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Journal of Organometallic Chemistry 606 (2000) 55–64

Journal of Organometallic Chemistry

Synthesis and evaluation of new $RuCl_2(p\text{-cymene})(ER_2R')$ and $(\eta^1{:}\eta^6\text{-phosphinoarene})RuCl_2$ complexes as ring-opening metathesis polymerization catalysts

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Received 9 December 1999; received in revised form 1 May 2000

Abstract

New $RuCl_2(p\text{-cymene})(ER_2R')$ complexes (E = P, As, Sb; R, R′ = H, alkyl, arylalkyl) have been synthesized and used as catalyst precursors for the ring-opening metathesis polymerization (ROMP) of cyclooctene, cyclopentene, and norbornene. When ER_2R' was a phosphinoarene, the *p*-cymene ligand could be displaced upon heating and tethered $(\eta^1{:}\eta^6\text{-phosphinoarene})RuCl_2$ complexes were obtained. Simple thermogravimetric analysis (TGA) of the complexes provided clear-cut indication on their potential catalytic activity in ROMP.

Keywords: Ruthenium; Carbene; Cyclooctene; Ring-opening metathesis polymerization; Cyclopropanation; Homogeneous catalysis

1. Introduction

Chemists can exert a profound influence on the reactivity of organometallic complexes through molecular engineering, i.e. modification of the ligand environment. Metal–carbene complexes are no exception to this rule and transition-metal mediated reactions of carbene fragments with substrates containing one or more unsaturations are among the most important catalytic strategies for constructing new hydrocarbon frameworks [1–4]. Whereas reactions of metal–carbene moieties with C=C double bonds result in cycloaddition products with some catalysts (in other words cyclopropanation takes place), other carbene complexes induce olefin metathesis. In some cases, cycloaddition and olefin metathesis occur as competing processes [5,6]. Thus, the reaction of metal–carbene bonds with olefins can yield different products depending on the nature of the metal, its oxidation state, and the ancillary ligands present. We have only a limited understanding of the parameters that govern the chemistry of different metal–carbene complexes, no 'unified theory' of metal–carbene reactivity being available nowadays.

The mechanism most commonly accepted for the metal-catalyzed olefin metathesis reaction involves the interconversion of metal–carbene–alkene complexes with metallacyclobutanes as key intermediates. The formation of metallacycles in olefin metathesis clearly points out the necessity of olefin coordination to the metal center. No metathesis occurs in the absence of olefin coordination. Many observations bear out this hypothesis. In particular, it was shown that some classical ruthenium- and rhodium-based cyclopropanation catalysts could also act as olefin metathesis catalysts simply by promoting coordinative unsaturation at the metal center [7–9].

Our laboratory has recently reported on the exceptional efficacy of $RuCl_2(arene)(PR_3)$ complexes as catalyst precursors for the ring-opening metathesis polymerization (ROMP) of low-strain cycloolefins after reaction with a stoichiometric amount of a diazo compound. This initiator is required to generate well-defined ruthenium–carbene species in situ [10,11]. It was shown unambiguously that in solution, the active

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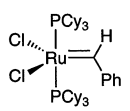
0022-328X/00/$ - see front matter
PII: S0022-328X(00)00287-4

ruthenium(II)–carbene species retain only one phosphane ligand and are no longer bound to the arene ligand. Moreover, the phosphane ligand has to be quite bulky and basic to afford high catalytic activities [10]. Practically, only bulky trialkylphosphanes and/or basic Arduengo-type carbenes [12] can impart sufficient activity and stability to the active species.

Attempts to improve the catalytic performances of the archetypical Grubbs' catalyst (**1**) have focused mainly on varying the carbene, the phosphane, or the anionic ligands. This search for better initiators has led in the last two years to the discovery inter alia of active cationic 18-electron allenylidene species [13], of cationic Grubbs-type catalysts with a rigid *cis*-stereochemistry of the phosphane ligands [14], and also of cationic carbynehydridoruthenium complexes [15]. Along with these metal–alkylidene or metal–alkylidyne complexes, $RuCl_2(p\text{-cymene})(PCy_3)$ (**2a**) remains an attractive catalyst precursor because of its ready availability and its air stability, even when ligated to the basic tricyclohexylphosphane. Complex **2a** can be prepared in situ by addition of the phosphane ligand to the ruthenium(II) dimer $[RuCl_2(p\text{-cymene})]_2$ (**3**). It promotes the ROMP of strained olefins [10] and the ring closing metathesis (RCM) of dienes in a photo-assisted manner simply by heating a solution of the diene substrate under neon light [16]. Upon activation with trimethylsilyldiazomethane (TMSD), it allows the synthesis of poly(norbornene-*g*-ε-caprolactone) copolymers with an excellent control of molecular weight distributions [17,18].



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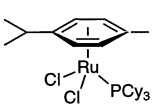


2a

We now report on various attempts at improving catalyst efficiency in the ROMP of strained and low-strain cycloolefins by fine-tuning the arene and the base ligands in $RuCl_2(arene)(ER_2R')$ complexes. Hereafter we also show that simple thermogravimetric analyses of type **2** precatalysts give a clear-cut indication of their potential catalytic activity in ROMP.

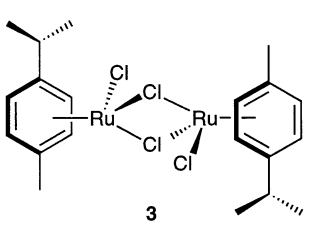
2. Results and discussion

Using the ROMP of cyclooctene as a test reaction, we have investigated the catalytic activity of type **2** complexes where the PCy_3 ligand has been replaced by: (i) the homologous $AsCy_3$ and $SbCy_3$ arsine and stibine; (ii) various simple PR_3 and PR_2R' phosphanes; or (iii) new chelating phosphinoarene ligands (Scheme 1).

2.1. Synthesis and catalytic activity of $RuCl_2(p\text{-cymene})(ECy_3)$ complexes (2a–c)

The tricyclohexylarsine and stibine ligands were synthesized by reacting $AsCl_3$ and $SbCl_3$, respectively, with cyclohexylmagnesium bromide [19,20]. Complexes **2b** and **2c** were obtained by addition of a stoichiometric amount of $[RuCl_2(p\text{-cymene})]_2$ (**3**) to the arsine and stibine ligands (see Section 4). Table 1 summarizes the results obtained for the polymerization of cyclooctene both with the preformed ruthenium(II) complexes and with the same complexes prepared in situ by addition of four equivalents of ligand to the ruthenium(II) dimer **3**. This corresponds to a phosphane-to-ruthenium ratio of 2, a value found optimum for the PCy_3-based catalytic system [10].

A comparison with the corresponding PCy_3 complexes indicates the superiority of the phosphine-based complexes over the arsine- and stibine-ones. It also appears that molecular weight distribution and σ_{cis} (which represents the relative amount of *cis* double bonds in the polyoctenamers) vary not only with the different ECy_3 ligands, but also with the way of preparing the catalyst (excess of phosphine). Monomer conversion decreases in the order $PCy_3 > AsCy_3 > SbCy_3$, as do polymer



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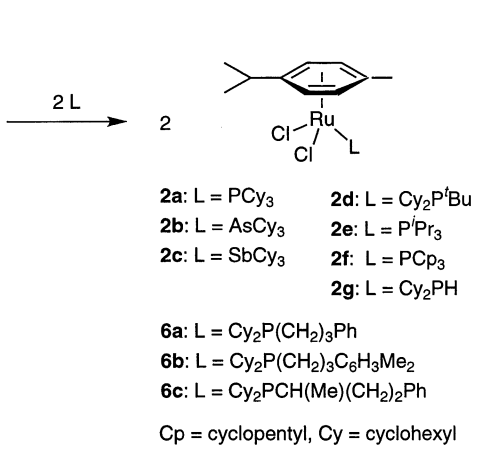


Scheme 1.

