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Dicationic ruthenium(II) complexes containing bridged η^1:η^6-phosphinoarene ligands for the ring-opening metathesis polymerization

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Abstract

Tertiary phosphines with pendant arenes R_2PR' (R = Cy, Ph; R′ = CH_2CH_2Ph or CH_2CHPh_2) (**1**–**4**) were synthesized and converted to the corresponding chelating ruthenium(II) complexes [$RuCl_2(\eta^1{:}\eta^6\text{-}R_2PR')$] (**1a**–**4a**). Halide exchange yielded [$RuI_2(\eta^1{:}\eta^6\text{-}R_2PR')$] (**1b**,**3b**), which were structurally characterized by single crystal X-ray diffraction. The systems (**1a**,**2a**,**4a**) were activated for ROMP of norbornene by addition of a diazo compound (trimethylsilyldiazomethane) and $AgBF_4$ (A), by a diazo compound alone (B) or by a combination of the sodium salt $NaB(Ar_f)_4$(Ar_f = 3,5-$(CF_3)_2C_6H_3$) and methanol (C). The influence of the thereby created differing number of accessible coordination sites on the polymerization activity and the polymer microstructure (*cis*/*trans* ratio) was investigated. The nucleophilicity of the counter ion was found to play a crucial role in terms of catalytic activity.

Keywords: Phosphine ligands; Ruthenium(II) complexes; Chelating complexes; Metathesis; Norbornene

1. Introduction

Over the past decades, olefin metathesis reactions have attracted growing interest from different fields. For instance, ring closing metathesis (RCM), acyclic diene metathesis (ADMET) or ring-opening metathesis polymerization (ROMP) have opened a new and elegant approach to low molecular weight compounds as well as to a wide variety of polymer materials [1]. Attention has been particularly focused on ruthenium-based catalytic systems due to their tolerance towards functional groups [2].

Ruthenium(II) carbene complexes of the type [$(PCy_3)_2Cl_2Ru{=}CH{-}CH{=}CPh_2$] and [$(PCy_3)_2$-$Cl_2Ru{=}CHPh$] (Cy = cyclohexyl) (Grubbs' catalyst) were used for the RCM of dienes, ROM of olefins or for ROMP [3–5]. Fürstner et al. [6] introduced cationic allenylidene ruthenium (II) complexes like [$Ru{=}C{=}C{=}CR_2(PCy_3)$ (arene)PF_6] as excellent catalysts for RCM. Phosphinoarene ruthenium(II) dichlorides [Ru-Cl_2(arene)(PR_3)] (PR_3 = phosphine) were already used by Hafner et al. [7,8] and Demonceau et al. [9] for ROMP of strained cyclic olefins like norbornene or even cyclooctene-type

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monomers where the double bond is less strained. In the case of ruthenium(II) dichlorides, the activation, i.e. the in situ formation of carbene complexes, is performed by the addition of diazo compounds like trimethylsilyldiazomethane (TMSD) [9], by heating or treatment with UV light [7,8].

Apart from the generation of carbene species, all these procedures involve the decoordination of either the phosphine ligand or the aromatic moiety to form flexible complexes with a low degree of control over the catalytic process. This drawback might be overcome by utilizing more rigid ligand frameworks, for instance phosphinoarene chelates, which are bound to the metal in a (η^1:η^6) fashion. Complexes of this type have been recently introduced by Therrien et al. [10] and Simal et al. [11]. First applications include the atom transfer radical polymerization (ATPR) [12] of vinyl monomers, olefin cyclopropanation and olefin metathesis [13], where the influence of chelating and non-chelating catalyst geometries was discussed [11].

In order to monitor the effect of increasing steric interaction between substrate and ligand sphere on activity and regioselectivity in metathesis reactions, we synthesized a series of phosphine ligands: 2-phenyl-1-diphenylphosphinoethane (**1**) (PDPPE) [10], 2-phenyl-1-dicyclohexylphosphinoethane (**2**) (PDCyPE) [14], 2,2-diphenyl-1-diphenylphosphinoethane (**3**) (DPDPPE) and 2,2-diphenyl-1-dicyclohexylphosphinoethane (**4**) (DPDCyPE) [15], which were subsequently converted to new chelating complexes [$RuCl_2(\eta^1:\eta^6$-1)] (**1a**), [$RuCl_2(\eta^1:\eta^6$-2)] (**2a**), [$RuCl_2(\eta^1:\eta^6$-3)] (**3a**) and [$RuCl_2(\eta^1:\eta^6$-4)] (**4a**) to be tested in the ROMP of norbornene. By applying several activation techniques we obtained catalytically active species which differ from the number of available coordination sites and, thus, the degree of steric interaction between ligand, growing polymer chain and coordinated monomer. This paper is focused on synthetic and structural aspects as well as on a discussion of first polymerization results.

