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Assessment of Catalysis by Arene-Ruthenium Complexes Containing Phosphane or NHC Groups bearing Pendant Conjugated Diene Systems

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Two *p*-cymene-ruthenium complexes **1** and **2** were isolated in high yields by treating the $[RuCl_2(p\text{-cymene})]_2$ dimer with new hybrid phosphane- or NHC-linked diene ligands. Both complexes were fully characterized by NMR spectroscopy, and the molecular structure of the ruthenium–*p*-cymene complex **1**, containing the phosphane–diene ligand system, was determined by X-ray diffraction analysis. The catalytic activities of both compounds were probed in atom-transfer radical addition (ATRA) and polymerization (ATRP), in the cyclopropanation of olefins, in the ring-opening metathesis polymerization (ROMP) of norbornene, and in the synthesis of enol esters from hex-1-yne and 4-acetoxybenzoic acid.

Introduction

Arene-ruthenium complexes associated with phosphane or *N*-heterocyclic carbene (NHC) ligands have been found to be particularly efficient precatalysts for a wide range of organic transformations.[1,2] Interestingly, these versatile complexes are believed to release the arene ligand in situ in some cases, thus leading to highly reactive coordinatively unsaturated catalytic species.[2a,2g,1] Aware of the low stability of these "naked species", some of us and others have developed the synthesis of arene-ruthenium complexes containing phosphane systems bearing pendant arene groups and of the resulting chelating complexes [i.e., the tethered (κP:η^6-phosphanoarene)ruthenium complexes].[3,4] We have notably shown that these complexes gain robustness from the chelate effect and can thus be used in catalysis at high temperatures, over prolonged reaction times, at low loadings.[5] Nevertheless, one drawback of this strategy is that the formation of over-stabilized complexes is accompanied by lower activity under standard conditions. In view of these results, we set out to replace the pendant arene groups with a potentially more labile function and thus designed ligands that incorporate either phosphane or NHC systems linked to diene groups through propylene spacers.[6–8] The alkyl spacers should allow the dienes to interact with the ruthenium centers once the arenes are released. Owing to the variety of possible binding modes of a linked diene,[9] we would expect it to be coordinatively flexible for Ru intermediates and able to stabilize highly reactive catalytic species while preserving sufficient catalytic activity. Here we describe the synthesis of these arene-ruthenium complexes incorporating new hybrid phosphane- or NHC-linked diene ligands. Preliminary assessment of the catalytic performances of these complexes in atom-transfer radical addition (ATRA) and polymerization (ATRP), olefin cyclopropanation, ring-opening metathesis polymerization (ROMP), and enol ester synthesis is reported.

Results and Discussion

The synthesis of the arene-ruthenium phosphane–diene complex **1** starts with isoprene, which is deprotonated with potassium diisopropylamide by Brandsma's procedure and added to ethylene oxide to generate 4-methylenehex-5-enol (Scheme 1).[10] Formation of the mesylate and addition of lithium diphenylphosphide give the phosphane–diene ligand. This can open the chloride bridges of the dimer $[(p\text{-cymene})RuCl_2]_2$ in benzene to afford the target complex **1** in good yield.

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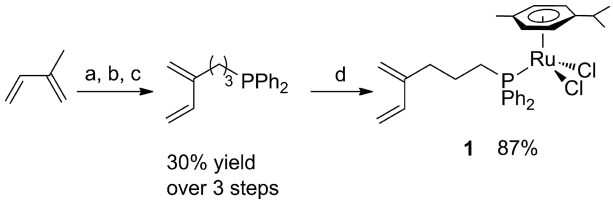
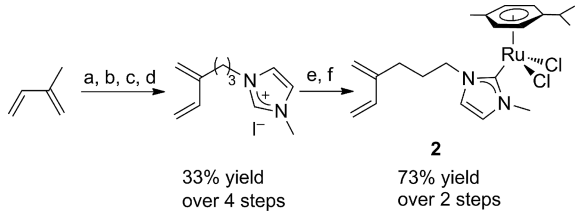


Scheme 1. Synthesis of the arene-ruthenium phosphane–diene complex **1**: (a) KDA, ethylene oxide, –80 °C→ room temp., 3 h; (b) MsCl, NEt_3, CH_2Cl_2, room temp., 1 h; (c) PPh_2Li, THF, 0 °C, 2 h; (d) 1/2 [(*p*-cymene)$RuCl_2]_2$, benzene, room temp., 4 h.



Scheme 2. Synthesis of the arene-ruthenium NHC–diene complex **2**: (a) KDA, ethylene oxide, –80 °C→ room temp., 3 h; (b) MsCl, NEt_3, CH_2Cl_2, room temp., 1 h; (c) imidazole, NaH, THF, room temp., 24 h; (d) CH_3I, AcOEt, 3 h, 65 °C; (e) Ag_2O, CH_2Cl_2, reflux, 24 h; (f) 1/2 [(*p*-cymene)$RuCl_2]_2$, CH_2Cl_2, room temp., 2 h.

The ^{31}P NMR chemical shift of **1** at δ = 23.2 ppm corresponds to a downfield shift of 26 ppm relative to the free ligand. In the ^1H NMR spectrum of **1**, the signals of the dienyl system show the same pattern as observed for the phosphane–diene. These results are indicative of the κP-coordination of the phosphane–diene. Single crystals of **1**, suitable for X-ray diffraction, were obtained by the layering technique. An ORTEP view of compound **1** is shown in Figure 1. The arene-ruthenium moiety has a three-legged piano stool structure with structural parameters in the range of those observed for related complexes.[3] In the solid state, the propylene spacer is roughly aligned with the Ru–P bond, keeping the dienyl system away from the Ru center.

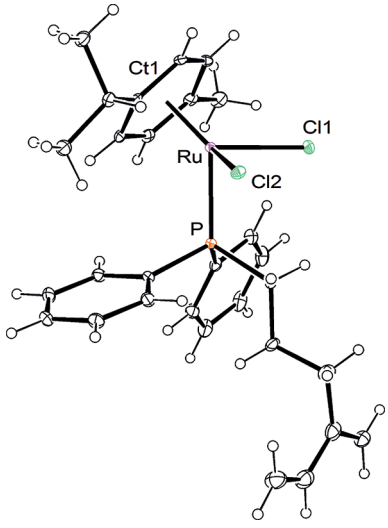


Figure 1. ORTEP view of complex **1**. Selected bonds (Å) and angles (°): Ru–Ct1 1.705(10), Ru–Cl1 2.4124(7), Ru–Cl2 2.4203(6), Ru–P 2.3373(6), Ct1–Ru–Cl1 126.08(4), Ct1–Ru–Cl2 127.68(4), Ct1–Ru–P 130.04(4), Cl1–Ru–Cl2 86.15(2), Cl1–Ru–P 88.23(2), Cl2–Ru–P 84.04(2).

The NHC-ruthenium complex **2** was synthesized from isoprene in a similar fashion. Addition of sodium imidazolate to the mesylate of 4-methylenehex-5-enol gives the imidazole–diene, which is next converted into the methylimidazolium salt by addition of CH_3I (Scheme 2). The target ruthenium complex **2** was next obtained in good yield by the commonly used silver carbene route.[11] The ^1H and ^{13}C NMR spectra of **2** show the expected signals with a singlet carbene at δ = 173.5 ppm.

With the aim of providing further insight into the influence of the diene moieties linked to the hybrid ligands on the catalytic properties of **1** and **2**, before starting the catalytic tests we tried to remove the *p*-cymene ligand from complexes **1** and **2** by heating at reflux in chlorobenzene. Despite our efforts, all attempts resulted in only partial decomposition of **1** and **2**. Nevertheless, molecular modelling performed on the basis of the crystal structure of **1** gives credit to the ability of the conjugated diene to bind the Ru center in the case of *p*-cymene being released, as shown in Figure 2. The geometry of the resulting 16-electron ruthenium complex is that of a distorted square-based pyramid with the P atom located in the apical position. The basal positions are occupied by the dienyl part of the hybrid ligand and the two chlorine atoms.

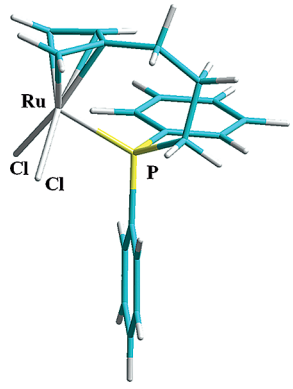


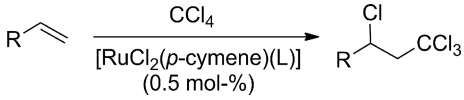
Figure 2. DFT-B3LYP-optimized geometry of [η^4-(4-methylenehex-5-enyl)diphenylphosphane-κ*P*]$RuCl_2$.

In the following discussion we compare the catalytic results obtained for **1** and **2** with those obtained for [$RuCl_2$(*p*-cymene)(PPh_3)] (**3**) and [$RuCl_2$(*p*-cymene){(4-methylhexyl)-diphenylphosphane}] (**4**). Compound **4**, a phosphane-alkyl complex analogue of **1**, was synthesized by a similar procedure including an extra intermediate step of hydrogenation of 4-methylenehex-5-enol to 4-methylhexanol (see the Supporting Information for spectroscopic and X-ray structure characterization of **4**).

In order to assess the catalytic efficiencies of complexes **1** and **2**, we first investigated atom-transfer radical addition, commonly named the Kharasch reaction.[12] Various types of ruthenium complexes,[13] including ruthenium–arene complexes,[14,15] are known to catalyze the addition of poly-

halogenated compounds to alkenes, thereby affording the corresponding 1:1 adducts in high yields and with excellent selectivities.

The addition of carbon tetrachloride to four representative olefins (methyl methacrylate, *n*-butyl acrylate, styrene, and dec-1-ene) was chosen as model set of reactions for these investigations (Scheme 3). Experimental protocols that had proved successful for evaluating the catalytic activities of [$RuCl_2$(*p*-cymene)(PR_3)] and [$RuCl_2$(*p*-cymene)-(NHC)] complexes in earlier studies were employed again.[14]



Scheme 3. Kharasch addition of carbon tetrachloride across olefins.

In a first series of experiments, we performed a rapid catalytic screening of both complexes at our disposal by use of pressure vials and a monomode microwave reactor.[16] As we had demonstrated in 2007, such a device was very convenient for quickly heating the reaction mixtures to temperatures well above the boiling points of the reaction partners and speeding up the Kharasch addition.[16] As a matter of fact, the microwave-assisted addition of CCl_4 to the four olefins under investigation afforded high levels of conversion after 10 min at 160 °C in the presence of the ruthenium phosphane–diene complex **1** (Table 1). Under the same conditions, however, the related ruthenium NHC–diene complex **2** was much less active, with three substrates remaining below the 50% threshold. In terms of yield, there was a marked dichotomy between dec-1-ene and readily polymerizable substrates such as methyl methacrylate, *n*-butyl acrylate, and styrene. These last three indeed furnished significant amounts of oligomers/polymers beside the desired 1:1 adducts (see Figures S1 and S2 in the Supporting Information), except for the reaction of styrene in the presence of the ruthenium phosphane complex **1**. With dec-1-ene, a substrate not inclined towards polymerization, the yields generally squared quite well with the levels of conversion (Table 1).