Table 1
ROMP of cyclooctene with $RuCl_2$(*p*-cymene)(ECy_3) catalysts **2a–c** preformed or generated in situ [a]

Catalyst	T (°C)	Conversion (%)	M_n (kg mol^{-1})	M_w/M_n	σ_{cis} [b]
2a	20	72	68.2	1.67	0.59
2b	20	39	31.1	1.76	0.78
2c	20	21	5.5	2.78	0.70
3 + $4PCy_3$	60	99	42.3	2.00	0.26
3 + $4AsCy_3$	60	41	51.3	1.55	0.72
3 + $4SbCy_3$	60	11	3.9	1.82	0.70

[a] Reaction conditions: 6×10^{-5} mol of **2a–c** with 1×10^{-4} mol of TMSD or 3×10^{-5} mol of **3** and 12×10^{-5} mol of ECy_3 with 2×10^{-4} mol of TMSD, 1 g of cyclooctene, 5 ml of PhCl, 4 h.
[b] Fraction of *cis* double bonds in the polyoctenamer.

molecular weights. Only oligomers are obtained with the stibine complex. These observations can be rationalized by invoking a combination of steric and electronic effects, the arsine and phosphine ligands being both less basic and less sterically demanding than the corresponding stibine [21].

2.2. Synthesis and catalytic activity of $RuCl_2$(*p*-cymene)(PR_2R') complexes **2d–g**

In an exploratory work from our laboratory, numerous phosphane ligands PR_3 were screened for use in conjunction with **3** as catalysts for the ROMP of cyclooctene [10]. To refine this study, we have tested new PR_2R' ligands whose basicities ($8.5 < pK_a < 10.5$) and steric bulk (defined by their cone angle θ, see Table 6) matched those of tricylohexylphosphane, our lead contender so far. Thus, complexes **2d–g** were synthesized (cf. Scheme 1) and their catalytic activities investigated. Results obtained for the polymerization of cylooctene are presented in Fig. 1 and Table 2. For comparison's sake, control experiments were also carried out with complexes **1** and **2a**.

Variations in catalyst activities are magnified when the polymerizations are carried out at room temperature. The different results obtained with catalyst precursors **2a**, **2d**, **2e**, and **2f** at 20°C highlight the fact that very small variations of the phosphane steric bulk induce large variations of catalyst efficiencies. Particularly striking is the difference brought about by replacing tricyclohexylphosphane by tricyclopentylphosphane (**2a** versus **2f**), two ligands of apparently very similar cone angles and basicities (but spatial conformation may vary). It also appears that **2d** is superior to **2a** for the ROMP of cyclooctene. Its overall relative efficacy is very much alike to that of **1**: same kinetics of polymerization, same molecular weight distributions, but higher content of *cis* double bonds and higher M_n for **2d** relative to **1**. Yet, the two catalytic systems show quite different behaviors for the polymerization of cyclopentene, a cycloolefin that has seldom been polymerized with ruthenium-based catalysts [15]. In that case, the superiority of **2a** and **2d** over **1** is blatant (Table 3).

2.3. Synthesis of phosphinoarene complexes **6a–c** and **7a–c**

Having established that the addition of a diazocompound to complexes **2** leads to arene disengagement, we considered tethering the phosphane and the arene into

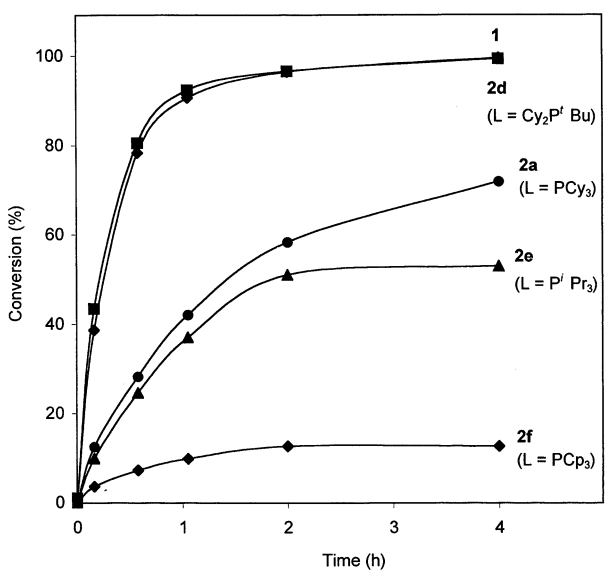


Fig. 1. Time course of the cyclooctene polymerization at 20°C using various $RuCl_2$(*p*-cymene)(PR_2R') complexes or **1** as catalysts (reaction conditions as in Table 2).

Table 2
ROMP of cyclooctene at 20°C with catalysts **1**, **2a**, and **2d–g** [a]

Catalyst	Conversion (%)	M_n (kg mol^{-1})	M_w/M_n	σ_{cis} [b]
1	99	49.1	1.80	0.26
2a	72	68.2	1.67	0.59
2d	99	80.3	1.72	0.45
2e	53	51.6	1.62	0.64
2f	13	26.2	1.77	0.66
2g	0	0	–	–

[a] Reaction conditions: 6×10^{-5} mol of ruthenium catalyst, 2×10^{-4} mol of TMSD, 1 g of cyclooctene, 5 ml of PhCl, 5 h, 20°C.
[b] Fraction of *cis* double bonds in the polyoctenamer.

Table 3
ROMP of cyclopentene at 20°C with catalysts **1**, **2a**, and **2d** [a]

Catalyst	Conversion (%)	M_n (kg mol^{-1})	M_w/M_n	σcis [b]	r_{cis} [c]	r_{trans} [c]	$r_{cis} \times r_{trans}$ [c]
1	8	3.2	1.86	–	–	–	–
2a	63	57.8	1.66	0.18	0.26	4.94	1.26
2d	64	45.3	1.72	0.17	0.09	5.20	0.50

[a] Reaction conditions: 6×10^{-5} mol of ruthenium catalyst, 2×10^{-4} mol of TMSD, 0.7 g of cyclopentene, 3 ml of PhCl, 2 h, 20°C.
[b] Fraction of *cis* double bonds in the polypentenamer.
[c] For a definition of r_{cis}, r_{trans}, and $r_{cis} \times r_{trans}$ see Ref. [1], pp. 242–243.

new phosphinoarene ligands that could act either as monodentate η^1 or as chelating η^1:η^6 ligands. Precedents for the synthesis and the chemistry of such three-legged piano-stool complexes are found in the work of Ward et al. [22,23].