2. Experimental

2.1. Materials

All reactions were performed under argon using standard Schlenk or vacuum-line techniques. Solvents were freshly distilled from standard drying agents and kept under argon. Norbornene, styrene (derivatives), dicyclohexylphosphine, 2-phenylethylbromide were reagent grade and used without further purification. $[RuCl_2(C_6H_5COOEt)]_2$ [10], DPDCyPE [15] and $NaB(Ar_f)_4$ (Ar_f = 3,5-$(CF_3)_2C_6H_3$) [16] were prepared according to literature procedures.

2.2. Ligands and complexes

2.2.1. Diphenylphospine, $(C_6H_5)_2PH$ [17]

50 g (0.19 mol) triphenylphosphine was dissolved in 500 ml dried and degassed THF and treated with 2.75 g (0.39 mmol) of lithium shavings. The mixture was stirred at room temperature until the lithium was dissolved. The deep-red solution was carefully hydrolyzed by dropwise addition of a stochiometric amount of degassed water (10 ml). After 1 h of additional stirring, the solvent was removed and the product was isolated by vacuum distillation. Yield 28.4 g (80%). ^{1}H NMR δ ($CDCl_3$): 7.63 ppm (m, 4H, Ar), 7.42 ppm (m, 6H, Ar). ^{31}P NMR δ ($CDCl_3$): -39.5 ppm.

2.2.2. 2-Phenyl-1-diphenylphosphinoethane (*1*)

6 ml (34 mmol) diphenylphosphine, 3.9 ml (34 mmol) styrene (free of inhibitor) and 280 mg (1.71 mmol) α,α'-azobis(isobutyronitrile) (AIBN) were dissolved in 20 ml degassed diethyl ether and irradiated with UV light for 24 h. The volatile materials were removed in vacuum, the oily residue was recrystallized from ethanol to afford colourless crystals. Yield 8.5 g (86%). ^{1}H NMR δ ($CDCl_3$): 7.46 ppm (m, 4H, Ar), 7.32 ppm (m, 6H, Ar), 7.25 ppm (m, 2H, Ar), 7.18 ppm (m, 3H, Ar), 2.73 ppm (m, 2H,

CH_2), 2.38 ppm (m, 2H, CH_2). ^{31}P NMR δ ($CDCl_3$): −14.8 ppm. MS (EI) m/z (rel intensity): 290 ([M^+], 100), 262 (39), 186 (24), 121 (59), 108 (32), 91 (16), 77 (24), 51 (18).

2.2.3. 2-Phenyl-1-dicyclohexylphosphinoethane (2)

To a solution of 4 g (20 mmol) dicyclohexylphosphine in 20 ml of dry THF, 12.5 ml of a 1.6 M solution of *n*-butyllithium in THF (20 mmol) was added at −20°C. The deep-red solution was stirred at room temperature for 1 h. At 0°C, 2.8 ml (20 mmol) 2-phenylethylbromide was slowly added and the solution became colorless. After treatment with a degassed, saturated aqueous solution of ammoniumchloride, the organic phase was separated and dried over Na_2SO_4. The solvent was evaporated. Since attempts for crystallization failed, the oily residue was used for complexation without further purification (purity about 75% according to ^{31}P NMR). Yield: 2.9 g (48%). ^{1}H NMR δ ($CDCl_3$): 7.20 ppm (m, 2H, Ar), 7.14 ppm (m, 3H, Ar), 2.87 ppm (m, 2H, CH_2), 2.68 ppm (m, 2H, CH_2), 1.70–1.16 ppm (several m, 22H, Cy). ^{31}P NMR δ ($CDCl_3$): −2.4 ppm. MS (EI) m/z (rel intensity): 302 ([M^+], 100), 219 (16), 117(42), 83 (9).

2.2.4. 2,2-Diphenyl-1-diphenylphosphinoethane (3)

DPDPPE was synthesized analogously to PDPPE (1) from 4 ml (23 mmol) diphenylphosphine, 4.1 ml (23 mmol) of (1,1′)-diphenylethene and 186 mg (1.1 mmol) of AIBN. Recrystallization from ethanol afforded colourless needles. Yield: 5.5 g (65%). ^{1}H NMR δ ($CDCl_3$): 7.37 ppm (m, 4H, Ar), 7.21 ppm (m, 6H, Ar), 3.93 ppm (m, 1H, CH), 2.83 ppm (d, 2H, CH_2). ^{31}P NMR δ ($CDCl_3$): −20.1 ppm. MS (EI) m/z (rel intensity): 366 ([M^+], 9), 262 (100), 199 (15), 121 (34), 77 (11).