To gauge better the influence of phosphane–diene and NHC–diene ligands on the outcomes of the reactions, we performed a second series of more thorough catalytic tests based on the addition of CCl_4 to styrene and dec-1-ene. These experiments were carried out on a larger scale in Schlenk tubes placed in an oil bath at 60 or 85 °C. With this revised setup, the Kharasch addition was slowed down and it was possible to monitor the reaction course more carefully and more conveniently than in the microwave reactor. The times needed to reach completion were considerably longer, and the differences between the two catalysts were more pronounced. Under these conditions, the ruthenium phosphane–diene complex **1** again proved to be more active than its NHC–diene counterpart **2** (Table 2 and Figure 3). Indeed, at 85 °C complex **1** afforded complete conversion of styrene together with an 80% yield of the Kharasch adduct within 100 h, whereas complex **2** gave 61% conversion and a 19% yield in the same period of time. As expected, dec-1-ene is a more sluggish substrate than styrene. Thus, with complex **1**, it took ca. 360 h at 85 °C to reach a quantitative yield, whereas **2** afforded a 68% yield in the same period of time. Interestingly, comparison between the phosphane–diene complex **1** and [$RuCl_2$(*p*-cymene)(PPh_3)] (**3**) or [$RuCl_2$(*p*-cymene){(4-methylhexyl)-diphenylphosphane}] (**4**) indicates the superiority of the last two compounds with use of a microwave heating mode,[16] but a better result for **1** with styrene as substrate after a prolonged reaction time at 60 °C in an oil bath.[14b]

Table 1. Microwave-assisted Kharasch addition of carbon tetrachloride across representative olefins.[a]

Substrate	Complex	Substrate conv./Kharasch add. [%][b] 135 °C, 30 min	160 °C, 10 min
Methyl methacrylate	**1**	16/4	67/45
	2	14/1	19/3
	3	99/92	100/80
	4	100/100	100/100
n-Butyl acrylate	**1**	72/21	94/47
	2	76/6	85/18
	3	100/58	100/51
	4	100/62	100/77
Styrene	**1**	26/16	95/88
	2	14/4	32/17
	3	100/92	99/85
	4	93/48	94/49
Dec-1-ene	**1**	38/36	79/77
	2	20/14	42/36
	3	88/87	92/91
	4	98/96	99/98

[a] $[Olefin]_0/[CCl_4]_0/[catalyst]_0$ = 200:800:1. [b] Determined by GC with dodecane as internal standard.

Table 2. Conventional Kharasch addition of carbon tetrachloride across styrene and dec-1-ene.[a]

Substrate	Complex, temp.	Substrate conv./Kharasch add. [%][b] 50 h	100 h	250 h
Styrene	**1**, 60 °C	19/6	40/19	98/77
	1, 85 °C	73/55	99/80	
	2, 60 °C	17/1	33/6	76/31
	2, 85 °C	41/8	61/19	95/43
	4, 60 °C	18/0	41/2	72/13
	4, 85 °C	100/55	–	–
Dec-1-ene	**1**, 60 °C	23/23	42/42	66/66
	1, 85 °C	52/51	73/73	95/95
	2, 60 °C	19/19	34/34	52/52
	2, 85 °C	39/39	49/49	64/63
	4, 60 °C	22/21	48/47	82/81
	4, 85 °C	86/84	96/94	99/97

[a] $[Olefin]_0/[CCl_4]_0/[catalyst]_0$ = 200:800:1. [b] Determined by GC with dodecane as internal standard.

Next, we focused our attention on the atom-transfer radical polymerization (ATRP)[17] of methyl methacrylate (MMA) initiated by carbon tetrachloride or ethyl 2-bromo-2-methylpropanoate (EiBr, Scheme 4). The initial mono-

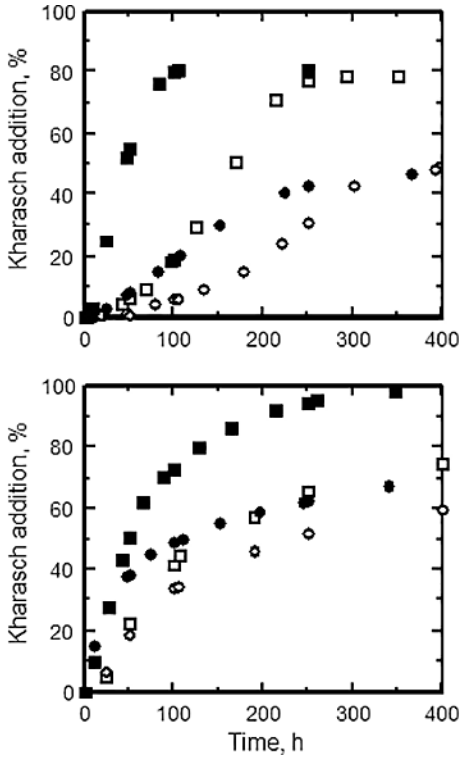
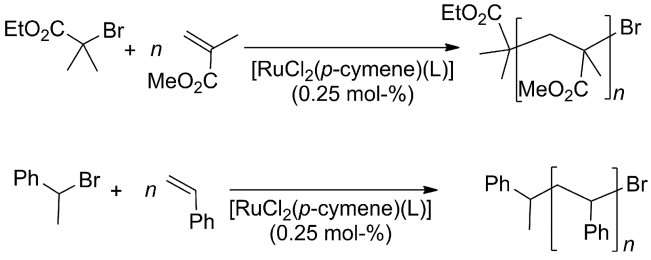


Figure 3. Influence of the temperature on the conventional Kharasch addition of carbon tetrachloride across styrene (top) and dec-1-ene (bottom) catalyzed by complexes **1** (□, ■) and **2** (○,●). Temperature: 60 °C (□,○) and 85 °C (■,●). See Table 2 for reaction conditions.

mer/initiator/ruthenium molar proportions were 800:2:1 and the polymerizations were performed in an oil bath at 85 °C under standard conditions.[18]



Scheme 4. Atom-transfer radical polymerization of methyl methacrylate and styrene.

Under these conditions, complex **1** bearing the phosphane–diene ligand afforded controlled polymerization. Indeed, the plots of $\ln([MMA]_0/[MMA]_t)$ versus time and of M_n versus monomer conversion were linear (Figure 4). Furthermore, complex **1** displayed high initiation efficiency and gave PMMA with molecular weights matching those expected for a well-behaved system (40 kg mol^{-1}). However, at M_w/M_n = 1.6–1.95 (Table 3), the polydispersity index denoted that control was not optimal. In contrast, complex **2**, with the NHC–diene ligand, displayed different behavior (Scheme S7 in the Supporting Information).

An induction period of 4–5 h was observed, after which the polymerization was controlled in terms of monomer

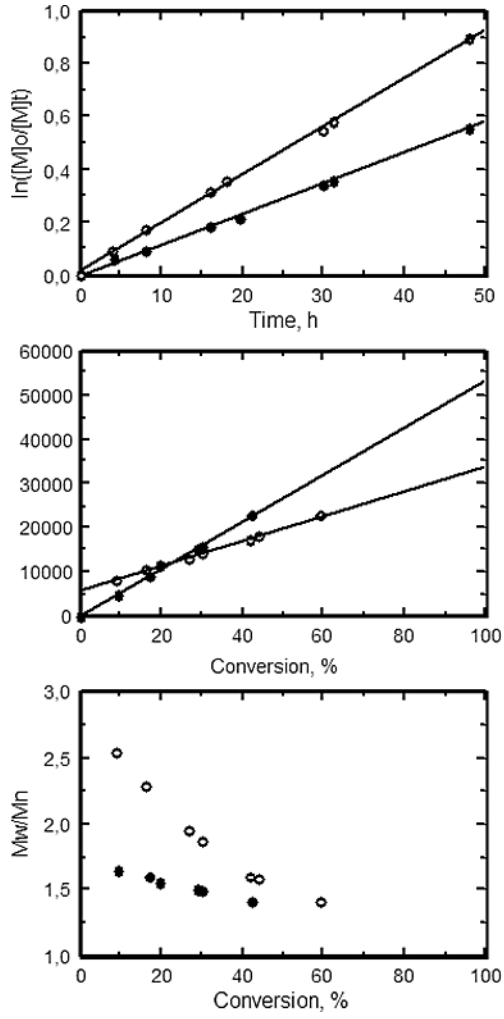


Figure 4. Polymerization of methyl methacrylate catalyzed by complex **1** and initiated by EiBr (●) and CCl_4 (○). See Table 3 for reaction conditions.

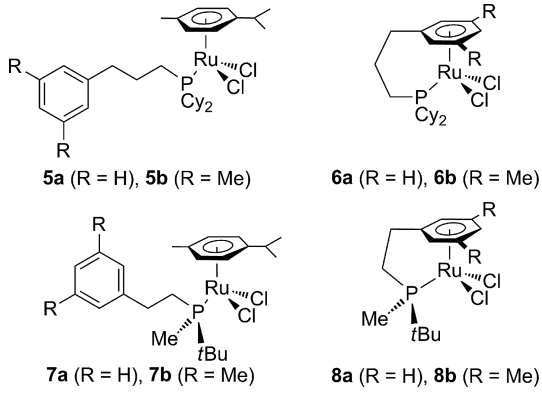
Table 3. Atom-transfer radical polymerization of methyl methacrylate and styrene.

Substrate	Complex	Inititiator	Polymer yield [%]	M_n [kg mol^{-1}][a]	M_w/M_n[a]
MMA[b]	**1**	EiBr	17	9	1.6
		CCl_4	27	13	1.95
	2	EiBr	99	70	4.3
		CCl_4	98	195	4.9
	3	EiBr	20	25	1.6
	4	EiBr	19	21	1.6
		CCl_4	33	26	1.85
Styrene[c]	**1**	PEBr	61	23	1.95
		CCl_4	63	22	1.9
	2	PEBr	77	40	1.9
		CCl_4	77	25	1.85
	3	PEBr	39	26	1.8
	4	PEBr	46	29	1.8
		CCl_4	43	27	1.9

[a] Determined by size-exclusion chromatography (SEC) in THF with PMMA or polystyrene calibration. [b] Initiator: ethyl 2-bromo-2-methylpropanoate (EiBr) or carbon tetrachloride; $[MMA]_0/[initiator]_0/[complex]_0$ = 800:2:1; 16 h at 85 °C. [c] Initiator: (1-bromoethyl)benzene (PEBr) or carbon tetrachloride; $[styrene]_0/[initiator]_0/[complex]_0$ = 750:2:1; 16 h at 110 °C.

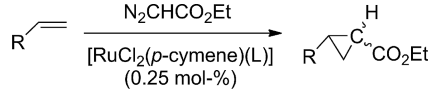
consumption. M_n also increased linearly with conversion, but the molecular weights were much higher than expected, thereby revealing a low initiation efficiency (Table S3 in the Supporting Information). Furthermore, the polydispersity was also very broad (M_w/M_n = 4–5, Table 3).