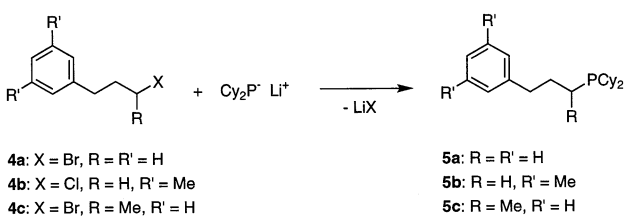
Ligand synthesis is straightforward and outlined in Scheme 2, starting from the appropriate halogenated arene molecules and Cy_2P^- Li^+. The yield decreases substantially when the secondary bromide **4c** is reacted in place of the primary halogenated derivatives **4a** and **4b**, because of the increased competition between elimination and nucleophilic substitution. Addition of a stoichiometric amount of ruthenium dimer **3** to ligands **5** affords the corresponding complexes **6** in good yield (see Section 4 and Scheme 1). Heating **6** in chlorobenzene for several hours results in the quantitative formation of **7** where the phosphinoarene molecule acts now as a chelating ligand (Scheme 3). Alternatively, the one-pot reaction of ligands **5** with dimer **3** at high temperature also affords complexes **7** in high yields. Structures of **7b** and **7c** were ascertained by X-ray crystallography [24].

Complexes **7**, where the phosphinoarene molecules act as chelating ligands could be seen as 'dormant species', arene disengagement (η^1:η^6 to η^1 ligation) providing room for the active species to form upon reaction with the diazocompound and, subsequently, the arene possibly acting as a two- or four-electron ligand during the polymerization process (η^1 to η^1:η^2 or η^1:η^4 ligation). It is also expected, if arene ligation is controlling the chemistry, that carbene transfer reactions might be favored, resulting in cyclopropane formation.

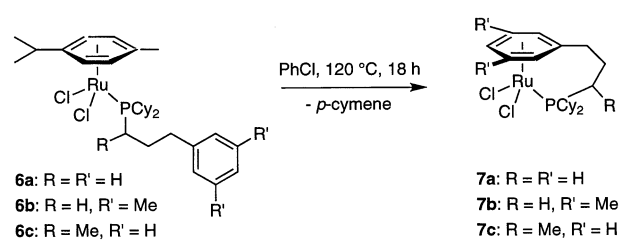
2.4. Catalytic activity of complexes *6a–c* and *7a–c* in ROMP and in olefin cyclopropanation

Complexes **6a–c** and **7a–c** yield poor ROMP catalysts after activation with TMSD or EtDA (ethyl diazoacetate). Some typical results obtained for the polymerization of cyclooctene in the presence of TMSD are summarized in Table 4. Among the 'open arm' series, compound **6c** (R = Me, R′ = H) comes out as the best catalyst precursor, probably because of a slightly higher basicity and higher steric hindrance at the phosphorus atom. The efficiency of **6c** remains, however, much lower than that of **2a** or **2d** (cf. Table 2), although chelation of the pending arm to yield **7c** is very slow under the polymerization conditions, as evidenced by NMR spectroscopy. Substitution on the remote arene ring is therefore expected not to have any significant influence on the metal center. Indeed, complexes **6a** and **6b** display identical behaviors and polymerize cyclooctene at the same very low rate.

Cyclooctene does not polymerize with catalysts of the series **7**. The reaction occurs with norbornene, a strained cycloolefin more prone to ring-opening, but conversion remains low (see Table 5). Again, the catalyst bearing ligand **5c** displays a higher efficiency than



Scheme 2.



Scheme 3.

Table 4
ROMP of cyclooctene at 20°C with catalysts **6a–c** [a]

Catalyst	Conversion (%)	M_n (kg mol^{-1})	M_w/M_n	σ_{cis} [b]
6a	5	0.8	–	–
6b	5	0.8	–	–
6c	57	71.7	1.64	0.61

[a] Reaction conditions: 6×10^{-5} mol of ruthenium catalyst, 2×10^{-4} mol of TMSD, 1 g of cyclooctene, 5 ml of PhCl, 5 h, 20°C.
[b] Fraction of *cis* double bonds in the polyoctenamer.

Table 5
ROMP of norbornene at 60°C with catalysts **7a–c** [a]

Catalyst	Isolated yield (%)	M_n (kg mol^{-1})	M_w/M_n [b]	σ_{cis} [c]	r_{cis} [d]	r_{trans} [d]	$r_{cis} \times r_{trans}$ [d]
7a	19	12.8	6.32	0.80	5.55	1.11	6.17
7b	5	35.8	15.47	0.74	4.00	1.20	4.80
7c	40	32.6	10.25	0.76	4.94	1.41	6.98

[a] Reaction conditions: 3×10^{-5} mol of ruthenium catalyst, 1×10^{-4} mol of TMSD, 1.0 g of norbornene, 30 ml of PhCl, 2 h, 60°C.
[b] Multimodal distributions.
[c] Fraction of *cis* double bonds in the polynorbornene.
[d] For a definition of r_{cis}, r_{trans}, and $r_{cis} \times r_{trans}$ see Ref. [1], pp. 242–243.

those based on **5a** or **5b**. The resulting polynorbornenes are somewhat blocky ($r_{cis} \times r_{trans} \gg 1$) and have a broad multimodal molecular weight distribution, indicating that different active species are operative and/or that initiation of the polymerization is slow. Indeed, it was checked that TMSD decomposition was very slow under our reaction conditions. Furthermore, when stoichiometric amounts of TMSD and cyclooctene were reacted with **7a** as catalyst, two new isomeric products were formed in a 78/22 ratio (80% yield, $m/z = 196$). Although these compounds were not fully characterized, the lack of C=C double bond absorption in their IR spectra and the lack of vinyl proton peaks in their ^{1}H-NMR spectra suggest that they are cyclopropanes resulting from carbene transfer to the double bond of cyclooctene.

A more thorough study revealed that with EtDA as the carbene source, cyclopropanation reactions take over metathesis. Activated olefins such as styrene derivatives are cyclopropanated in up to 82% yield based on EtDA. The scope and limitations of complexes **6** and **7** as cyclopropanation catalysts have been reported elsewhere [25]. Experimental observations support the idea that arene de-coordination is crucial for observing ROMP, the more labile the arene, the more efficient the catalyst. Arene disengagement requires a close spatial fit between the phosphane and arene ligands. The role of the diazocompound in promoting arene removal remains, however, largely speculative so far.

3. Predictive value of TGA measurements

The existence of a relationship between the *p*-cymene release from a ruthenium–phosphane complex and the catalyst activity was proposed by Hafner et al. to rationalize differential scanning calorimetry (DSC) measurements carried out on $RuCl_2$(*p*-cymene)(PR_3) complexes used as photoinitiators in ROMP [26]. It was confirmed and substantiated by thermogravimetric analysis (TGA) of catalyst precursors in our group. An easy liberation of the arene ligand (corresponding to a low T_D value in DSC or TGA) is indicative of a good catalytic efficiency. Experimental data supporting this assumption are provided in Table 6, which links the temperature at which the *p*-cymene ligand is liberated from complexes **2a–g** and the activity of the resulting active species in the ROMP of cyclooctene at room temperature. Coupled TGA–MS and TGA–IR analyses unambiguously confirmed that it is indeed the arene ligand that is disengaged from the metal complexes **2** upon heating.