2.2.5. $[RuCl_2(\eta^1{:}\eta^6\text{-}PR_2R')]$ (1a–4a)

To a solution of the phosphine **1**–**4** (1.55 mmol) in dry chloroform, 500 mg (0.77 mmol) $[RuCl_2(\eta^6\text{-}C_6H_5COOEt)]_2$ was added. After stirring at room temperature, the solution became clear and was refluxed until the chelating process was complete (according to ^{31}P NMR of the reaction solution). The addition of *n*-pentane caused the precipitation of the chelating complexes in quantitative yield.

2.2.5.1. $[RuCl_2(\eta^1{:}\eta^6\text{-}(PDPPE))]$ (1a)

450 mg (1.55 mmol) PDPPE (**1**), orange-colored solid; ^{1}H NMR δ ($CDCl_3$): 7.87 ppm (m, 4H, Ar), 7.50 ppm (m, 6H, Ar), 6.24 ppm (m, 2H, Ar), 6.04 ppm (m, 1H, Ar), 5.00 ppm (d, 2H, Ar), 2.63 ppm (m, 2H, CH_2), 2.63 ppm (m, 2H, CH_2). ^{31}P NMR δ ($CDCl_3$): 46.8 ppm. Anal. Calcd. for **1a**: C, 51.95; H, 4.11. Found: C, 51.43; H, 4.13.

2.2.5.2. $[RuCl_2(\eta^1{:}\eta^6\text{-}(PDCYPE))]$ (2a)

268 mg (1.55 mmol) PDCyPE (**2**), reddish-brown solid; ^{1}H NMR δ ($CDCl_3$): 6.22 ppm (m, 1H, Ar), 5.83 ppm (m, 2H, Ar), 5.04 ppm (m, 2H, Ar), 2.93 ppm (m, 2H, CH_2), 2.61 ppm (m, 2H, CH_2), 2.31–1.29 ppm (several m, 22H, Cy). ^{31}P NMR δ ($CDCl_3$): 70.4 ppm. Anal. Calcd for **2a**: C, 50.63; H, 6.54. Found: C, 51.07; H, 6.74.

2.2.5.3. $[RuCl_2(\eta^1{:}\eta^6\text{-}(DPDPPE))]$ (3a)

567 mg (1.55 mmol) DPDPPE (**3**), orange, microcrystalline solid; ^{1}H NMR δ ($CDCl_3$): 8.02 ppm (m, 2H, Ar), 7.58 ppm (m, 2H, Ar), 7.47 ppm (m, 3H, Ar), 7.36 ppm (m, 8H, Ar), 6.23 ppm (m, 1H, Ar), 6.15 ppm (m, 1H, Ar), 6.00 ppm (m, 1H, Ar), 5.39 ppm (m, 1H, Ar), 4.94 ppm (m, 1H, Ar), 4.00 ppm (m, 2H, CH_2), 3.76 ppm (m, 1H, CH). ^{31}P NMR δ ($CDCl_3$): 33.5 ppm. Anal. Calcd. for **3a**: C, 57.99; H, 4.28. Found: C, 57.35; H, 4.01.

2.2.5.4. $[RuCl_2(\eta^1{:}\eta^6\text{-}(DPDCYPE))]$ (4a)

486 mg (1.55 mmol) DPDCyPE (**4**), light-orange solid; ^{1}H NMR δ ($CDCl_3$): 7.37 ppm (m, 5H, Ar), 6.25 ppm (m, 1H, Ar), 6.12 ppm (m, 1H, Ar), 5.65 ppm (m, 1H, Ar), 5.18 ppm (m, 2H, Ar), 3.94 ppm (m, 1H, CH), 3.36–3.13 ppm (m,