We then investigated the ATRP of styrene initiated by (1-bromoethyl)benzene (PEBr) or carbon tetrachloride as initiators, with an initial monomer/initiator/catalyst molar ratio of 750:2:1. The temperature was raised to 110 °C, a usual value for this monomer (Table 3). Under these conditions, none of the polymerizations was controlled. Indeed, the levels of conversion of styrene did not exceed 75–90%, even after a prolonged reaction time, thus resulting in a deviation in the plot of $\ln([styrene]_0/[styrene]_t)$ versus time (Figures S8 and S9 in the Supporting Information). The molecular weights of the polymers remained fairly constant throughout the whole runs and the polydispersity indices were around 2. For purposes of comparison, it is worth noting that [$RuCl_2$(*p*-cymene)(PPh_3)] (**3**) and [$RuCl_2$(*p*-cymene){(4-methylhexyl)diphenylphosphane}] (**4**) were as active as phosphane–diene complex **1** for the polymerization of MMA but less active for the polymerization of styrene.[2g,18a] On the other hand, it has been shown in a similar investigation that with non-chelated ruthenium-*p*-cymene complexes **5** (Scheme 5) as catalyst precursors, ATRP proceeded efficiently, whereas the chelated analogues **6** were inefficient (<10% yield) under the same conditions.[18b]

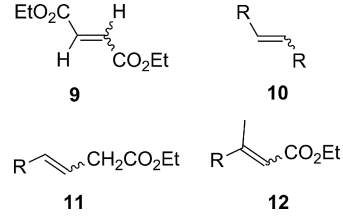


Scheme 5. Structures of non-chelated (**5** and **7**) and chelated (**5** and **8**) phosphane-arene-ruthenium complexes.

Over the past few decades, olefin cyclopropanation has grown tremendously in synthetic utility. Furthermore, carbene moieties generated from diazo compounds provide attractive atom-efficient and environmentally friendly protocols, because nitrogen is the only byproduct. Ruthenium complexes,[19] including ruthenium–arene complexes,[20] have recently emerged as powerful catalysts in olefin cyclopropanation. To evaluate the catalytic activities of complexes **1** and **2** further, the cyclopropanation of various olefins with ethyl diazoacetate was explored by use of a well-established protocol (Scheme 6).[21] Thus, dropwise addition of the diazo compound to a solution of styrene and **1** or **2** at 60 °C resulted in instantaneous gas evolution (Figure S10 in the Supporting Information). In terms of decomposition rate of the diazo compound, complex **1**, [$RuCl_2$(*p*-cymene)(PPh_3)] (**3**), and [$RuCl_2$(*p*-cymene){(4-methylhexyl)diphenylphosphane}] (**4**) were equivalent, slightly more active than the non-chelated complexes **5** but significantly more active than the chelated complex **6**.[3b] With complexes **1** and **2**, cyclopropanes were formed in 67–72% yields along with significant amounts (ca. 25%) of dimerization of the diazo reagent to form diethyl maleate and diethyl fumarate (**9**, Scheme 7). Homologation products **11** and **12** (ca. 5%) resulting from the formal insertion of the carbene moiety into the olefinic C–H bonds of styrene, were also formed, as well as *trans*-stilbene, the metathesis product of styrene (ca. 5% based on styrene). It is worth noting that cyclopropanes were formed with comparable yields and selectivities when complex **4** was used (76% yield, *cis*/*trans* ratio = 0.44). Performing the reaction at room temperature resulted in a significant lowering of the rate of decomposition of the diazo compound, with a concomitant decrease in yields of cyclopropanes (30–43%, Table 4), stilbene, and homologation products, and a corresponding increase in dimerization of the diazo reagent. The sum of the yields for cyclopropanation, dimerization, and homologation corresponded to complete conversion of ethyl diazoacetate. With regard to the mechanism of the reaction, competitive formation of cyclopropanes, homologation compounds, and stilbene might be explained by the involvement of a metallacyclobutane intermediate in the catalytic cycle.[19f,21b,22]



Scheme 6. Cyclopropanation of olefins with ethyl diazoacetate.



Scheme 7. Byproducts of the cyclopropanation of olefins with ethyl diazoacetate.

Table 4. Cyclopropanation of olefins with ethyl diazoacetate.[a]

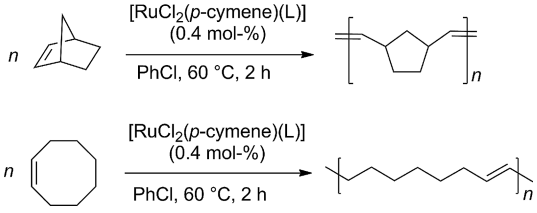
Olefin	Yield [%] (*cis*/*trans* ratio)[b]	
	1	**2**
Styrene (20 °C)	30 (0.59)	43 (0.60)
Styrene	67 (0.54)	72 (0.58)
4-Methoxystyrene	71 (0.47)	78 (0.49)
4-Methylstyrene	73 (0.45)	78 (0.43)
4-*tert*-Butylstyrene	69 (0.48)	75 (0.49)
4-Chlorostyrene	65 (0.52)	70 (0.54)
α-Methylstyrene	82 (0.89)	88 (0.64)
Cyclooctene	13 (0.53)	49 (1.0)

[a] Reaction conditions: catalyst (0.005 mmol), olefin (20 mmol), ethyl diazoacetate (1 mmol) diluted by the olefin to 1 mL; addition time 4 h; temperature 60 °C. [b] Determined by GC.

This method was cleanly extended to *p*-substituted styrenes, affording the corresponding cyclopropanes in 65–78% yields. α-Methylstyrene, a substrate that is more electron-rich than styrene, was accordingly more reactive, with 82–88% yields. In contrast, cyclooctene, an internal non-activated olefin, required longer reaction times than styrene (Figure S10 in the Supporting Information). Yields for this substrate were lower (13–49%) and dimerization became dominant. Polymers generated by the ring-opening metathesis polymerization of cyclooctene also formed in minute amounts.

Examination of Table 4 also reveals that complex **2**, containing the NHC–diene ligand, was always slightly more efficient in the cyclopropanation than its phosphane–diene analogue **1**. In terms of selectivity, both complexes behaved similarly with styrene and its *p*-substituted derivatives, favoring the *trans* cyclopropanes with *cis*/*trans* ratios from 0.43 to 0.60. In contrast, with α-methylstyrene, complex **2** was more *trans*-selective than **1**, whereas the reverse was observed with cyclooctene (Table 4). Furthermore, in all cases, diethyl maleate predominated over diethyl fumarate (*cis*/*trans* ratio: 5–6).

In accordance with earlier observations,[21a,21b] with Ru-arene complexes, norbornene did not undergo cyclopropanation with ethyl diazoacetate. Instead, ring-opening metathesis polymerization (ROMP) occurred readily.[2c,2d,23,24] In order to assess the catalytic efficiency of ruthenium–*p*-cymene complexes **1** and **2**, ROMP of norbornene was attempted in chlorobenzene at 60 °C for 2 h with a monomer-to-catalyst ratio of 250 (Scheme 8).



Scheme 8. ROMP of norbornene and cyclooctene.

Under these conditions, complexes **1** and **2** were completely inefficient. In contrast, when trimethylsilyldiazomethane (TMSD) was added to generate metathetically active ruthenium–carbene species[23b] from [$RuCl_2$(*p*-cymene)(L)] precursors **1** and **2**, ROMP occurred with 91% and 67% yields, respectively (Table 5). Interestingly, similar trends were found with [(*p*-cymene)$RuCl_2(PPh_3)$] (**3**) and [$RuCl_2$(*p*-cymene){(4-methylhexyl)diphenylphosphane}] (**4**) (Table 5),[23b] and chelated ruthenium complexes **5** were poorly active.[23c] With complexes **1** and **2**, the molecular weights of the polymers were rather low (63 and 16 kg mol^{-1}, respectively) in comparison with those obtained with related ruthenium–arene complexes,[23a,23b,24m] and the polydispersities were quite broad (M_w/M_n = 4.5–5). Furthermore, the double bonds of the polymers were mostly *trans*.

Cyclooctene is significantly more difficult to ring-open than norbornene. Hence, formation of polyoctenamer at a reasonable rate occurs only with highly active catalytic systems. With this monomer, complexes **1** and **2** did not afford any reaction after 2 h at 60 °C, even in the presence of TMSD or under visible light irradiation (Table S5 in the Supporting Information), thereby underlining the limitations of these catalysts in olefin metathesis. Both [(*p*-cymene)$RuCl_2(PPh_3)$] (**3**) and chelated ruthenium complexes **5** were inactive with cyclooctene.[23c]

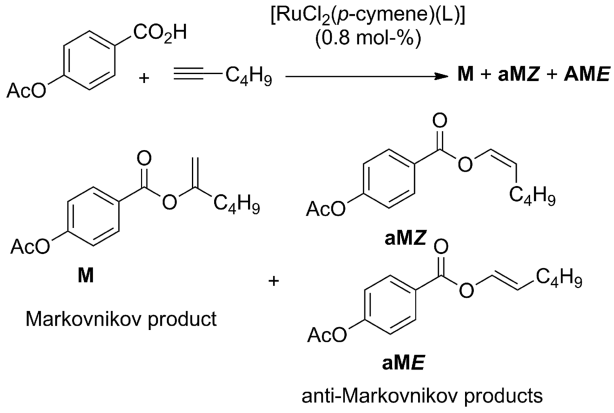
To gauge the potentials of complexes **1** and **2** in homogeneous catalysis further, we probed their activity in the synthesis of enol esters. Various types of ruthenium–arene complexes are known to catalyze the addition of carboxylic acids to terminal alkynes, thereby affording vinyl esters in high yields and with excellent selectivities.[25,26] The hydrooxycarbonylation of hex-1-yne with 4-acetoxybenzoic acid was chosen as a model reaction for these investigations (Scheme 9).

Experimental protocols that proved successful in earlier studies[5,27] were employed again. Thus, dry toluene was used as a solvent and sodium carbonate was added as an activator. Separation and quantification of the three possible products – hex-1-en-2-yl 4-acetoxybenzoate (Markovnikov addition product, **M**) and the *E* and *Z* isomers of hex-1-en-1-yl 4-acetoxybenzoate (anti-Markovnikov addition products, **aM*E*** and **aM*Z***) – were achieved by gas chromatography in the presence of *n*-dodecane as an internal standard. Because hex-1-yne was introduced in excess relative to the carboxylic acid (1.5 equiv.), dimerization products of this terminal alkyne were also detected in the reaction media (Scheme 10). In all cases, however, they represented less than 3% of the total conversion.