4. Experimental

4.1. General considerations

All syntheses were carried out under a dry argon atmosphere using standard Schlenk and glove-box techniques. NMR spectra were recorded on a Brucker AM 400 spectrometer. ^{1}H and ^{13}C chemical shifts are listed in parts per million downfield from TMS and are referenced by the solvent peaks (7.25 and 77.0 in $CDCl_3$ for ^{1}H and ^{13}C spectra, respectively). ^{31}P data are listed in parts per million downfield from 85% H_3PO_4 and are externally referenced. Infrared spectra were recorded on a Perkin–Elmer 1720X series FT-IR spectrometer with a selected resolution of 2 cm^{-1}. Gel permeation chromatographic (GPC) analyses of the polymers were performed in THF on a Hewlett–Packard HP 1090

Table 6
Influence of the phosphane cone angle and of the arene lability on the catalytic activity of complexes **2**

Catalyst	θ (°) [a]	T_D (°C) [b]	Cyclooctene conversion (%) [c]
2a	170	162	72
2b	166	212	39
2c	161	219	21
2d	174	139	99
2e	160	172	53
2f	n.a.	165	13
2g	145	222	0

[a] Cone angle of the phosphane ligand.
[b] Temperature at which the *p*-cymene ligand is liberated as determined by TGA.
[c] Reaction at 20°C (same conditions as in Table 2).

instrument equipped with a HP 1037A refractive index detector and a battery of four PL gel columns fitted in series (particle size: 5 μm; pore sizes: 100 000, 10 000, 1000, and 100 Å). The molecular weights (not corrected) are reported versus monodisperse polystyrene standards used to calibrate the instrument. The GPC values are internally consistent but are not necessary directly comparable to values obtained in different solvents. The polymer microstructures were determined by comparison of their ^{1}H- and ^{13}C-NMR spectra with those reported in the literature. Results are accurate within 2% when the integrations of the vinyl and allyl protons and of all carbon atoms are averaged. For analogous complexes, elemental analyses were performed only on select representative materials.

4.2. Materials

Solvents and monomers were distilled from appropriate drying agents and deoxygenated prior to use. 1-Bromo-3-phenylpropane, 1,2-dichloroethane, and 1,3,5-trimethylbenzene were dried over calcium chloride and distilled before use. Cyclohexyl bromide, $AsCl_3$, $SbCl_3$, PBr_3, $RuCl_3{\cdot}xH_2O$, trimethylsilyldiazomethane (2.0 M in hexanes), 4-phenylbutan-2-one, *n*-butyllithium (2.5 M in hexanes), PCy_3, Cy_2PH, and $[RuCl_2(p\text{-cymene})]_2$ were purchased from commercial suppliers and used without further purification. Tricyclopentylphosphine (PCp_3, 50% wt solution in toluene) was a generous loan from CYTEC Canada Inc. $AsCy_3$ [19], $SbCy_3$ [20], $RuCl_2(p\text{-cymene})(PCy_3)$ (**2a**), and $RuCl_2(p\text{-cymene})(P^iPr_3)$ (**2e**) [10] were synthesized according to published procedures. 4-Phenylbutan-2-ol was obtained by reduction of 4-phenylbutan-2-one with sodium borohydride.

4.3. Synthesis of phosphine and phosphinoarene ligands

4.3.1. tert-Butyldicyclohexylphosphine

To a solution of chlorodicyclohexylphosphine (5.75 g, 24.7 mmol) in THF (20 ml) cooled at −78°C were added dropwise 18 ml of *tert*-butyllithium (1.5 M in pentane, 27.2 mmol). The yellow suspension was allowed to warm to room temperature (r.t.) and was stirred overnight at this temperature. The reaction mixture was evaporated to dryness and the phosphine was extracted twice with 20 ml of pentane. The pentane solution was filtered through Celite, concentrated to 20 ml, and cooled to −78°C. After 2 h, the white crystals obtained were filtered under inert atmosphere and washed with small fractions of cold pentane. Cy_2P^tBu is highly air-sensitive and melts at r.t. Yield 5.60 g (89%). ^{1}H-NMR ($CDCl_3$, δ ppm): 1.90–1.05 (m, 22H, C_6H_{11}), 1.10 (d, 9H, $C(CH_3)_3$, $^3J_{H-P} = 10.8$ Hz). ^{13}C-NMR: 33.11 (d, CMe_3, $^1J_{C-P} = 19.4$ Hz), 33.61 (d, C_1 C_6H_{11}, $^1J_{C-P} = 16.2$ Hz), 30.96, 27.82 (2 d, C_2 C_6H_{11}, $^2J_{C-P} = 9.7$ Hz), 30.33 (d, $C(CH_3)_3$, $^2J_{C-P} = 13.2$ Hz), 27.69, 27.61 (2 s, C_3 C_6H_{11}), 26.41 (s, C_4, C_6H_{11})′. ^{31}P-NMR: 28.58.

4.3.2. 1-Chloro-3-(3,5-dimethyl)phenylpropane (**4b**)

To a solution of 1,3,5-trimethylbenzene (6.30 g, 52.4 mmol) in THF (20 ml) cooled at −78°C were added 22 ml of a *n*-butyllithium solution (2.5 M in hexanes, 55 mmol). The solution was stirred overnight at r.t. and was then added dropwise at 0°C to 49 g of 1,2-dichloroethane (505 mmol). The mixture was stirred for 2 h at r.t. and the fine white precipitate was removed by filtration through Celite. Evaporation of the volatile fraction and distillation under reduced pressure afforded the title product as a colorless liquid. Yield 3.10 g (33%); b.p. 70°C (0.07 mm Hg). GC–MS: *m*/*z* (%) 184 (13), 182 (35) [M^+], 119 (100), 105 (38). ^{1}H-NMR ($CDCl_3$, δ ppm): 6.91 (s, ^{1}H, CH_{para}), 6.88 (s, 2H, CH_{ortho}), 3.58 (t, 2H, CH_2Cl, $^3J_{H-H} = 6.8$ Hz), 2.76 (t, 2H, CH_2Ar, $^3J_{H-H} = 7.2$ Hz), 2.36 (s, 6H, CH_3Ar), 2.12 (pseudo-quint, 2H, $CH_2CH_2CH_2$, $^3J_{H-H} = 7$ Hz). ^{13}C-NMR: 140.57 (C_{ipso} Ar), 137.87 (CCH_3), 127.68 (C_{para} Ar), 126.32 (C_{ortho} Ar), 44.29 (CH_2Cl), 34.08 (CH_2CH_2Cl), 32.61 (CH_2Ar), 21.14 (CH_3). IR (cm^{-1}): 3014 (m), 2952 (s), 2919 (s), 2860 (m), 1607 (s), 1443 (m), 837 (m), 703 (m).

4.3.3. 2-Bromo-4-phenylbutane (**4c**)

Phosphorus tribromide (3.25 g, 12 mmol) was slowly added at 0°C to 4.95 g of neat 4-phenylbutan-2-ol (33 mmol). The resulting yellow solution was stirred 2 h at 0°C and overnight at r.t. The reaction mixture was carefully hydrolyzed with 15 ml of water and extracted twice with 30 ml of diethyl ether. The ethereal phase was washed with a saturated Na_2CO_3 solution, dried over Na_2SO_4, and the solvent was evaporated. Distillation under reduced pressure afforded the pure product as a colorless liquid. Yield 4.57 g (65%); b.p. 64°C (0.08 mm Hg). GC–MS: *m*/*z* (%) 214 (26), 212 (27) [M^+], 117 (53), 91 (100). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.35–7.22 (m, 5H, Ph), 4.11 (m, ^{1}H, CHBr), 2.83 (m, 2H, CH_2Ph), 2.15 (m, 2H, CH_2CH), 1.75 (d, 3H, CH_3, $^3J_{H-H} = 10.7$ Hz). ^{13}C-NMR: 140.87, 128.47, 128.44, 126.05 (C_6H_5), 50.84 (CHBr), 42.64 (CH_2CH), 33.92 (CH_2Ph), 26.47 (CH_3). IR (cm^{-1}): 3063 (m), 3027 (s), 2980 (m), 2922(s), 2861 (m), 1603 (m), 1495 (s), 1455 (s), 1209 (m), 700 (s).