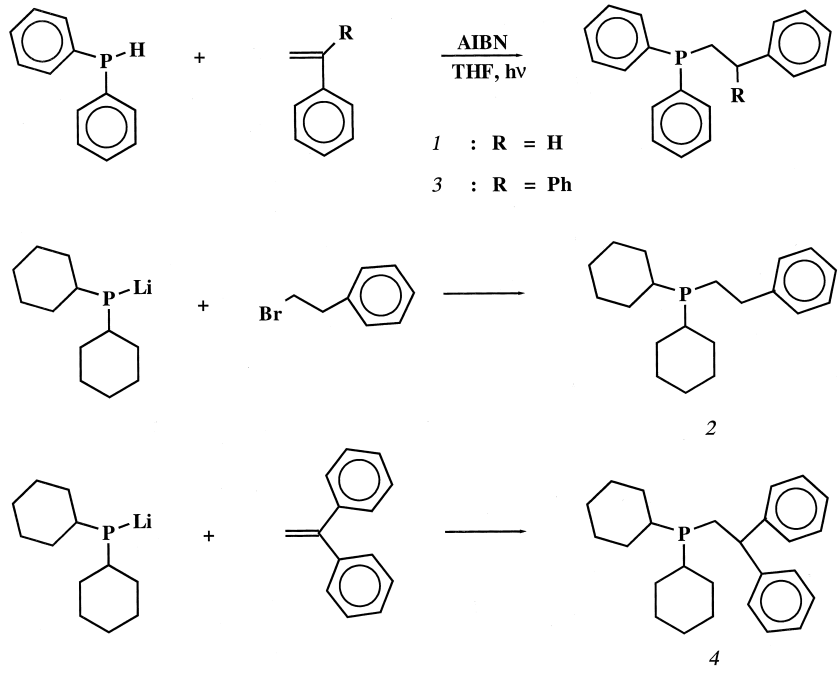

Fig. 1. Synthesis of phosphine ligands with pendant arene moieties (**1**–**4**).

2H, CH_2), 2.41–1.28 ppm (several m, 22H, Cy). ^{31}P NMR δ ($CDCl_3$): 53.4 ppm. Anal. Calcd. for **4a**: C, 56.72; H, 6.36. Found: C, 56.14; H, 6.24.

2.2.6. Halide exchange

0.043 mmol of **1a** or **3a** were suspended in 20 ml of degassed acetone. After adding 195 mg (1.29 mmol) NaI, the mixture was stirred for

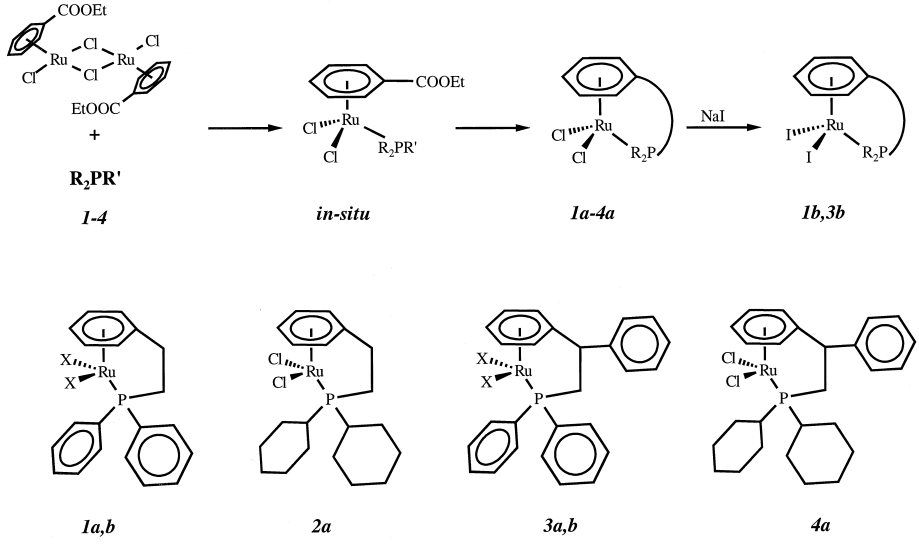

Fig. 2. Synthesized chelating complexes (a: X = Cl; b: X = I).