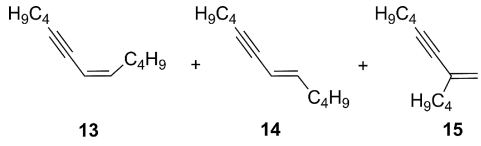
Table 5. Ring-opening metathesis polymerization of norbornene catalyzed by complexes **1**, **2**, and **3**.[a]

Complex	Additive	Monomer conv. [%][b]	Polymer yield [%]	M_n[c] [kg mol^{-1}]	M_w/M_n[c]	σ_c[d]
1	–	<5	traces	–	–	–
1	TMSD	95	91	63	4.6	0.37
2	–	<5	traces	–	–	–
2	TMSD	74	67	16	4.7	0.38
3	–	<5	traces	–	–	–
3	TMSD	70	65	–	–	0.35
4	–	<5	traces	–	–	–
4	TMSD	99	97	65	4.5	0.40

[a] Norbornene (7.5 mmol), catalyst (0.03 mmol), TMSD (0.1 mmol), chlorobenzene; 2 h at 60 °C, under argon. [b] Determined by GC with norbornane as an internal standard. [c] Determined by SEC in THF with polystyrene calibration. [d] Fraction of *cis* double bonds in the polymer, determined by ^{1}H and ^{13}C NMR spectroscopy.



Scheme 9. Synthesis of enol esters from 4-acetoxybenzoic acid and hex-1-yne.



Scheme 10. Dimerization products of hex-1-yne.

Under these conditions, complex **1** afforded a quantitative reaction within 55 h (Figure 5), whereas complex **2** led to a 58% yield within the same period of time. For the sake of comparison, it is worth emphasizing that [$RuCl_2$(*p*-cymene)(PPh_3)] (**3**), a representative catalyst in this field, as well as [$RuCl_2$(*p*-cymene){(4-methylhexyl)diphenylphosphane}] (**4**), were more efficient than **1** (Figure 5),[27a] and that chelated phosphane-arene-ruthenium complexes **7** were equivalent to complex **2**.[5] Altogether, the duration needed to reach completion followed the sequence **4** (30 h) > **3** (40 h) > **1** (55 h) > **7** (120–150 h) > **2** (150 h). The ruthenium–phosphane complexes **1**, **3**, and **4** were also highly selective catalyst precursors and strongly favored the formation of the Markovnikov adduct (94–99% selectivity against 83% with complex **2**).

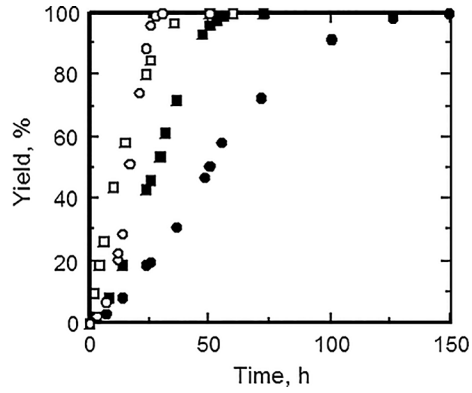


Figure 5. Addition of hex-1-yne to 4-acetoxybenzoic acid catalyzed by [$RuCl_2$(*p*-cymene)(PPh_3)] (**3**, □), [$RuCl_2$(*p*-cymene){(4-methylhexyl)diphenylphosphane}] (**4**, ○), and complexes **1** (■) and **2** (●), temperature: 60 °C, see Table 6 for reaction conditions.

In the next series of experiments, we investigated the effect of the temperature on the hydrooxycarbonylation of hex-1-yne with 4-acetoxybenzoic acid (Scheme 9). Owing to the low boiling point of hex-1-yne (71–72 °C), we made recourse to a monomodal microwave reactor. As expected, the reaction rate significantly increased with the temperature (Figure S12 in the Supporting Information), and after only 30 min at 160 °C, 84% and 67% yields were obtained with catalyst precursors **1** and **2**, respectively. Furthermore, the reactivity order [**4** = **3** (100%) > **1** (84%) > **2** (67%), Table 6] was similar to that previously observed at 60 °C. Raising the temperature to 160 °C also resulted in a lower proportion of hex-1-en-2-yl 4-acetoxybenzoate (**M**), this trend being more pronounced with complex **2** than with **1**. These data confirm the crucial importance of choosing a phosphane ligand rather than an NHC to achieve high catalytic efficiencies in the synthesis of enol esters.

Table 6. Synthesis of enol esters from 4-acetoxybenzoic acid and hex-1-yne.

Complex	Enol esters						Enynes	
	Yield [%][a]					Selectivities [%][b]	Yield [%][a]	Selectivities [%][b]
	0.5 h	25 h	50 h	100 h	150 h	**M**/a**MZ**/a**ME**		13:14:15
Conventional heating at 60 °C[c]								
1		46	96	100		94:4:2	2	44:21:35
2		20	51	92	100	83:13:4	3	26:46:28
3		85	100			94:5:1	3	50:17:33
4		96	100			99:1[e]		
Microwave heating at 160 °C[d]								
1	84					82:14:4	2	45:21:34
2	67					65:26:9	traces	–
3	100					87:11:2	2	51:18:31
4	100					87:10.5:2.5	traces	–

[a] Based on 4-acetoxybenzoic acid and determined by GC with dodecane as an internal standard. [b] Based on hex-1-yne and determined by GC with dodecane as an internal standard. [c] [Hex-1-yne]$_0$/[4-acetoxybenzoic acid]$_0$/[catalyst]$_0$/[Na_2CO_3]$_0$ = 150:100:0.8:1.6. [d] [Hex-1-yne]$_0$/[4-acetoxybenzoic acid]$_0$/[catalyst]$_0$ = 150:100:0.8. No base. [e] a**MZ** + a**ME** = 1%.

Conclusions

By treating the $[RuCl_2(p\text{-cymene})]_2$ dimer with 2 equiv. of phosphane–diene or NHC–diene ligands, we were able to synthesize the two new ruthenium–arene complexes **1** and **2**, respectively. These compounds were isolated in high yields and fully characterized by various analytical techniques. Complexes **1** and **2** remained stable in the solid state for more than five years in the open air. In chlorobenzene at reflux, however, they partially decomposed and the desired 16-electron complexes with the conjugated diene coordinated to the ruthenium center could not be obtained.

In several reactions catalyzed by saturated 18-electron $[RuCl_2(arene)(PR_3)]$ or $[RuCl_2(arene)(NHC)]$ precursors, the mechanism is believed to begin with arene dissociation to provide a highly coordinatively unsaturated 12-electron species,[2a,2g,1] which might be stabilized by the solvent and/or the reaction partners. In the particular case of complexes **1** and **2**, a further stabilization of the 12-electron species was expected as a result of the ligation of the pendant diene moiety of the phosphane or the NHC, generating thereby a 16-electron complex, with an open site for activation of a carbon–halogen bond in atom-transfer radical processes, initial coordination of the diazo compound and subsequent carbene complex formation in olefin cyclopropanation and olefin metathesis, or activation of a terminal alkyne. Although the formation of a chelated ruthenium–phosphane-(or NHC)–diene complex could not be substantiated by the isolation of a well-defined structure, its intermediacy in a catalytic process might be quite plausible, as determined by molecular modeling (Figure 2). The catalytic activities of the two complexes were probed in the atom-transfer radical addition of carbon tetrachloride to olefins, in the atom-transfer radical polymerization of methyl methacrylate and styrene, in olefin cyclopropanation, in the ring-opening metathesis polymerization of norbornene and cyclooctene, and in the synthesis of enol esters from hex-1-yne and 4-acetoxybenzoic acid. Except in the case of the cyclopropanation reaction, complex **1** surpassed complex **2**. It gave results comparable with those obtained with its phosphane-alkyl complex analogue **4** in cyclopropanation, ATRP, and ROMP reactions. Catalytic results for **1** and **2** in these three reaction classes are also similar to those obtained with $[RuCl_2(p\text{-cymene})(PPh_3)]$ (**3**) or the previously described non-chelated phosphane-arene-ruthenium complexes **5** and **7**. These data strongly suggest that the in situ formation of the chelated phosphane- or NHC–diene-ruthenium complexes starting from **1** or **2** either does not operate or is marginal under our catalytic conditions. On the contrary, complexes **1/2** and **4** showed different catalytic behavior for the Kharasch addition and enol ester synthesis. These differences indicate possible coordination of the dienyl fragment to the ruthenium center, which would slow down the catalytic reaction, as described previously with chelated arene-ruthenium complexes. Another hypothesis that cannot be excluded at this stage is that the butadienyl moiety could react with the substrates to give a new phosphane ligand with a pendant function that would alter the catalytic performances of the complex. Further efforts to design new phosphane- and NHC–diene ligands able to give stable chelated ruthenium complexes are in progress.

Experimental Section

General: All reactions were carried out under purified argon with use of vacuum line techniques. Solvents were dried and distilled under argon before use. 3-Methylenehex-5-enol was prepared by the literature method.[10] All other reagents were commercially available and used as received. All the analyses were performed at the "Plateforme d'Analyses Chimiques et de Synthèse Moléculaire de l'Université de Bourgogne". Elemental analyses were performed with an EA 1112 CHNS-O FISONS instrument. ^1H (300.13, 500.13 MHz), ^{13}C (75.5, 125.8 MHz), and ^{31}P (121.5, 202.5 MHz) NMR spectra were recorded with Bruker 300 and 500 Avance spectrometers. Chemical shifts are quoted in ppm (δ) relative to TMS (^1H), with the residual protonated solvent as internal standard, or with external 85% H_3PO_4 (^{31}P). Coupling constants are reported in Hertz. Gas chromatography was carried out with a Varian 3900 instrument equipped with a flame ionization detector and a WCOT fused silica column (stationary phase CP-Sil 5CB, column length 15 m, inside diameter 0.25 mm, outside diameter 0.39 mm, film thickness 0.25 μm).

Synthetic Procedures

4-Methylenehex-5-enyl Methanesulfonate: Triethylamine (4.35 mL, 32 mmol) and methanesulfonyl chloride (2.48 mL, 32 mmol) were added successively, dropwise, at 0 °C to a stirred solution of 4-methylenehex-5-enol (3 g, 26.7 mmol) in dichloromethane (80 mL). After having been stirred for 1 h at room temperature, the reaction mixture was treated with a saturated solution of $NaHCO_3$ (30 mL) and extracted with dichloromethane (50 mL). The combined organics were washed with H_2O, dried, and concentrated. The resulting residue was purified by chromatography on silica gel with pentane/diethyl ether 2:1 to recover the mesylate (4.16 g, 82%). ^1H NMR ($CDCl_3$, 300.13 MHz, 298 K): δ = 2.18 (pseudo quint, $^3J_{H,H}$ = 6.5 Hz, 2 H, $CH_2CH_2CH_2$), 2.57 (t, $^3J_{H,H}$ = 7.8 Hz, 2 H, $MsOCH_2CH_2CH_2$), 3.22 (s, 3 H, OSO_2CH_3), 4.47 (t, $^3J_{H,H}$ = 6.4 Hz, 2 H, CH_2OMs), 5.24 [pseudo s, 1 H, $H_2C(CH)CCH_2$], 5.30 [pseudo s, 1 H, $H_2C(CH)CCH_2$], 5.31 [d, $^3J_{H,H}$ = 9.0 Hz, 1 H, $H_2C(CH)$], 5.44 [d, $^3J_{H,H}$ = 17.6 Hz, 1 H, $H_2C(CH)$], 6.58 [dd, $^3J_{H,H}$ = 9.0, 17.6 Hz, 1 H, $H_2C(CH)$] ppm. ^{13}C NMR ($CDCl_3$, 75.47 MHz, 298 K): δ = 27.3 (CH_2CH_2OMs), 27.7 ($CH_2CH_2CH_2OMs$), 37.6 (OSO_2CH_3), 69.6 (CH_2OMs), 113.9 [$H_2CC(CH)CH_2$], 117.0 [$H_2C(CH)$], 138.5 [$H_2C(CH)$], 144.6 [$H_2C(CH)CCH_2$] ppm. $C_8H_{14}O_3S$ (190.26): calcd. C 50.50, H 7.42; found C 50.68, H 7.67.