4.3.4. Dicyclohexyl(3-phenylpropyl)phosphine (**5a**)

To a solution of dicyclohexylphosphine (1.79 g, 9 mmol) in THF (25 ml) cooled at −78°C were added 3.6 ml of a *n*-butyllithium solution (2.5 M in hexanes, 9 mmol). The resulting deep yellow suspension was stirred for 2 h at r.t. 1-Bromo-3-phenylpropane (2.19 g, 11 mmol) was added at −78°C and the mixture was stirred 18 h at r.t. After evaporation of the solvent, the

phosphine was extracted with pentane and the resulting solution was filtered through Celite. Evaporation of the solvent and recrystallization from cold (− 78°C) diethyl ether afforded the product as white crystals which gave an air-sensitive, oily liquid at ambient temperature. Yield 2.24 g (78%). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.25–7.13 (m, 5H, Ph), 2.65 (t, 2H, CH_2Ph, $^3J_{H-H} = 7.6$ Hz), 1.76–1.09 (m, 26H, C_6H_{11} and CH_2CH_2P). ^{13}C-NMR: 144.22, 128.44, 128.21, 125.67 (C_6H_5), 37.58 (d, CH$_2$Ph, $^3J_{C-P} = 12.7$ Hz), 33.28 (d, C_1 C_6H_{11}, $^1J_{C-P} = 11.4$ Hz), 30.41, 28.99 (both d, C_2 C_6H_{11}, $^2J_{C-P} = 8.1$ Hz), 30.15 (d, CH$_2$P, $^1J_{C-P} = 19.5$ Hz), 27.43, 27.26 (both s, C_3 C_6H_{11}), 27.32, 26.53 (2 s, C_4, C_6H_{11}), 20.86 (d, CH$_2$$CH_2CH_2$, $^2J_{C-P} = 16.5$ Hz). ^{31}P-NMR: − 4.09.

4.3.5. Dicyclohexyl(3-(3,5-dimethyl)phenylpropyl)-phosphine (**5b**)

The procedure given above for **5a** was followed using 2.65 g (13.3 mmol) of dicyclohexylphosphine, 5.4 ml (13.5 mmol) of *n*-butyllithium solution and 2.77 g (13.3 mmol) of 1-chloro-3-(3,5-dimethyl)phenylpropane (**4b**). Yield 3.40 g (74%). ^{1}H-NMR ($CDCl_3$, δ ppm): 6.81 (s, 3H, CH arom), 2.62 (t, 2H, CH_2Ar, $^3J_{H-H} = 7.6$ Hz), 2.28 (s, 6H, CH_3), 1.75–1.20 (m, 26H, C_6H_{11} and CH_2CH_2P). ^{13}C-NMR: 142.14, 137.66, 127.31, 126.31 (C_6H_3), 37.37 (d, CH$_2$Ar, $^3J_{C-P} = 11.4$ Hz), 33.30 (d, C_1 C_6H_{11}, $^1J_{C-P} = 11.4$ Hz), 30.35, 29.02 (both d, C_2 C_6H_{11}, $^2J_{C-P} = 7.2$ Hz), 30.11 (d, CH$_2$P, $^1J_{C-P} = 17.9$ Hz), 27.45, 27.27 (both s, C_3 C_6H_{11}), 27.34, 26.54 (both s, C_4, C_6H_{11}), 21.24 (ArCH$_3$), 20.86 (d, CH$_2$$CH_2CH_2$, $^2J_{C-P} = 16.3$ Hz). ^{31}P-NMR: − 4.02.

4.3.6. Dicyclohexyl(2-(4-phenyl)butyl)phosphine (**5c**)

The procedure given above for **5a** was followed using 2.88 g (14.5 mmol) of dicyclohexylphosphine, 6.1 ml (15.2 mmol) of *n*-butyllithium solution and 3.09 g (14.5 mmol) of 2-bromo-4-phenylbutane (**4c**). Yield 2.73 g (57%). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.30–7.10 (m, 5H, Ph), 2.70 (m, PCHCH$_3$ and CH_2Ph, 3H), 2.14–1.13 (m, C_6H_{11} and PCH(CH_3)CH_2, 27H). ^{13}C-NMR: 141.09, 128.49, 128.32, 126.14 (C_6H_5), 37.40–23.28 (m, C_6H_{11} and PCHCH$_2$CH$_2$), 17.26 (d, PCHCH$_3$, $^2J_{C-P} = 8.2$ Hz). ^{31}P-NMR: 11.64.

4.4. Synthesis of $RuCl_2$(*p*-cymene)(ER_2R') complexes

4.4.1. $RuCl_2$(*p*-cymene)($AsCy_3$) (**2b**)

To a solution of $[RuCl_2(p\text{-cymene})]_2$ (0.10 g, 0.16 mmol) in dichloromethane (8 ml) were added 0.32 g (0.98 mmol) of $AsCy_3$ and the mixture was stirred 14 h at r.t. The solvent was then evaporated to dryness and the orange–red residue was washed with pentane (2 × 15 ml) and with diethyl ether (8 ml). Yield 0.17 g (82%); m.p. 165°C (dec.). ^{1}H-NMR (CD_2Cl_2, δ ppm): 5.53 (m, 4H, CH_{arom} *p*-cym), 2.88 (sept, ^{1}H, CHMe$_2$, $^3J_{H-H} = 7.2$ Hz), 2.51 (pseudo t, 3H, CH C_6H_{11}), 2.15–1.15 (m, 30H, C_6H_{11}), 2.10 (s, 3H, CH_3 *p*-cym), 1.26 (d, 6H, CHCH_3, $^3J_{H-H} = 7.2$ Hz). ^{13}C-NMR: 106.75 (*C*–Me *p*-cym), 93.65 (*C*–CHMe$_2$ *p*-cym), 85.85, 81.21 (*C*H *p*-cym), 36.78 (C_1 C_6H_{11}), 30.56 (*C*HMe$_2$ and C_2 C_6H_{11}), 27.93 (C_3 C_6H_{11}), 26.54 (C_4 C_6H_{11}), 22.35 (CH*C*H$_3$), 18.04 (Ar*C*H$_3$).