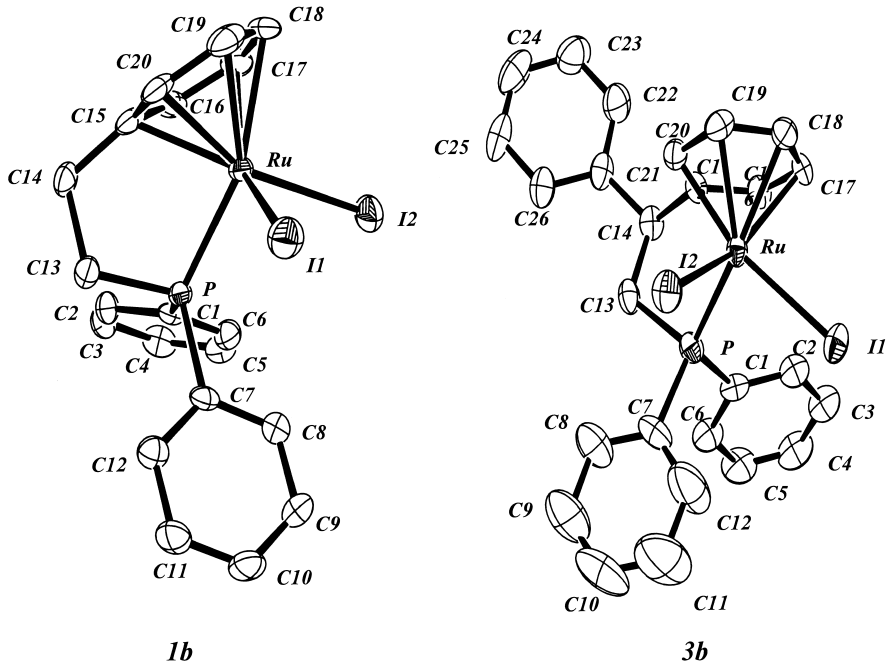

Fig. 3. Molecular structure of complexes **1b** and **3b** (ORTEP plot). **1b** represents only one of the two independent species present in the unit cell. In the case of **3b**, the enclosed acetone molecule has been omitted. Thermal ellipsoids are at the 50% probability level.

2 h at room temperature. The solvent was removed and the residue dissolved in CH_2Cl_2 in order to remove NaCl and excess NaI by filtration. CH_2Cl_2 was evaporated and single crystals

Table 1
Crystal data and structure refinement for **1b**

$[RuI_2(\eta^1{:}\eta^6-1)]$ (**1b**)			
Empirical formula	$C_{20}H_{19}I_2PRu$	Crystal size (mm)	$0.38 \times 0.20 \times 0.12$
Formula weight	645.19	Θ range (°)	2.74–25.00
Temperature (K)	193(2)	Index ranges	$17\Delta h\Delta$-14, $17\Delta k\Delta$-17, $11\Delta l\Delta$-11
Wavelength (Å)	0.71073	Reflections collected/unique	8071/6566 [$R_{int} = 0.0212$]
Crystal system	triclinic		
Space group	P-1	Refinement method	Full-matrix least-squares on F^2
Unit cell dimensions (Å, °)	$a = 14.385(4)$, $\alpha = 95.67(2)$	Data/restraints/parameters	6566/36/433
	$b = 14.923(4)$, $\beta = 99.40(3)$	Goodness-of-fit on F^2	1.023
	$c = 9.513(3)$, $\gamma = 99.36(2)$	Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0370$, $wR2 = 0.0874$
Volume (Å^3)	1971.3(10)	R indices (all data)	$R1 = 0.0435$, $wR2 = 0.0905$
Z, calculated density (g/cm^3)	4, 2.174	Largest diffraction peak and hole (e/Å^{-3})	0.950 and −1.971
Absorption coefficient (mm^{-1})	4.008		
F (000)	1216		

Data collection, cell refinement and data reduction were performed with TEXSAN (Molecular Structure Corporation, 1993). A psi-scan absorption correction was performed, $0.579 < T < 0.786$ [28]. Intensities were corrected for Lorentz and polarization effects. For structure solution SHELXS-97 and structure refinement SHELXL-97 (both Sheldrick, 1997) were used. Molecular Graphics: ORTEP III. Non-hydrogen atom positions were obtained with direct methods and anisotropically refined. Hydrogen atoms were refined on calculated positions. Displacement factors of the H atoms were 1.2 × to that of the host atom. There are two independent $C_{20}H_{19}I_2PRu$ molecules (and their symmetry equivalents) in one unit cell, $Z = 4$.

of $[RuI_2(\eta^1{:}\eta^6\text{-(PDPPE)})]$ (**1b**) and $[RuI_2(\eta^1{:}\eta^6\text{-(DPDPPE)})]$ (**3b**) were grown from acetone by slow evaporation of the solvent.