(4-Methylenehex-5-enyl)diphenylphosphane: A solution of PPh_2Li (4.95 mmol) in THF (20 mL) was added dropwise under argon at 0 °C to a stirred solution of 4-methylenehex-5-enyl methanesulfonate (0.94 g, 4.95 mmol) in THF (30 mL). The solution was then stirred at room temperature for 2 h and filtered through a Celite® pad. The filtrate was concentrated in vacuo and purified on silica gel with diethyl ether/pentane 5:1 as eluent (0.97 g, 70%). ^1H NMR (C_6D_6, 300.13 MHz, 298 K): δ = 1.79 (pseudo quint, $J_{H,H}$ = 7.7 Hz, 2 H, $CH_2CH_2CH_2$), 2.06 (m, 2 H, CH_2P), 2.34 (t, $^3J_{H,H}$ = 7.4 Hz, 2 H, $Ph_2PCH_2CH_2CH_2$), 4.97 [pseudo s, 1 H, $H_2C(CH)CCH_2$], 5.02 [pseudo s, 1 H, $H_2C(CH)CCH_2$], 5.03 [d, $^3J_{H,H}$ = 9.0 Hz, 1 H, $H_2C(CH)$], 5.23 [d, $^3J_{H,H}$ = 17.8 Hz, 1 H, $H_2C(CH)CCH_2$], 6.39 [dd, $^3J_{H,H}$ = 9.0, 17.8 Hz, 1 H, $H_2C(CH)$], 7.14–7.23 (m, 6 H, Ph), 7.50–7.58 (m, 4 H, Ph) ppm. ^{13}C NMR (C_6D_6, 75.47 MHz, 298

K): δ = 24.8 (d, $^{1}J_{C,P}$ = 17.2 Hz, *C*H_2P), 28.2 (d, $^{2}J_{C,P}$ = 13.1 Hz, *C*H_2CH_2P), 32.9 (d, $^{3}J_{C,P}$ = 12.5 Hz, *C*H_2CH_2CH_2P), 113.4 [s, H_2*C*(CH)CCH_2], 116.3 [s, H_2C(CH)C*C*H_2], 128.6 (s, C_{meta}), 128.7 (s, C_{para}), 133.1 (d, $^{2}J_{C,P}$ = 18.0 Hz, C_{ortho}), 139.1 [s, H_2C(*C*H)], 139.8 (d, $^{1}J_{C,P}$ = 14.5 Hz, C_{ipso}), 146.0 [s, H_2C(CH)*C*CH$_2$] ppm. ^{31}P{^{1}H} NMR (C_6D_6, 121.49 MHz, 298 K): δ = –3.4 (s, PPh_2) ppm. $C_{19}H_{21}P$ (280.34): calcd. C 81.40, H 7.55; found C 81.17, H 7.93.

[(4-Methylenehex-5-enyl)diphenylphosphane-κ*P*][η^6-(*p*-cymene)]-RuCl_2 (1): A 25 mL Schlenk flask was charged under argon with (4-methylenehex-5-enyl)diphenylphosphane (0.34 g, 1.21 mmol), [(*p*-cymene)RuCl_2]$_2$ (0.37 g, 0.6 mmol), and degassed benzene (5 mL). The mixture was stirred at room temperature for 4 h, during which time a brick-red precipitate slowly formed. The solvent was removed by filtration and the red residue was dried under vacuum (0.61 g, 87%). ^{1}H NMR ($CDCl_3$, 500.13 MHz, 298 K): δ = 0.82 [d, $^{3}J_{H,H}$ = 6.9 Hz, 6 H, CH(C*H*$_3$)$_2$], 1.25 (m, 2 H, C*H*$_2$), 1.90 (s, 3 H, C*H*$_3$), 2.06 (t, $^{3}J_{H,H}$ = 7.5 Hz, 2 H, C*H*$_2$CH$_2$CH$_2$P), 2.55 [hept, $^{3}J_{H,H}$ = 7.0 Hz, 1 H, C*H*(CH$_3$)$_2$], 2.61 (pseudo q, $^{3}J_{H,H}$ = $^{2}J_{H,P}$ = 8.0 Hz, 2 H, C*H*$_2$P), 4.73 [pseudo s, 1 H, H_2C(CH)CC*H*$_2$], 4.86 [pseudo s, 1 H, H_2C(CH)CC*H*$_2$], 4.89 [d, $^{3}J_{H,H}$ = 11.0 Hz, 1 H, *H*$_2$C(CH)], 4.95 [d, $^{3}J_{H,H}$ = 17.5 Hz, 1 H, *H*$_2$C(CH)], 5.10 (d, $^{3}J_{H,H}$ = 6.0 Hz, 2 H, *p*-cymene), 5.26 (d, $^{3}J_{H,H}$ = 6.0 Hz, 2 H, *p*-cymene), 6.11 [dd, $^{3}J_{H,H}$ = 11.0, 17.5 Hz, 1 H, H$_2$C(C*H*)], 7.46–7.50 (m, 6 H, Ph), 7.87–7.90 (m, 4 H, Ph) ppm. ^{13}C NMR ($CDCl_3$, 125.75 MHz, 298 K): δ = 17.3 (s, CH$_3$), 21.3 [s, CH(*C*H$_3$)$_2$], 21.7 (d, $^{2}J_{C,P}$ = 7.0 Hz, CH$_2$P), 22.7 (d, $^{1}J_{C,P}$ = 29.3 Hz, *C*H$_2$CH$_2$P), 30.0 [s, *C*H(CH$_3$)$_2$], 32.4 (d, $^{3}J_{C,P}$ = 12.1 Hz, *C*H$_2$CH$_2$CH$_2$P), 85.6 (d, $^{2}J_{C,P}$ = 6.0 Hz, *C*H *p*-cymene), 90.5 (d, $^{2}J_{C,P}$ = 5.5 Hz, *C*H *p*-cymene), 93.5 (s, *p*-cymene), 108.0 (s, *p*-cymene), 113.2 [s, H_2*C*(CH)], 115.9 [s, H$_2$C(CH)C*C*H$_2$], 128.3 (d, $^{3}J_{C,P}$ = 9.2 Hz, Ph C_{meta}), 130.5 (s, Ph C_{para}), 132.7 (d, $^{1}J_{C,P}$ = 41.4 Hz, Ph C_{ipso}), 133.2 (d, $^{2}J_{C,P}$ = 9.0 Hz, Ph C_{ortho}), 138.5 [s, H_2C(*C*H)], 145.4 [s, H_2C(CH)*C*CH$_2$] ppm. ^{31}P{^{1}H} NMR ($CDCl_3$, 202.45 MHz, 298 K): δ = 23.6 (s, PPh_2) ppm. $C_{29}H_{35}Cl_2PRu$ (586.54): calcd. C 59.38, H 6.01; found C 59.15, H 6.13.

1-(4-Methylenehex-5-enyl)-1*H*-imidazole: NaH (0.38 g, 9.5 mmol) was added in small portions at 0 °C under argon to a solution of imidazole (0.646 g, 9.5 mmol) in THF (20 mL). The solution was then stirred at room temperature for 12 h, after which 4-methylenehex-5-enyl methanesulfonate (1.9 g, 10 mmol) was added. After 24 h of stirring at room temperature, the solution was filtered through a Celite® pad. The filtrate was concentrated in vacuo and purified on silica gel with acetonitrile as eluent (1.26 g, 82%). ^{1}H NMR ($CDCl_3$, 300.13 MHz, 298 K): δ = 2.01 (pseudo quint, $J_{H,H}$ = 7.0 Hz, 2 H, CH$_2$C*H*$_2$CH$_2$), 2.24 [t, $^{3}J_{H,H}$ = 7.6 Hz, 2 H, H$_2$C(CH)CC*H*$_2$], 3.97 (t, $^{3}J_{H,H}$ = 7.2 Hz, 2 H, C*H*$_2$N), 5.00 [pseudo s, 1 H, H$_2$C(CH)CC*H*$_2$], 5.09 [pseudo s, 1 H, H$_2$C(CH)CC*H*$_2$], 5.10 [d, $^{3}J_{H,H}$ = 10.9 Hz, 1 H, *H*$_2$C(CH)], 5.16 [d, $^{3}J_{H,H}$ = 17.7 Hz, 1 H, *H*$_2$C(CH)], 6.38 [dd, $^{3}J_{H,H}$ = 10.9, 17.7 Hz, 1 H, H$_2$C(C*H*)], 6.94 (pseudo s, 1 H, H_{imid}), 7.09 (pseudo s, 1 H, H_{imid}), 7.54 (pseudo s, 1 H, NC*H*N) ppm. ^{13}C NMR ($CDCl_3$, 75.47 MHz, 298 K): δ = 28.1 (*C*H$_2$CH$_2$N), 29.2 [*C*H$_2$(CH$_2$)$_2$N], 46.5 (*C*H$_2$N), 113.7 [H$_2$C(CH)C*C*H$_2$], 116.6 [H$_2$*C*(CH)], 118.7 (N*C*H=*C*HN), 129.5 (NCH=*C*HN), 137.1 (N*C*HN), 138.3 [H$_2$C(*C*H)], 144.5 [H$_2$C(CH)*C*CH$_2$] ppm. $C_{10}H_{14}N_2$ (162.23): calcd. C 74.03, H 8.70; found C 73.19, H 8.85.