4.4.2. $RuCl_2$(*p*-cymene)($SbCy_3$) (**2c**)

To a solution of $[RuCl_2(p\text{-cymene})]_2$ (0.26 g, 0.42 mmol) in dichloromethane (15 ml) were added 0.91 g (2.45 mmol) of $SbCy_3$ and the mixture was stirred 14 h at r.t. The solvent was then evaporated to dryness and the orange–red residue was washed with pentane (2 × 15 ml) and with diethyl ether (8 ml). Yield 0.38 g (67%); m.p. 179°C (dec.). ^{1}H-NMR (CD_2Cl_2, δ ppm): 5.54 (m, 4H, CH_{arom} *p*-cym), 2.82 (sept, ^{1}H, CHMe$_2$, $^3J_{H-H} = 7.2$ Hz), 2.47 (pseudo t, 3H, CH C_6H_{11}), 2.15–1.15 (m, 30H, C_6H_{11}), 2.08 (s, 3H, CH_3 *p*-cym), 1.26 (d, 6H, CHCH_3, $^3J_{H-H} = 7.3$ Hz). ^{13}C-NMR: 105.86 (*C*-Me *p*-cym), 93.40 (*C*-CHMe$_2$ *p*-cym), 84.74, 81.29 (*C*H *p*-cym), 32.21 (*C*1 C_6H_{11}), 31.41 (C_2 C_6H_{11}), 31.03 (*C*HMe$_2$), 29.07 (C_3 C_6H_{11}), 27.02 (C_4 C_6H_{11}), 22.40 (CH*C*H$_3$), 18.57 (Ar*C*H$_3$).

4.4.3. $RuCl_2$(*p*-cymene)($Cy_2P'Bu$) (**2d**)

To 0.47 g (1.84 mmol) of *tert*-butyldicyclohexylphosphine in dichloromethane (20 ml) were added 0.47 g of $[RuCl_2(p\text{-cymene})]_2$. The red–brown solution was stirred 1 h at r.t. and was then evaporated to dryness. The crude product was washed with pentane (2 × 20 ml) and with diethyl ether (2 × 8 ml). The complex was obtained as a red microcrystalline powder. Yield 0.70 g (81%); m.p. 108°C (dec.). ^{1}H-NMR ($CDCl_3$, δ ppm): 5.57 (s, 4H, CH_{arom} *p*-cym), 2.87 (sept, ^{1}H, CHMe$_2$, $^3J_{H-H} = 7.2$ Hz), 2.43 (m, 2H, CH C_6H_{11}), 2.25–1.11 (m, 26H, C_6H_{11} and CH_2CH_2CH_2P), 2.11 (s, 3H, CH_3 *p*-cym), 1.41 (d, 9H, C(CH_3)$_3$, $^3J_{H-P} = 12.4$ Hz), 1.30 (d, 6H, CH(CH_3)$_2$, $^3J_{H-H} = 7.2$ Hz). ^{13}C-NMR: 108.43 (*C*–Me *p*-cym), 107.46, 94.24, 89.20, 83.66, 81.29, 80.53 (*C* *p*-cym), 38.81 (d, C_1 C_6H_{11}, $^1J_{C-P} = 24.7$ Hz), 38.27 (d, *C*Me$_3$, $^1J_{C-P} = 11.5$ Hz), 30.49 (*C*HMe$_2$), 32.14, 30.03 (both s, C_2 C_6H_{11}), 29.78 (d, C(*C*H$_3$)$_3$, $^2J_{C-P} = 3.3$ Hz), 28.55, 26.43 (both d, C_3 C_6H_{11}, $^3J_{C-P} = 8.6$ Hz), 26.63 (s, C_4 C_6H_{11}), 22.24 (CH*Me*$_2$), 22.63 (Ar(*C*H$_3$)$_2$), 17.71 (d, *C*H$_2$CH$_2$P, $^2J_{C-P} = 22.8$ Hz), 18.02 (Ar*C*H$_3$ *p*-cym). ^{31}P-NMR: 35.68. Anal. Calc. for $C_{26}H_{45}Cl_2PRu$: C, 55.71; H, 8.09. Found: C, 55.17; H, 8.99%.

4.4.4. $RuCl_2$(*p*-cymene)($P(C_5H_9)_3$) (**2f**)

A solution of tricyclopentylphosphine (50% wt in toluene, 0.90 g, 1.88 mmol) was added to 0.51 g of $[RuCl_2(p\text{-cymene})]_2$ (0.83 mmol) in 10 ml of dichloromethane. The reaction mixture was stirred 1 h at r.t. and evaporated to dryness. The crude product

was washed several times with pentane and diethyl ether. The complex was obtained as an orange microcrystalline powder. Yield 0.73 g (82%); m.p. 149°C (dec.). ^{1}H-NMR ($CDCl_3$, δ ppm): 5.55 (s, 4H, CH_{arom} *p*-cym), 2.78 (sept, ^{1}H, CHMe$_2$, $^3J_{H-H} = 6.8$ Hz), 2.66 (m, 3H, CHP), 2.05 (s, 3H, ArCH_3), 1.98–1.50 (m, 24H, C_5H_9), 1.25 (d, 6H, CHCH_3, $^3J_{H-H} = 6.8$ Hz). ^{13}C-NMR: 106.23 (*C*-Me *p*-cym), 93.63 (*C*–CHMe$_2$ *p*-cym), 89.79, 84.01 (both d, CH *p*-cym, $J = 3.3$ Hz), 37.22 (d, C_1 C_5H_9, $^1J_{C-P} = 22.8$ Hz), 30.46 (*C*HMe$_2$), 29.78 (C_2 C_5H_9), 25.63 (d, C_3 C_5H_9, $^2J_{C-P} = 8.1$ Hz), 22.47 (CH*Me*$_2$), 17.78 (Ar*C*H$_3$). ^{31}P-NMR: 51.78.

4.4.5. $RuCl_2$(*p*-cymene)(Cy_2PH) (**2g**)

A solution of dicyclohexylphosphine (0.31 g, 1.44 mmol) in 5 ml of dichloromethane was added via a cannula to 0.40 g of [$RuCl_2$(*p*-cymene)]$_2$ (0.65 mmol) in 12 ml of dichloromethane. The resulting red–brown solution was stirred 1 h at r.t. The volatiles were evaporated under vacuum and the crude product was washed several times with pentane and diethyl ether to afford a deep orange powder. Yield 0.61 g (93%); m.p. 222°C (dec.). ^{1}H-NMR ($CDCl_3$, δ ppm): 5.49 (m, 4H, CH_{arom} *p*-cym), 4.34 (dt, ^{1}H, P*H*, $^1J_{H-P} = 366.9$ Hz, $^3J_{H-H} = 3.3$ Hz), 2.82 (sept, ^{1}H, CHMe$_2$, $^3J_{H-H} = 6.8$ Hz), 2.30 (m, 2H, CH C_6H_{11}), 2.15–1.15 (m, 20H, C_6H_{11}), 2.09 (s, 3H, CH_3 *p*-cym), 1.21 (d, 6H, CHCH_3, $^3J_{H-H} = 6.8$ Hz). ^{13}C-NMR: 107.15 (*C*-Me *p*-cym), 95.86 (*C*–CHMe$_2$ *p*-cym), 87.45, 87.42, 84.12, 84.09 (*C*H *p*-cym), 34.28 (C_1 C_6H_{11}, $^1J_{C-P} = 22.8$ Hz), 32.50, 30.50 (both d, C_2 C_6H_{11}, $^2J_{C-P} = 3.2$ Hz), 30.48 (*C*HMe$_2$), 27.19, 26.98 (both s, C_3 C_6H_{11}), 27.08, 25.70 (both s, C_4 C_6H_{11}), 22.05 (CH(*C*H$_3$)$_2$), 18.05 (Ar*C*H$_3$). ^{31}P-NMR: 40.91. Anal. Calc. for $C_{22}H_{37}Cl_2PRu$: C, 51.55; H, 8.84. Found: C, 52.04; H, 8.55%.