2.3. Polymerization procedure

In a typical polymerization experiment, 5.6×10^{-2} mmol of $[RuCl_2(\eta^1{:}\eta^6\text{-}PR_2R')]$ (**1a**,**2a**,**4a**) was dissolved in dry CH_2Cl_2. Sodium salt (133 mg (0.15 mmol) $NaB(Ar_f)_4$) or silver salt (32.8 mg (0.17 mmol) $AgBF_4$ or 57.7 mg (0.17 mmol) $AgSbF_6$) were added (methods A,C), the solution was filtered under argon and 1 g (10.6 mmol) norbornene was introduced. Thereafter, 1 ml of a 0.2 M solution of TMSD in hexanes/CH_2Cl_2 (0.2 mmol TMSD) (methods A,B) or 0.5 ml dry methanol (method C) was added and the mixture was stirred at room temperature. The polymer was precipitated into methanol, washed thoroughly with methanol and dried under vacuum at room temperature.

2.4. Physical measurements

^1H and ^{31}P NMR spectra were recorded on a Bruker AMX 500 spectrometer; ^1H chemical shifts are given in ppm relative to internal standard TMS, ^{31}P chemical shifts were referenced to external 85% H_3PO_4. Mass Spectra were recorded on a Varian GC/MS 2000. Elemental analyses were performed in the Microanalytical Section of the University of Ulm. X-ray structure determination was carried out on a Rigaku AFC7S diffractometer. The measurements utilized Mo($K\alpha$) radiation (wavelength 0.71073 Å; fine-focused sealed tube) with a graphite monochromator.

3. Results and discussion

3.1. Ligand and complex synthesis

Phosphine ligands with pendant arene groups (PR_2R') were prepared (Fig. 1) starting from secondary phosphines and styrene (derivatives). The tertiary phosphines (PR_2R', **1** and **3** [15]) were formed in a radical reaction upon addition

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$) for **1b**

1b	*X*	*Y*	*Z*	U_{eq}
I1	1850(1)	2604(1)	2411(1)	30(1)
I2	1014(1)	4079(1)	5469(1)	32(1)
I3	3213(1)	7463(1)	3396(1)	37(1)
I4	3700(1)	5671(1)	602(1)	40(1)
Ru1	2680(1)	3570(1)	5046(1)	21(1)
Ru2	2155(1)	6373(1)	1044(1)	21(1)
P1	2250(1)	2357(1)	6298(2)	22(1)
P2	2449(1)	7384(1)	−608(2)	19(1)
C1	2793(4)	1343(4)	6013(7)	25(1)
C2	3288(5)	1213(4)	4898(7)	29(1)
C3	3715(5)	448(5)	4726(8)	36(2)
C4	3668(5)	−185(5)	5690(8)	39(2)
C5	3179(5)	−57(5)	6832(8)	39(2)
C6	2743(5)	700(5)	6979(7)	31(2)
C7	1026(4)	1847(4)	6360(7)	26(1)
C8	426(6)	1435(7)	5123(9)	63(3)
C9	−509(6)	1036(8)	5124(10)	73(3)
C10	−840(5)	1004(6)	6385(9)	45(2)
C11	−255(5)	1387(5)	7631(9)	40(2)
C12	678(5)	1816(5)	7636(8)	34(2)
C13	2802(5)	2861(5)	8133(7)	30(1)
C14	3840(5)	3330(5)	8111(8)	37(2)
C15	3869(4)	3869(5)	6834(7)	31(2)
C16	3451(5)	4654(5)	6722(8)	35(2)
C17	3376(5)	5059(5)	5433(8)	37(2)
C18	3672(5)	4668(5)	4223(9)	42(2)
C19	4073(5)	3868(5)	4320(8)	38(2)
C20	4221(5)	3489(5)	5606(8)	37(2)
C21	2000(4)	8454(4)	−394(6)	21(1)
C22	1225(4)	8634(4)	−1342(7)	26(1)
C23	892(5)	9453(5)	−1150(7)	31(1)
C24	1324(5)	10109(5)	−14(8)	35(2)
C25	2107(5)	9941(5)	946(8)	33(2)
C26	2434(5)	9123(4)	758(7)	29(1)
C27	3630(4)	7745(4)	−1015(7)	24(1)
C28	4389(5)	8153(5)	87(7)	34(2)
C29	5296(5)	8442(6)	−189(8)	42(2)
C30	5463(5)	8334(6)	−1569(9)	43(2)
C31	4715(5)	7944(5)	−2683(8)	38(2)
C32	3804(5)	7651(4)	−2404(7)	29(1)
C33	1735(4)	6731(4)	−2274(7)	25(1)
C34	743(4)	6266(5)	−1981(7)	28(1)
C35	840(4)	5959(4)	−527(7)	27(1)
C36	1234(4)	5169(4)	−242(8)	32(2)
C37	1425(5)	4957(5)	1188(10)	45(2)
C38	1258(5)	5526(6)	2335(9)	46(2)
C39	883(5)	6336(6)	2078(8)	40(2)
C40	644(4)	6520(5)	655(7)	31(2)