3-Methyl-1-(4-methylenehex-5-enyl)-1*H*-imidazolium Iodide: CH_3I (0.57 mL, 9.24 mmol) was added to a solution of 1-(4-methylenehex-5-enyl)-1*H*-imidazole (1 g, 6.16 mmol) in ethyl acetate (5 mL). The solution was then stirred at 65 °C for 3 h, during which time an oily product not miscible with the solvent was formed. The supernatant solvent was removed by cannula filtration and the residue was washed three times with ethyl acetate (5 mL portions). The volatile material was removed from the resulting yellow oil under reduced pressure (1.74 g, 93%). No satisfactory elemental analysis could be obtained for this compound. ^{1}H NMR ($CDCl_3$, 300.13 MHz, 298 K): δ = 2.18 (pseudo quint, $J_{H,H}$ = 7.0 Hz, 2 H, CH$_2$C*H*$_2$CH$_2$), 2.38 [t, $^{3}J_{H,H}$ = 7.2 Hz, 2 H, H$_2$C(CH)CC*H*$_2$], 4.11 (s, 3 H, C*H*$_3$), 4.51 (t, $^{3}J_{H,H}$ = 7.4 Hz, 2 H, C*H*$_2$N), 5.07 [d, $^{3}J_{H,H}$ = 7.4 Hz, 1 H, *H*$_2$C(CH)], 5.08 [pseudo s, 1 H, H$_2$C(CH)CC*H*$_2$], 5.10 [pseudo s, 1 H, H$_2$C(CH)CC*H*$_2$], 5.33 [d, $^{3}J_{H,H}$ = 17.9 Hz, 1 H, *H*$_2$C(CH)], 6.40 [dd, $^{3}J_{H,H}$ = 7.4, 17.9 Hz, 1 H, H$_2$C(C*H*)], 7.80 (pseudo t, $^{4}J_{H,H}$ = 1.5, $^{3}J_{H,H}$ = 2.0 Hz, 1 H, H_{imid}), 7.91 (pseudo t, $^{4}J_{H,H}$ = 1.7, $^{3}J_{H,H}$ = 2.0 Hz, 1 H, H_{imid}), 9.65 (m, 1 H, NC*H*N) ppm. ^{13}C NMR ($CDCl_3$, 75.47 MHz, 298 K): δ = 28.5 (*C*H$_2$CH$_2$N), 29.9 [*C*H$_2$(CH$_2$)$_2$N], 36.9 (*C*H$_3$), 50.1 (*C*H$_2$N), 114.5 [H$_2$C(CH)*C*CH$_2$], 117.0 [H$_2$*C*(CH)], 123.4 (N*C*H=*C*HN), 124.7 (N*C*H=*C*HN), 138.0 (N*C*HN), 139.3 [H$_2$C(*C*H)], 145.9 [H$_2$C(CH)*C*CH$_2$] ppm.

[3-Methyl-1-(4-methylenehex-5-enyl)-1*H*-imidazolidene][η^6-(*p*-cymene)]RuCl_2 (2): Ag_2O (0.46 g, 1.94 mmol) was added to a solution of 3-methyl-1-(4-methylenehex-5-enyl)-1*H*-imidazolium iodide (1 g, 3.28 mmol) in dichloromethane (20 mL). The solution was stirred at reflux under Ar for 12 h and filtered. [(*p*-cymene)RuCl_2]$_2$ (0.50 g, 1.64 mmol) was next added to the filtrate, and the resulting mixture was further stirred for 2 h during which time a white precipitate was formed. The solution was filtered through a Celite® pad and concentrated in vacuo. The solid residue was washed three times with diethyl ether (5 mL portions) to afford the product as brick-red powder (1.15 g, 73%). ^{1}H NMR ($CDCl_3$, 300.13 MHz, 298 K): δ = 1.23 [d, $^{3}J_{H,H}$ = 7.0 Hz, 6 H, CH(C*H*$_3$)$_2$], 2.03 (s, 3 H, C*H*$_3$), 2.30–2.45 (m, 4 H, C*H*$_2$), 2.91 [hept, $^{3}J_{H,H}$ = 6.9 Hz, 1 H, C*H*(CH$_3$)$_2$], 3.96 (s, 3 H, NC*H*$_3$), 4.45–4.70 (m, 2 H, C*H*$_2$), 5.04 [pseudo s, 2 H, H$_2$C(CH)CC*H*$_2$], 5.08 (d, $^{3}J_{H,H}$ = 6.0 Hz, 2 H, *p*-cymene), 5.09 [d, $^{3}J_{H,H}$ = 10.5 Hz, 1 H, *H*$_2$C(CH)], 5.32 [d, $^{3}J_{H,H}$ = 17.7 Hz, 1 H, *H*$_2$C(CH)], 5.37 (d, $^{3}J_{H,H}$ = 6.0 Hz, 2 H, *p*-cymene), 6.36 [dd, $^{3}J_{H,H}$ = 17.7, $^{3}J_{H,H}$ = 10.5 Hz, 1 H, H$_2$C(C*H*)], 6.98 (d, $^{3}J_{H,H}$ = 2.0 Hz, 1 H, NC*H*=C*H*N), 7.02 (d, $^{3}J_{H,H}$ = 2.0 Hz, 1 H, NC*H*=C*H*N) ppm. ^{13}C NMR ($CDCl_3$, 75.47 MHz, 298 K): δ = 18.7 [CH(*C*H$_3$)$_2$], 22.5 [*C*H(CH$_3$)$_2$], 28.5 (CH$_3$), 30.3 (*C*H$_2$CH$_2$N), 30.8 [*C*H$_2$(CH$_2$)$_2$N], 39.5 (*C*H$_3$N), 51.1 (*C*H$_2$N), 82.7 (*C*H *p*-cymene), 85.0 (*C*H *p*-cymene), 99.0 (*p*-cymene), 108.6 (*p*-cymene), 114.1 [H$_2$*C*(CH)], 116.4 [H$_2$*C*C(CH)CH$_2$], 121.5 (N*C*H=*C*HN), 124.0 (N*C*H=*C*HN), 138.4 [H$_2$C(*C*H)], 145.3 [H$_2$C*C*(CH)CH$_2$], 173.5 (N*C*N) ppm. $C_{21}H_{30}Cl_2N_2Ru$ (482.45): calcd. C 52.28, H 6.27; found C 51.90, H 6.32.

[(4-Methylhexyl)diphenylphosphane-κ*P*][η^6-(*p*-cymene)]RuCl_2 (4): [(*p*-cymene)RuCl_2]$_2$ (245 mg, 0.400 mmol) and (4-methylhexyl)diphenylphosphane (250 mg, 0.879 mmol) in toluene (10 mL) were stirred at room temperature for 4 h. The reacting mixture was concentrated, and the residue was washed with pentane and dried to afford a red powder (392 mg, 83%). ^{1}H NMR ($CDCl_3$, 500.13 MHz, 298 K): δ = 0.58 (d, $^{3}J_{H,H}$ = 6.3 Hz, 3 H, CHC*H*$_3$), 0.69 (t, $^{3}J_{H,H}$ = 7.2 Hz, 3 H, CH$_2$C*H*$_3$), 0.80 [d, $^{3}J_{H,H}$ = 7.1 Hz, 6 H, CH(C*H*$_3$)$_2$], 0.86–1.01 (m, 1 H + 1 H + 1 H, C*H*$_2$CH$_3$, PCH$_2$C*H*$_2$, PCH$_2$CH$_2$C*H*$_2$), 1.02–1.18 (m, 1 H + 1 H + 1 H + 1 H, C*H*$_2$CH$_3$, C*H*CH$_3$, PCH$_2$C*H*$_2$, PCH$_2$CH$_2$C*H*$_2$), 1.88 (s, 3 H, C*H*$_3$ *p*-cymene), 2.46–2.58 [m, 2 H + 1 H, PC*H*$_2$, C*H*(CH$_3$)$_2$], 5.07 (d, $^{3}J_{H,H}$ = 6.0 Hz, 2 H, *p*-cymene), 5.26 (d, $^{3}J_{H,H}$ = 5.8 Hz, 2 H, *p*-cymene), 7.43–7.51 (m, 6 H, Ph), 7.85–7.92 (m, 4 H, Ph), 7.43–7.51 (m, 6 H, Ph), 7.85–7.92 (m, 4 H, Ph) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 125.75 MHz, 298 K): δ = 11.3 (s, CH$_2$*C*H$_3$), 17.4 (s, *C*H$_3$ *p*-cymene), 19.0 (s, CH*C*H$_3$), 20.6 (d, $^{2}J_{C,P}$ = 8.9 Hz, PCH$_2$*C*H$_2$), 21.40 [s, CH(*C*H$_3$)$_2$], 21.41 [s, CH(*C*H$_3$)$_2$], 22.9 (d, $^{1}J_{C,P}$ = 28.5 Hz,

PCH_2), 29.4 (s, CH_2CH_3), 30.1 [s, $CH(CH_3)_2$], 33.8 (s, $CHCH_3$), 37.8 (d, $^3J_{C,P}$ = 11.7 Hz, $PCH_2CH_2CH_2$), 85.7 (d, $^2J_{C,P}$ = 5.3 Hz, *C*H *p*-cymene), 90.7 (d, $^2J_{C,P}$ = 3.4 Hz, *C*HC *p*-cymene), 93.6 (s, *p*-cymene), 108.1 (s, *p*-cymene), 128.4 (d, $^3J_{C,P}$ = 9.9 Hz, Ph C_{meta}), 130.6 (d, $^4J_{C,P}$ = 1.9 Hz, C_{para} Ph), 133.0 (d, $^1J_{C,P}$ = 42.0 Hz, C_{ipso} Ph), 133.1 (d, $^1J_{C,P}$ = 42.1 Hz, C_{ipso} Ph), 133.40 (d, $^2J_{C,P}$ = 8.3 Hz, C_{ortho} Ph), 133.43 (d, $^2J_{C,P}$ = 8.5 Hz, C_{ortho} Ph) ppm. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.45 MHz, 298 K): δ = 24.0 (s, PPh_2) ppm. $C_{29}H_{39}Cl_2PRu$ (590.57): calcd. C 59.5, H 6.99; found C 58.87, H 7.37.

X-ray Crystallography Analysis: Intensity data for compound **1** were collected with a Nonius Kappa CCD at 115 K. The structures were solved by direct methods (SIR92)[28] and refined with full-matrix, least-squares methods based on F^2 (SHELXL-97)[29] with the aid of the WINGX program.[30] All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were included in their calculated positions and refined with a riding model. Crystallographic data are reported in Table 7.

Table 7. Crystal data and structure refinement for **1**.

Formula	$C_{29}H_{35}Cl_2PRu$
M	586.51
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	7.59560(10)
b [Å]	10.99070(10)
c [Å]	16.7132(2)
α [°]	74.9330(6)
β [°]	83.1030(6)
γ [°]	86.0960(7)
V [Å^3]	4374.25(9)
Z	2
F(000)	604
D_{calcd} [g cm^{-3}]	1.457
Diffractometer	Nonius Kappa CCD
Scan type	ϕ rot. and ω scans
λ [Å]	0.71073
μ [mm^{-1}]	0.862
Crystal size [mm^3]	0.3 × 0.3 × 0.3
sin(θ)/λ max [Å^{-1}]	0.65
T; *k*	115
Index ranges	*h*: –9; 9 *k*: –14; 13 *l*: –21; 21
RC = reflections collected	11361
IRC = independent RC	6091 [*R*(int) = 0.0195]
IRCGT = IRC and [$I > 2\sigma(I)$]	5741
Refinement method	full-matrix least squares on F^2
data/restraints/param.	6091/0/299
R for IRCGT	R_1[a] = 0.035, wR_2[b] = 0.092
R for IRC	R_1[a] = 0.038, wR_2[b] = 0.093
Goodness-of-fit[c]	1.059
Δ*ρ* (max./min.) [e Å^{-3}]	1.730/–0.093

[a] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma 2(F_o^2 + (0.048P)^2 + 2.18P)]$. [c] Goodness of fit: $[\Sigma w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2}$.

CCDC-1023384 (for **1**) and -1056295 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Molecular Modeling: Geometry optimization was performed with Jaguar v. 5.5[31] at the DFT B3LYP/6-31G** level and use of the LANL2DZ effective core basis set for the metal. The equilibrium geometry was checked by a frequencies calculation. All calculations were performed with the aid of HPC resources from DSI-CCUB (Université de Bourgogne).