4.4.6. $RuCl_2$(*p*-cymene)($Cy_2P(CH_2)_3Ph$) (**6a**)

A solution of phosphine **5a** (0.50 g, 1.57 mmol) in dichloromethane (5 ml) was added to 0.42 g of [$RuCl_2$(*p*-cymene)]$_2$ (0.68 mmol) in 10 ml of dichloromethane. The reaction mixture was stirred for 1 h and then evaporated to dryness. The crude product was washed several times with pentane and diethyl ether. The complex was obtained as an orange microcrystalline powder. Yield 0.72 g (84%); m.p. 152°C (dec.). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.24–7.21 (m, 2H, CH_{ortho} Ph), 7.15–7.11 (m, 3H, C$H_{meta+para}$ Ph), 5.51 (s, 4H, CH_{arom} *p*-cym), 2.80 (sept, ^{1}H, CHMe$_2$, $^3J_{H-H} = 6.8$ Hz), 2.55 (m, 2H, C_1 C_6H_{11}), 2.21–1.16 (m, 26H, C_6H_{11} and $CH_2CH_2CH_2$P), 2.05 (s, 3H, CH_3 *p*-cym), 1.24 (d, 6H, CH(CH_3)$_2$, $^3J_{H-H} = 6.8$ Hz). ^{13}C-NMR: 141.91, 128.47, 128.28, 125.79 (C_6H_5), 108.48 (*C*–Me *p*-cym), 93.82 (*C*–CHMe$_2$ *p*-cym), 88.45 (d, *C*H *p*-cym, $J = 3.2$ Hz), 82.99 (d, *C*H *p*-cym, $J = 4.9$ Hz), 37.75 (d, *C*H$_2$Ph, $^3J_{C-P} = 11.1$ Hz), 37.38 (d, C_1 C_6H_{11}, $^1J_{C-P} = 21.1$ Hz), 30.67 (*C*HMe$_2$), 29.21, 27.39 (both d, C_2 C_6H_{11}, $^2J_{C-P} = 3.2$ Hz), 28.58, 26.43 (both s, C_3 C_6H_{11}), 27.37 (d, *C*H$_2$P, $^1J_{C-P} = 22.8$ Hz), 27.09, 27.01 (both s, C_4 C_6H_{11}), 22.29 (CH*Me*$_2$), 18.54 (d, *C*H$_2$CH$_2$P, $^2J_{C-P} = 24.4$ Hz), 18.02 (Ar*C*H$_3$ *p*-cym). ^{31}P-NMR: 24.96.

4.4.7. $RuCl_2$(*p*-cymene)($Cy_2P(CH_2)_3C_6H_3Me_2$) (**6b**)

This complex was prepared in the same way as **6a** by using 0.42 g (0.68 mmol) of [$RuCl_2$(*p*-cymene)]$_2$ and 0.55 g (1.60 mmol) of phosphine **5b**. Yield 0.69 g (78%); m.p. 161°C (dec.). ^{1}H-NMR ($CDCl_3$, δ ppm): 6.78 (s, ^{1}H, CH_{para} Ar), 6.74 (s, 2H, CH_{ortho} Ar), 5.51 (s, 4H, CH_{arom} *p*-cym), 2.82 (sept, ^{1}H, CHMe$_2$, $^3J_{H-H} = 6.8$ Hz), 2.48 (m, 2H, CH C_6H_{11}), 2.23–1.18 (m, 26H, C_6H_{11} and $CH_2CH_2CH_2$P), 2.26 (s, 6H, ArCH_3), 2.06 (s, 3H, CH_3 *p*-cym), 1.24 (d, 6H, CH(CH_3)$_2$, $^3J_{H-H} = 6.8$ Hz). ^{13}C-NMR: 141.79, 137.69, 127.41, 126.26 (C_6H_5), 108.43 (*C*–Me *p*-cym), 93.76 (*C*–CHMe$_2$ *p*-cym), 88.4 (d, C*H* *p*-cym, $J = 3.2$ Hz), 82.96 (d, C*H* *p*-cym, $J = 4.9$ Hz), 37.62 (d, *C*H$_2$Ar, $^3J_{C-P} = 11.1$ Hz), 37.26 (d, C_1 C_6H_{11}, $^1J_{C-P} = 21.1$ Hz), 30.64 (*C*HMe$_2$), 29.18, 27.37 (both d, C_2 C_6H_{11}, $^2J_{C-P} = 3.2$ Hz), 28.55, 26.43 (both s, C_3 C_6H_{11}), 27.35 (d, *C*H$_2$P, $^1J_{C-P} = 22.8$ Hz), 27.08, 27.00 (both s, C_4 C_6H_{11}), 22.24 (CH*Me*$_2$), 21.19 (Ar(*C*H$_3$)$_2$), 18.65 (d, *C*H$_2$CH$_2$P, $^2J_{C-P} = 22.8$ Hz), 18.02 (Ar*C*H$_3$ *p*-cym); ^{31}P-NMR: 24.88. Anal. Calc. for $C_{33}H_{51}Cl_2PRu$: C, 60.91; H, 7.90. Found: C, 61.40; H, 9.13%.

4.4.8. $RuCl_2$(*p*-cymene)($Cy_2PCH(Me)(CH_2)_2Ph$) (**6c**)

This complex was prepared in the same way as **6a** by using 0.37 g (0.60 mmol) of [$RuCl_2$(*p*-cymene)]$_2$ and 0.50 g (1.50 mmol) of phosphine **5c**. Yield 0.50 g (66%); m.p. 96°C (dec.). ^{1}H-NMR ($CDCl_3$, δ ppm): 7.21–7.17 (m, 5H, C*H* Ph), 5.53–5.49 (m, 4H, CH_{arom} *p*-cym), 2.80 (sept, ^{1}H, CHMe$_2$, $^3J_{H-H} = 6.8$ Hz), 2.75–1.24 (m, 28H, C_6H_{11} and CH_2CH(CH_3)P), 2.03 (s, 3H, CH_3 *p*-cym), 1.24 (d, 6H, CH(CH_3)$_2$, $^3J_{H-H} = 6.8$ Hz). ^{13}C-NMR: 141.82, 128.64, 128.33, 125.87 (C_6H_5), 107.04 (*C*–Me *p*-cym), 94.57 (*C*–CHMe$_2$ *p*-cym), 88.94, 87.91 (both d, C*H* *p*-cym, $J = 3.2$ Hz), 84.37, 83.62 (both d, C*H* *p*-cym, $J = 4.8$ Hz), 36.35, 36.18 (both d, C_1 C_6H_{11}, $^1J_{C-P} = 13.1$ Hz), 35.19 (s, *C*H$_2$Ph), 34.55 (d, P*C*HMe, $^1J_{C-P} = 10.1$ Hz), 30.57 (*C*HMe$_2$), 29.72, 27.67 (both d, C_2 C_6H_{11}, $^3J_{C-P} = 5.0$ Hz), 29.57, 26.47 (both s, C_4 C_6H_{11}), 29.23, 29.04 (both s, C_3 C_6H_{11}), 22.74 (PCH*C*H$_3$), 22.26 (CH(*C*H$_3$)$_2$), 17.89 (Ar*C*H$_3$ *p*-cym), 16.40 (CH_2CH_2CH). ^{31}P-NMR: 30.30.