Table 3
Crystal data and structure refinement for **3b** · acetone

$[RuI_2(\eta^1{:}\eta^6-3)]\cdot$ acetone			
Empirical formula	$C_{29}H_{29}I_2OPRu$	Crystal size (mm)	$0.25\times0.24\times0.12$
Formula weight	779.36	Θ range (°)	2.71–25.00
Temperature (K)	193(2)	Index ranges	$15\Delta h\Delta0$, $17\Delta k\Delta0$, $17\Delta l\Delta$-18
Wavelength (Å)	0.71073	Reflections collected/unique	4758/4549 [$R_{int}=0.0401$]
Crystal system	monoclinic		
Space group	P 21/c	Refinement method	Full-matrix least-squares on F^2
Unit cell dimensions (Å, °)	$a=12.799(5)$, $\alpha=90$	Data/restraints/parameters	4758/27/307
	$b=15.032(6)$, $\beta=110.56(2)$	Goodness-of-fit on F^2	1.043
	$c=15.547(4)$, $\gamma=90$	Final R indices [$I>2\sigma(I)$]	$R1=0.0452$, $wR2=0.1012$
Volume (Å^3)	2800.6(17)	R indices (all data)	$R1=0.0576$, $wR2=0.1066$
Z, calculated density (g/cm^3)	4, 1.848	Largest diff. peak and hole (e/Å^{-3})	0.741 and −0.792
Absorption coefficient (mm^{-1})	2.841		
F (000)	1504		

Data collection, cell refinement and data reduction were performed with TEXSAN (Molecular Structure, 1993). A psi-scan absorption correction was performed, $0.700<T<0.997$ [28]. Intensities were corrected for Lorentz and polarization effects. For structure solution SHELXS-97 and structure refinement SHELXL-97 (both Sheldrick, 1997) were used. Molecular Graphics: ORTEP III. Non-hydrogen atom positions were obtained with direct methods and anisotropically refined. Hydrogen atoms were refined on calculated positions. Displacement factors of the H atoms were 1.2 × to that of the host atom. The acetone molecule present within the unit cell is more or less disordered as can be seen from the values of the anisotropic displacement parameters.

of AIBN and treatment with either UV light or by heating up [10]. A second possibility is to use metal phosphides (metal = sodium, potassium or lithium, phosphides = diphenylphosphide or dicyclohexylphosphide) and add either 2-phenylethylbromide (**2**) or a styrene(derivative) (**4**) (Fig. 1) [14,15].

This variety of reaction pathways allows access to phosphine ligands with different substitution patterns at the pendant arene moiety or in the bridge.[1]

Arene ruthenium(II) complexes $[RuCl_2(arene)]_2$ (arene = C_6H_6, PhMe, *p*-$C_6H_4Me_2$, 1,3,5,-$C_6H_3Me_3$ or *p*-$MeC_6H_4CHMe_2$) are accessible by dehydrogenation of the corresponding cyclohexadienes with an ethanolic solution of ruthenium(III) trichloride [19,20]. These complexes are used as precursor for the synthesis of phosphinoarene ruthenium(II) dichlorides $[RuCl_2(arene)PR_3]$ (PR_3 = tertiary phosphines): addition of tertiary phosphines to a suspension of the dimeric arene ruthenium(II) complexes $[RuCl_2(arene)]_2$ cleaves the chlorine bridges to afford orange to red, air-stable phosphinoarene ruthenium(II) dichloride complexes $[RuCl_2(arene)PR_3]$ [9,21] (Fig. 2).

Even in the case of electron-rich ligands, the chelating effect was insufficient for the desired displacement of the coordinated arene, which is necessary in order to create the corresponding chelating complexes $[RuCl_2(\eta^1{:}\eta^6\text{-}PR_2R')]$ (**1a**–**4a**)[10,18a,18b]. Examples for the problems with arene displacement reactions at ruthenium(II) are known from the literature [20]. A strategy to facilitate arene exchange has been proposed by Therrien et al. [10] who suggested the use of labile ruthenium(II) arene dimers comprising of electron-poor arenes like C_6H_5COOEt, which were expected to be more easily replaced by the pendant arene group (Fig. 2). Accordingly, we obtained the phosphinoarene ruthenium(II) dichloride complexes $[RuCl_2(\eta^6\text{-}C_6H_5COOEt)(PR_2R')]$ by reacting $[RuCl_2(arene)]_2$ (arene = C_6H_5COOEt) and the desired phosphines **1**–**4** in chloroform at room

