Viñas, C.; Nuñez, R.; Teixidor, F. *Tetrahedron Lett.* **1997**, *38*, 7879–7882; (g) Felekidis, A.; Goblet-Stachow, M.; Liégeois, J. F.; Pirotte, B.; Delarge, J.; Demonceau, A.; Fontaine, M.; Noels, A. F.; Chizhevsky, I. T.; Zinevich, T. V.; Bregadze, V. I.; Dolgushin, F. M.; Yanovsky, A. I.; Struchkov, Yu. T. *J. Organomet. Chem.* **1997**, *536–537*, 405–412; (h) Simal, F.; Sebille, S.; Demonceau, A.; Noels, A. F.; Nuñez, R.; Abad, M.; Teixidor, F.; Viñas, C. *Tetrahedron Lett.* **2000**, *41*, 5347–5351; (i) Teixidor, F.; Núñez, R.; Flores, M. A.; Demonceau, A.; Viñas, C. *J. Organomet. Chem.* **2000**, *614–615*, 48–56; (j) Tutusaus, O.; Delfosse, S.; Demonceau, A.; Noels, A. F.; Núñez, R.; Viñas, C.; Teixidor, F. *Tetrahedron Lett.* **2002**, *43*, 983–987; (k) Delfosse, S.; Guillaume, B.; Richel, A.; Demonceau, A.; Noels, A. F.; Tutusaus, O.; Núñez, R.; Viñas, C.; Teixidor, F.; Baran, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43*, 5–6; (l) Richel, A.; Delfosse, S.; Demonceau, A.; Noels, A. F.; Paavola, S.; Kivekäs, R.; Viñas, C.; Teixidor, F. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2002**, *43*, 177–178; (m) Teixidor, F.; Cirera, M^{a} R.; Viñas, C.; Kivekäs, R.; Sillanpää, R.; Demonceau, A. *J. Organomet. Chem.* **2003**, *680*, 89–99; (n) Teixidor, F.; Viñas, C.; Demonceau, A.; Núñez, R. *Pure Appl. Chem.* **2003**, *75*, 1305–1313.
6. (a) Gossage, R. A.; van de Kuil, L. A.; van Koten, G. *Acc. Chem. Res.* **1998**, *31*, 423–431; (b) Simal, F.; Demonceau, A.; Noels, A. F. In *Recent Research Developments in Organic Chemistry*; Pandalai, S. G., Ed.; Transworld Research Network: Trivandrum, 1999; Vol. 3, pp. 455–464.
7. (a) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921–2990; (b) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689–3745.
8. (a) Simal, F.; Demonceau, A.; Noels, A. F. *Angew. Chem.* **1999**, *111*, 559–562; *Angew. Chem., Int. Ed.* **1999**, *38*, 538–540; (b) Simal, F.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **1999**, *40*, 5689–5693; (c) Simal, F.; Delfosse, S.; Demonceau, A.; Noels, A. F.; Denk, K.; Kohl, F. J.; Weskamp, T.; Herrmann, W. A. *Chem. Eur. J.* **2002**, *8*, 3047–3052.
9. (a) Tutusaus, O.; Teixidor, F.; Núñez, R.; Viñas, C.; Sillanpää, R.; Kivekäs, R. *J. Organomet. Chem.* **2002**, *657*, 247–255; (b) Tutusaus, O.; Viñas, C.; Núñez, R.; Teixidor, F.; Demonceau, A.; Delfosse, S.; Noels, A. F.; Mata, I.; Molins, E. *J. Am. Chem. Soc.* **2003**, *125*, in press; (c) Tutusaus, O.; Núñez, R.; Viñas, C.; Teixidor, F. to be published.
10. For the use of complexes **1**–**6** in ATRP, see: (a) Tutusaus, O.; Delfosse, S.; Simal, F.; Demonceau, A.; Noels, A. F.; Núñez, R.; Viñas, C.; Teixidor, F. *Inorg. Chem. Commun.* **2002**, *5*, 941–945; (b) Delfosse, S.; Richel, A.; Simal, F.; Demonceau, A.; Noels, A. F.; Tutusaus, O.; Núñez, R.; Viñas, C.; Teixidor, F. In *Advances in Controlled/Living Radical Polymerization*; Matyjaszewski, K., Ed.; ACS Symposium Series, American Chemical Society: Washington, DC, 2003; Vol. 854, pp. 116–129.
11. (a) Simal, F.; Wlodarczak, L.; Demonceau, A.; Noels, A. F. *Tetrahedron Lett.* **2000**, *41*, 6071–6074; (b) Simal, F.; Wlodarczak, L.; Demonceau, A.; Noels, A. F. *Eur. J. Org. Chem.* **2001**, 2689–2695.
12. van de Kuil, L. A.; Grove, D. M.; Gossage, R. A.; Zwikker, J. W.; Jenneskens, L. W.; Drenth, W.; van Koten, G. *Organometallics* **1997**, *16*, 4985–4994.
13. (a) Del Zotto, A.; Baratta, W.; Rigo, P. *J. Chem. Soc., Perkin Trans. 1* **1999**, 3079–3081; (b) Baratta, W.; Herrmann, W. A.; Kratzer, R. M.; Rigo, P. *Organometallics* **2000**, *19*, 3664–3669.