4.5. Synthesis of tethered phosphinoarene–ruthenium complexes

4.5.1. $RuCl_2$(η^1:η^6-$Cy_2P(CH_2)_3Ph$) (**7a**)

A solution of complex **6a** (0.36 g, 0.58 mmol) in 20 ml of chlorobenzene was heated overnight at 120°C. The volatiles were removed under vacuum and the

orange residue was washed several times with pentane and diethyl ether. Yield 0.23 g (82%); m.p. 252°C (dec.). ^{1}H-NMR ($CDCl_3$, δ ppm): 6.25 (t, ^{1}H, CH_{para} Ph, $^3J_{H-H} = 6.0$ Hz), 5.66 (t, 2H, CH_{meta} Ph, $^3J_{H-H} = 6.0$ Hz), 5.08 (d, 2H, CH_{ortho} Ph, $^3J_{H-H} = 6.0$ Hz), 2.52 (m, 2H, CH C_6H_{11}), 2.39 (t, 2H, CH_2Ph, $^3J_{H-H} = 4.8$ Hz), 2.36–1.15 (m, 24H, C_6H_{11} and CH_2CH_2P). ^{13}C-NMR: 97.17, 97.06, 95.96, 93.27, 93.24, 80.09 (*arene*), 33.05 (d, C_1 C_6H_{11}, $^1J_{C-P} = 24.3$ Hz), 29.89, 25.00 (both s, CH_2Ph), 29.04 (s, C_2 C_6H_{11}), 27.68 (d, C_3 C_6H_{11}, $^3J_{C-P} = 3.3$ Hz), 27.46, 26.77 (both d, CH_2P, $^1J_{C-P} =$ 10.5 Hz), 26.08 (s, C_4 C_6H_{11}), 15.43, 15.19 (both s, CH_2C$H_2$$CH_2$P). ^{31}P-NMR: 29.57.

4.5.2. $RuCl_2(\eta^1{:}\eta^6$-$Cy_2P(CH_2)_3C_6H_3Me_2)$ (**7b**)

Heating **6b** (0.40 g, 0.62 mmol) in chlorobenzene as described above for **7a** afforded the title complex as an orange solid. Yield 0.30 g (95%); m.p. 272°C (dec.). ^{1}H-NMR ($CDCl_3$, δ ppm): 5.63 (s, ^{1}H, CH_{para} Ar), 4.60 (s, 2H, CH_{ortho} Ar), 2.43 (m, 2H, CH C_6H_{11}), 2.29 (t, 2H, CH_2Ph, $^3J_{H-H} = 5.6$ Hz), 2.09 (s, 3H, CH_3Ar), 2.00–1.10 (m, 24H, C_6H_{11} and CH_2CH_2P). ^{13}C-NMR: 107.23, 107.20, 96.39, 95.99, 95.86, 77.47 (*arene*), 33.69 (d, C_1 C_6H_{11}, $^1J_{C-P} = 24.3$ Hz), 30.31, 24.41 (both s, CH_2Ar), 29.18 (s, C_2 C_6H_{11}), 27.72 (d, C_3 C_6H_{11}, $^3J_{C-P} = 3.3$ Hz), 27.56, 27.01 (both d, CH_2P, $^1J_{C-P} =$ 10.5 Hz), 26.27 (s, C_4 C_6H_{11}), 18.23 (ArCH_3), 16.32, 16.09 (both s, CH_2C$H_2$$CH_2$P). ^{31}P-NMR: 28.61. Anal. Calc. for $C_{22}H_{35}Cl_2PRu$: C, 53.49; H, 7.22. Found: C, 53.56; H, 8.13%.

4.5.3. $RuCl_2(\eta^1{:}\eta^6$-$Cy_2PCH(Me)(CH_2)_2Ph)$ (**7c**)

Heating **6c** (0.77 g, 1.22 mmol) in chlorobenzene as described above for **7a** afforded the title complex as an orange solid. Yield 0.38 g (63%); m.p. 242°C (dec.). ^{1}H-NMR ($CDCl_3$, δ ppm): 6.21 (m, 2H, CH_{ortho} Ph), 5.28 (m, ^{1}H, CH_{meta} Ph), 5.23 (m, ^{1}H, CH_{meta} Ph), 4.83 (m, ^{1}H, CH_{para} Ph), 2.69–0.90 (m, 30H, C_6H_{11} and CH_2CH_2CH(CH_3)P). ^{13}C-NMR: 102.83, 102.75 (C_{ipso} Ph), 97.95, 97.84, 91.64, 85.62, 81.88, 76.01 (C$H_{ortho+meta+para}$Ph), 36.02–13.34 (m, not completely assigned because of the multiplicity of the signals). ^{31}P-NMR: 36.44.

4.5.4. Alternative preparation of **7a–c**

The reaction of $[RuCl_2(p\text{-cymene})]_2$ (0.7 mmol) with the chelating phosphines **5a–c** (1.6 mmol) in chlorobenzene (20 ml) at 120°C for 16 h led to the corresponding tethered phosphinoarene–ruthenium complexes after washing with pentane and diethyl ether. Complexes **7a–c** were obtained in 91, 85 and 80% yield, respectively.

4.6. Typical procedure for the ROMP of cyclooctene

To a ruthenium complex (6×10^{-5} mol) placed in a flask under argon were added 3 ml of chlorobenzene and 1.0 g of cyclooctene (9.1 mmol). The mixture was stirred for 5 min and 2 ml of trimethylsilyldiazomethane (TMSD, 0.1 M in chlorobenzene, 0.2 mmol) were added via a syringe. The conversion was followed by gas chromatography using the cyclooctane impurity of cyclooctene as an internal standard. The solution was kept at 20°C for 5 h, then diluted in $CHCl_3$ before precipitation in a large volume of methanol acidified with HF (600 ml). The resulting polymer was dried overnight under vacuum and analyzed by GPC and NMR spectroscopy.

4.7. Typical procedure for the ROMP of norbornene

To a ruthenium complex (3×10^{-5} mol) placed in a flask under argon were added 25 ml of chlorobenzene and 1.0 g of norbornene (10.6 mmol) dissolved in 4 ml of chlorobenzene. The flask was heated to 60°C over 5 min and 1 ml of trimethylsilyldiazomethane (TMSD, 0.1 M in chlorobenzene, 0.10 mmol) was added via a syringe. The solution was kept at 60°C for 2 h, cooled to r.t. and diluted in $CHCl_3$ before precipitation in a large volume of methanol acidified with HF (600 ml). The resulting polymer was dried overnight under vacuum and analyzed by GPC and NMR spectroscopy.

Acknowledgements

D.J. thanks the 'Services Fédéraux des Affaires Scientifiques, Techniques et Culturelles' for financial support in the frame of the PAI 4/11-Supramolecular Chemistry and Supramolecular Catalysis. Support of the 'Fonds National de la Recherche Scientifique' (FNRS) for the purchase of major instrumentation is gratefully acknowledged. TGA-MS and TGA-FTIR analyses were kindly performed by M. Alexandre (University of Mons-Hainaut).

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