Supporting Information (see footnote on the first page of this article): NMR spectra of compounds **1** and **2** and of the intermediates.

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[1] For recent reviews, see: a) B. Therrien, *Coord. Chem. Rev.* **2009**, *253*, 493–519; b) L. Delaude, A. Demonceau, *Dalton Trans.* **2012**, *41*, 9257–9268; c) P. Kumar, R. K. Gupta, D. S. Pandey, *Chem. Soc. Rev.* **2014**, *43*, 707–733.

[2] See for instance: a) A. W. Stumpf, E. Saive, A. Demonceau, A. F. Noels, *J. Chem. Soc., Chem. Commun.* **1995**, 1127–1128; b) H. Nishiyama, K. Aoki, H. Itoh, T. Iwamura, N. Sakata, O. Kurihara, Y. Motoyama, *Chem. Lett.* **1996**, 1071–1072; c) C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1997**, 507–512; d) A. Fürstner, M. Picquet, C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1998**, 1315–1316; e) E. L. Dias, R. H. Grubbs, *Organometallics* **1998**, *17*, 2758–2767; f) F. Simal, A. Demonceau, A. F. Noels, *Tetrahedron Lett.* **1998**, *39*, 3493–3496; g) F. Simal, A. Demonceau, A. F. Noels, *Angew. Chem. Int. Ed.* **1999**, *38*, 538–540; *Angew. Chem.* **1999**, *111*, 559; h) L. Jafarpour, J. Huang, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 3760–3763; i) A. Fürstner, M. Liebl, C. W. Lehmann, M. Picquet, R. Kunz, C. Bruneau, D. Touchard, P. H. Dixneuf, *Chem. Eur. J.* **2000**, *6*, 1847–1857; j) L. Delaude, A. Demonceau, A. F. Noels, *Chem. Commun.* **2001**, 986–987; k) X. Sauvage, Y. Borguet, A. F. Noels, L. Delaude, A. Demonceau, *Adv. Synth. Catal.* **2007**, *349*, 255–265; l) A. B. Chaplin, P. J. Dyson, *Organometallics* **2007**, *26*, 2447–2455; m) L. Delaude, X. Sauvage, A. Demonceau, J. Wouters, *Organometallics* **2009**, *28*, 4056–4064.

[3] a) B. Therrien, T. R. Ward, M. Pilkington, C. Hoffmann, F. Gilardoni, J. Weber, *Organometallics* **1998**, *17*, 330–337; b) F. Simal, D. Jan, A. Demonceau, A. F. Noels, *Tetrahedron Lett.* **1999**, *40*, 1653–1656; c) A. Abele, R. Wursche, M. Klinga, B. Rieger, *J. Mol. Catal. A* **2000**, *160*, 23–33; d) K. Umezawa-Vizzini, I. Y. Guzman-Jimenez, K. H. Whitmire, T. R. Lee, *Organometallics* **2003**, *22*, 3059–3065; e) J. W. Faller, P. P. Fontaine, *Organometallics* **2005**, *24*, 4132–4138; f) D. J. Morris, A. M. Hayes, M. Wills, *J. Org. Chem.* **2006**, *71*, 7035–7044; g) D. Arquier, L. Vendier, K. Miqueu, J.-M. Sotiropoulos, S. Bastin, A. Igau, *Organometallics* **2009**, *28*, 4945–4957; h) B. Lastra-Barreira, J. Díez, P. Crochet, I. Fernández, *Dalton Trans.* **2013**, *42*, 5412–5420; i) R. Aznar, A. Grabulosa, A. Mannu, G. Muller, D. Sainz, V. Moreno, M. Font-Bardia, T. Calvet, J. Lorenzo, *Organometallics* **2013**, *32*, 2344–2362; j) P. Clavero, A. Grabulosa, M. Font-Bardia, G. Muller, *J. Mol. Catal. A* **2014**, *391*, 183–190.

[4] Ruthenium complexes with chelating arene carbene ligands have been described, see: a) B. Çetinkaya, S. Demir, I. Özdemir, L. Toupet, D. Sémeril, C. Bruneau, P. H. Dixneuf, *New J. Chem.* **2001**, *25*, 519–521; b) B. Çetinkaya, S. Demir, I. Özdemir, L. Toupet, D. Sémeril, C. Bruneau, P. H. Dixneuf, *Chem. Eur. J.* **2003**, *9*, 2323–2330.

[5] F. Nicks, R. Aznar, D. Sainz, G. Muller, A. Demonceau, *Eur. J. Org. Chem.* **2009**, 5020–5027.

[6] For leading references on the chemistry of phosphane–olefin ligands, see: a) M. Herberhold, K. Bauer, W. Milius, *J. Organomet. Chem.* **1997**, *545–546*, 267–275; b) J. Yin, M. P. Rainka, X.-X. Zhang, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 1162–1163; c) P. Maire, S. Deblon, F. Breher, J. Geier, C. Böhler, H. Rüegger, H. Schönberg, H. Grützmacher, *Chem. Eur. J.* **2004**, *10*, 4198–4205; d) R. Shintani, W.-L. Duan, T. Nagano, A. Okada, T. Hayashi, *Angew. Chem. Int. Ed.* **2005**, *44*, 4611–4614; *Angew. Chem.* **2005**, *117*, 4687; e) C. Thoumazet, L. Ricard, H. Grützmacher, P. Le Floch, *Chem. Commun.* **2005**, 1592–1594; f) G. Mora, S. Van Zutphen, C. Thoumazet, F. X. Le Goff, L. Ricard, H. Grützmacher, P. Le Floch, *Organometallics* **2006**, *25*, 5528–5532; g) C. Defieber, M. A. Ariger, P. Moriel, E. M. Carreira, *Angew. Chem. Int. Ed.* **2007**, *46*, 3139–3143; *Angew. Chem.* **2007**, *119*, 3200; h) J. C. Lewis, A. M. Berman, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2008**, *130*, 2493–2500; i) E. Drinkel, A. Briceño, R. Dorta, R. Dorta, *Organometallics* **2010**, *29*, 2503–2514; j) R. Shintani, R. Narui, Y. Tsutsumi, S. Hayashi, T. Hayashi, *Chem. Commun.* **2011**, *47*, 6123–6125.

[7] For N,S- and N,N-heterocyclic carbene–olefin ligands, see: a) F. E. Hahn, C. Holtgrewe, T. Pape, M. Martin, E. Sola, L. A. Oro, *Organometallics* **2005**, *24*, 2203–2209; b) E. F. Hahn, B. Heidrich, A. Hepp, T. Pape, *J. Organomet. Chem.* **2007**, *692*, 4630–4638; c) L. Benhamou, J. Wolf, V. César, A. Labande, R. Poli, N. Lugan, G. Lavigne, *Organometallics* **2009**, *28*, 6981–6993; d) C. Gandolfin, M. Heckenroth, A. Neels, G. Laurenczy, M. Albrecht, *Organometallics* **2009**, *28*, 5112–5121; e) N. Ding, W. Zhang, T. S. A. Hor, *Dalton Trans.* **2012**, *41*, 5988–5994.

[8] Only a few phosphane-conjugated diene ligands have been described, see: a) M. Herberhold, K. Bauer, W. Milius, *J. Organomet. Chem.* **1997**, *545–546*, 267–276; b) H. Kaddouri, V. Vicente, A. Ouali, F. Ouazzani, M. Taillefer, *Angew. Chem. Int. Ed.* **2009**, *48*, 333–336; *Angew. Chem.* **2009**, *121*, 339; A. Massard, V. Rampazzi, A. Perrier, E. Bodio, M. Picquet, P. Richard, J.-C. Hierso, P. Le Gendre, *Organometallics* **2012**, *31*, 947–958.

[9] a) M. Murakami, K. Itami, Y. Ito, *Organometallics* **1999**, *18*, 1326–1336; b) C. Elschenbroich, *Organometallics*, 3rd ed., Wiley-VCH, Weinheim, Germany, **2006**, p. 405–409.

[10] P. A. A. Klusener, L. Tip, L. Brandsma, *Tetrahedron* **1991**, *47*, 2041–2064.

[11] H. M. J. Wang, I. J. B. Lin, *Organometallics* **1998**, *17*, 972–975.

[12] a) L. Delaude, A. Demonceau, A. F. Noels, *Top. Organomet. Chem.* **2004**, *11*, 155–171; b) K. Severin, *Curr. Org. Chem.* **2006**, *10*, 217–224.

[13] a) F. Simal, A. Demonceau, A. F. Noels, *Tetrahedron Lett.* **1999**, *40*, 5689–5693; b) F. Simal, S. Sebille, A. Demonceau, A. F. Noels, R. Núñez, M. Abad, F. Teixidor, C. Viñas, *Tetrahedron Lett.* **2000**, *41*, 5347–5350; c) F. Simal, L. Wlodarczak, A. Demonceau, A. F. Noels, *Tetrahedron Lett.* **2000**, *41*, 6071–6074; d) F. Simal, L. Wlodarczak, A. Demonceau, A. F. Noels, *Eur. J. Org. Chem.* **2001**, 2689–2695; e) O. Tutusaus, C. Viñas, R. Núñez, F. Teixidor, A. Demonceau, S. Delfosse, A. F. Noels, I. Mata, E. Molins, *J. Am. Chem. Soc.* **2003**, *125*, 11830–11831; f) O. Tutusaus, S. Delfosse, A. Demonceau, A. F. Noels, C. Viñas, F. Teixidor, *Tetrahedron Lett.* **2003**, *44*, 8421–8425; g) B. De Clercq, F. Verpoort, *J. Organomet. Chem.* **2003**, *672*, 11–16; h) K. Thommes, B. Içli, R. Scopelliti, K. Severin, *Chem. Eur. J.* **2007**, *13*, 6899–6907; i) A. E. Díaz-Álvarez, P. Crochet, M. Zablocka, C. Duhayon, V. Cadierno, J.-P. Majoral, *Eur. J. Inorg. Chem.* **2008**, 786–794; j) R. J. Lundgren, M. A. Rankin, R. McDonald, M. Stradiotto, *Organometallics* **2008**, *27*, 254–258; k) M. A. Fernández-Zúmel, K. Thommes, G. Kiefer, A. Sienkiewicz, K. Pierzchala, K. Severin, *Chem. Eur. J.* **2009**, *15*, 11601–11607; l) R. P. Nair, T. H. Kim, B. J. Frost, *Organometallics* **2009**, *28*, 4681–4688; m) M. A. Fernández-Zúmel, G. Kiefer, K. Thommes, R. Scopelliti, K. Severin, *Eur. J. Inorg. Chem.* **2010**, 3596–3601; n) A. D. Phillips, K. Thommes, R. Scopelliti, C. Gandolfi, M. Albrecht, K. Severin, D. F. Schreiber, P. J. Dyson, *Organometallics* **2011**, *30*, 6119–6132; o) R. P. Nair, J. A. Pineda-Lanorio, B. J. Frost, *Inorg. Chim. Acta* **2012**, *380*, 96–103; p) Z. Liu, J. Xu, W. Ruan, C. Fu, H.-J. Zhang, T.-B. Wen, *Dalton Trans.* **2013**, *42*, 11976–11980.

[14] a) A. Richel, S. Delfosse, C. Cremasco, L. Delaude, A. Demonceau, A. F. Noels, *Tetrahedron Lett.* **2003**, *44*, 6011–6015; b) A. Richel, A. Demonceau, A. F. Noels, *Tetrahedron Lett.* **2006**, *47*, 2077–2081; c) L. Delaude, A. Demonceau, A. F. Noels, *Curr. Org. Chem.* **2006**, *10*, 203–215.

[15] a) J. Wolf, K. Thommes, O. Briel, R. Scopelliti, K. Severin, *Organometallics* **2008**, *27*, 4464–4474; b) K. Parkhomenko, L. Barloy, J.-B. Sortais, J.-P. Djukic, M. Pfeffer, *Tetrahedron Lett.* **2010**, *51*, 822–825.

[16] Y. Borguet, A. Richel, S. Delfosse, A. Leclerc, L. Delaude, A. Demonceau, *Tetrahedron Lett.* **2007**, *48*, 6334–6338.

[17] a) K. Matyjaszewski, J. Xia, *Chem. Rev.* **2001**, *101*, 2921–2990; b) M. Kamigaito, T. Ando, M. Sawamoto, *Chem. Rev.* **2001**, *101*, 3689–3745; c) N. V. Tsarevsky, K. Matyjaszewski, *Chem. Rev.* **2007**, *107*, 2270–2299; d) T. Pintauer, K. Matyjaszewski, *Chem. Soc. Rev.* **2008**, *37*, 1087–1097; e) T. Pintauer, K. Matyjaszewski, *Top. Organomet. Chem.* **2009**, *26*, 221–251; f) K. Matyjaszewski, N. V. Tsarevsky, *J. Am. Chem. Soc.* **2014**, *136*, 6513–6533.

[18] a) F. Simal, S. Sebille, L. Hallet, A. Demonceau, A. F. Noels, *Macromol. Symp.* **2000**, *161*, 73–85; b) F. Simal, D. Jan, A. Demonceau, A. F. Noels, in: *ACS Symposium Series*, 768, *Controlled/Living Radical Polymerization: Progress in ATRP, NMP and RAFT* (Ed.: K. Matyjaszewski), American Chemical Society, Washington, DC, **2000**, p. 223–233; c) F. Simal, D. Jan, L. Delaude, A. Demonceau, M.-R. Spirlet, A. F. Noels, *Can. J. Chem.* **2001**, *79*, 529–535; d) F. Simal, S. Delfosse, A. Demonceau, A. F. Noels, K. Denk, F. J. Kohl, T. Weskamp, W. A. Herrmann, *Chem. Eur. J.* **2002**, *8*, 3047–3052; e) L. Delaude, S. Delfosse, A. Richel, A. Demonceau, A. F. Noels, *Chem. Commun.* **2003**, 1526–1527; f) S. Delfosse, Y. Borguet, L. Delaude, A. Demonceau, *Macromol. Rapid Commun.* **2007**, *28*, 492–503.

[19] a) G. Maas, *Chem. Soc. Rev.* **2004**, *33*, 183–190; b) T. Werle, L. Schäffler, G. Maas, *J. Organomet. Chem.* **2005**, *690*, 5562–5569; c) S. Buck, G. Maas, *J. Organomet. Chem.* **2006**, *691*, 2774–2784; d) M. K.-W. Choi, W.-Y. Yu, M.-H. So, C.-Y. Zhou, Q.-H. Deng, C.-M. Che, *Chem. Asian J.* **2008**, *3*, 1256–1265; e) C. S. Gill, K. Venkatasubbaiah, C. W. Jones, *Adv. Synth. Catal.* **2009**, *351*, 1344–1354; f) M. Basato, C. Tubaro, A. Biffis, M. Bonato, G. Buscemi, F. Lighezzolo, P. Lunardi, C. Vianini, F. Benetollo, A. Del Zotto, *Chem. Eur. J.* **2009**, *15*, 1516–1526; g) B. Saha, T. Ghatak, A. Sinha, S. M. W. Rahaman, J. K. Bera, *Organometallics* **2011**, *30*, 2051–2058; h) S. Chanthamath, K. Phomkeona, K. Shibatomi, S. Iwasa, *Chem. Commun.* **2012**, *48*, 7750–7752; i) G. A. Ardizzoia, S. Brenna, S. Durini, B. Therrien, *Organometallics* **2012**, *31*, 5427–5437.

[20] a) D. Huber, A. Mezzetti, *Tetrahedron: Asymmetry* **2004**, *15*, 2193–2197; b) D. Huber, P. G. A. Kumar, P. S. Pregosin, A. Mezzetti, *Organometallics* **2005**, *24*, 5221–5223; c) D. Huber, P. G. A. Kumar, P. S. Pregosin, I. S. Mikhel, A. Mezzetti, *Helv. Chim. Acta* **2006**, *89*, 1696–1715; d) C. del Pozo, A. Corma, M. Iglesias, F. Sánchez, *Green Chem.* **2011**, *13*, 2471–2481; e) A. Grabulosa, A. Mannu, A. Mezzetti, G. Muller, *J. Organomet. Chem.* **2012**, *696*, 4221–4228.

[21] a) F. Simal, A. Demonceau, A. F. Noels, *Tetrahedron Lett.* **1998**, *39*, 3493–3496; b) F. Simal, A. Demonceau, A. F. Noels, D. R. T. Knowles, S. O'Leary, P. M. Maitlis, O. Gusev, *J. Organomet. Chem.* **1998**, *558*, 163–170; c) A. Tudose, A. Demonceau, L. Delaude, *J. Organomet. Chem.* **2006**, *691*, 5356–5365.

[22] a) A. F. Noels, A. Demonceau, *J. Phys. Org. Chem.* **1998**, *11*, 602–609; b) A. F. Noels, A. Demonceau, D. Jan, *Russ. Chem. Bull.* **1999**, *48*, 1206–1211; c) I. Dragutan, V. Dragutan, F. Ver-

poort, *Appl. Organomet. Chem.* **2014**, *28*, 211–215; d) F. Ding, Y.-G. Sun, F. Verpoort, V. Dragutan, I. Dragutan, *J. Mol. Catal. A* **2014**, *386*, 86–94.
[23] a) A. Demonceau, A. F. Noels, E. Saive, A. J. Hubert, *J. Mol. Catal. A* **1992**, *76*, 123–132; b) A. Demonceau, A. W. Stumpf, E. Saive, A. F. Noels, *Macromolecules* **1997**, *30*, 3127–3136; c) L. Delaude, A. Demonceau, A. F. Noels, *Macromolecules* **1999**, *32*, 2091–2103; d) D. Jan, L. Delaude, F. Simal, A. Demonceau, A. F. Noels, *J. Organomet. Chem.* **2000**, *606*, 55–64; e) L. Delaude, M. Szypa, A. Demonceau, A. F. Noels, *Adv. Synth. Catal.* **2002**, *344*, 749–756; f) L. Delaude, A. Demonceau, A. F. Noels, *Macromolecules* **2003**, *36*, 1446–1456.
[24] a) A. Hafner, A. Mühlebach, P. A. van der Schaaf, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2121–2124; *Angew. Chem.* **1997**, *109*, 2213; b) M. Picquet, C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1998**, 2249–2250; c) D. Sémeril, C. Bruneau, P. H. Dixneuf, *Helv. Chim. Acta* **2001**, *84*, 3335–3341; d) B. De Clercq, F. Verpoort, *J. Mol. Catal. A* **2002**, *180*, 67–76; e) D. Sémeril, C. Bruneau, P. H. Dixneuf, *Adv. Synth. Catal.* **2002**, *344*, 585–595; f) R. Castarlenas, D. Sémeril, A. F. Noels, A. Demonceau, P. H. Dixneuf, *J. Organomet. Chem.* **2002**, *663*, 235–238; g) T. Opstal, K. Couchez, F. Verpoort, *Adv. Synth. Catal.* **2003**, *345*, 393–401; h) R. Castarlenas, I. Alaoui-Abdallaoui, D. Sémeril, B. Mernari, S. Guesmi, P. H. Dixneuf, *New J. Chem.* **2003**, *27*, 6–8; i) Y. Zhang, D. Wang, P. Lönnecke, T. Scherzer, M. R. Buchmeiser, *Macromol. Symp.* **2006**, *236*, 30–37; j) M. R. Buchmeiser, D. Wang, Y. Zhang, S. Naumov, K. Wurst, *Eur. J. Inorg. Chem.* **2007**, 3988–4000; k) N. Ledoux, B. Allaert, F. Verpoort, *Eur. J. Inorg. Chem.* **2007**, 5578–5583; l) M. Ahr, C. Thieuleux, C. Copéret, B. Fenet, J.-M. Basset, *Adv. Synth. Catal.* **2007**, *349*, 1587–1591; m) Y. Kong, S. Xu, H. Song, B. Wang, *Organometallics* **2012**, *31*, 5527–5532.
[25] a) C. Bruneau, P. H. Dixneuf, *Chem. Commun.* **1997**, 507–512; b) F. Alonso, I. P. Beletskaya, M. Yus, *Chem. Rev.* **2004**, *104*, 3079–3159.
[26] a) P. Le Gendre, V. Comte, A. Michelot, C. Moïse, *Inorg. Chim. Acta* **2003**, *350*, 289–292; b) K. Melis, F. Verpoort, *J. Mol. Catal. A* **2003**, *194*, 39–47; c) S. Doherty, J. G. Knight, R. K. Rath, W. Clegg, R. W. Harrington, C. R. Newman, R. Campbell, H. Amin, *Organometallics* **2005**, *24*, 2633–2644; d) P. Pelagatti, A. Bacchi, M. Balordi, S. Bolaño, F. Calbiani, L. Elviri, L. Gonsalvi, C. Pelizzi, M. Peruzzini, D. Rogolino, *Eur. J. Inorg. Chem.* **2006**, 2422–2436; e) S. Ye, W. K. Leong, *J. Organomet. Chem.* **2006**, *691*, 1117–1120; f) C. S. Yi, R. Gao, *Organometallics* **2009**, *28*, 6585–6592; g) K.-C. Cheung, W.-L. Wong, M.-H. So, Z.-Y. Zhou, S.-C. Yan, K.-Y. Wong, *Chem. Commun.* **2013**, *49*, 710–712.
[27] a) F. Nicks, L. Libert, L. Delaude, A. Demonceau, *Aust. J. Chem.* **2009**, *62*, 227–231; b) Q. Willem, F. Nicks, X. Sauvage, L. Delaude, A. Demonceau, *J. Organomet. Chem.* **2009**, *694*, 4049–4055; c) M. Hans, Q. Willem, J. Wouters, A. Demonceau, L. Delaude, *Organometallics* **2011**, *30*, 6133–6142.
[28] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.
[29] G. M. Sheldrick, Institute for Inorganic Chemistry, University of Göttingen, Germany, **1998**.
[30] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
[31] Jaguar 5.5, *Schrodinger*, LLC, Portland, Oregon, **2003**.

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