[1] These included $R_2PCH_2CH_2Ar$ (R = Ph, Cy; Ar = 2,5-$C_6H_3Me_2$, 2,4,6-$C_6H_2Me_3$ or 4-$C_6H_4C(CH_3)_3$ or R_2PCHR'-CH_2Ar (R = Ph, Cy; R′ = Me, Ph; Ar = Ph); see also Refs. [18a,18b].

temperature [10]. After refluxing these solutions, the chelating complexes [$RuCl_2(\eta^1{:}\eta^6\text{-}PR_2R')$] (**1a**–**4a**) precipitated by the addition of *n*-pentane to yield red microcrystalline solids (Fig. 2). All phosphines were observed to act as ($\eta^1{:}\eta^6$)-chelates, and no substitution pattern at the arene or in the bridge hindered the exchange process. Single crystals of **1b** and **3b** were grown after halide exchange by slow evaporation of an acetone solution. The structure of [$RuI_2(\eta^1{:}\eta^6$-1)] (**1b**) and [$RuI_2(\eta^1{:}\eta^6$-3)] (**3b**) was determined by X-ray crystallography and is presented as ORTEP plot (Fig. 3). The unit cell of **1b** encloses two independent molecules (and their symmetry equivalents). In the case of **3b**, an acetone molecule is present in the unit cell that is more or less disordered — as can be seen from the values of the anisotropic displacement parameters. Crystallographic data and structure refinement for **1b** and **3b** are given in Tables 1 and 2 (**1b**) and Tables 3 and 4 (**3b**).

Table 4
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for **3b**

3b · Acetone	*X*	*Y*	*Z*	U_{eq}
I1	3073(1)	1349(1)	4568(1)	37(1)
I2	3316(1)	−589(1)	6273(1)	41(1)
Ru	4310(1)	1027(1)	6361(1)	26(1)
P	3001(2)	1671(1)	6873(1)	30(1)
O	8388(10)	1823(10)	8157(10)	182(5)
C1	2647(6)	2849(5)	6601(5)	34(2)
C2	3026(6)	3311(5)	5992(5)	39(2)
C3	2693(7)	4186(5)	5749(6)	45(2)
C4	1993(8)	4595(5)	6136(6)	55(2)
C5	1636(8)	4156(6)	6746(6)	54(2)
C6	1958(6)	3275(5)	6978(5)	42(2)
C7	1634(7)	1202(5)	6704(6)	44(2)
C8	1351(10)	894(10)	7403(11)	111(5)
C9	258(12)	578(11)	7234(14)	145(7)
C10	−494(11)	550(9)	6389(12)	98(5)
C11	−214(11)	862(13)	5718(10)	134(7)
C12	862(10)	1178(11)	5874(8)	108(5)
C13	3735(6)	1627(5)	8131(4)	33(2)
C14	4953(6)	1919(4)	8371(4)	32(2)
C15	5404(6)	1563(4)	7643(4)	28(2)
C16	5499(6)	2127(5)	6947(5)	34(2)
C17	5733(6)	1747(5)	6203(5)	34(2)
C18	5984(6)	837(5)	6182(5)	35(2)
C19	5939(6)	288(5)	6893(5)	34(2)
C20	5631(6)	638(4)	7615(4)	30(2)
C21	5684(7)	1632(5)	9331(5)	35(2)
C22	6829(7)	1832(6)	9620(5)	52(2)
C23	7533(9)	1584(7)	10491(6)	63(3)
C24	7123(9)	1143(6)	11080(6)	61(3)
C25	6025(9)	945(5)	10811(5)	51(2)
C26	5303(8)	1191(5)	9937(5)	44(2)
C27	10040(2)	1843(14)	9395(13)	251(15)
C28	9248(10)	2202(8)	8539(10)	110(5)
C29	9574(15)	3028(11)	8162(12)	164(8)

3.2. Polymerization

In order to be active for ROMP, established ruthenium catalysts, e.g. ruthenium(II) arene dimers or phosphinoarene ruthenium(II) dichlorides, require an activation step [7–9]. That means, initial carbene species must either be generated in situ by adding diazo compounds [9,22,23] or be formed in a reaction between precatalyst and monomer under UV irradiation or by heating [24,25]. Alternatively, catalysts may be utilized in which the required carbene fragment has been preformed by reacting a suitable complex precursor with certain reagents to generate stable carbene complexes, which can be isolated and stored over longer periods of time without significant decomposition [2].

All these pathways lead to active species in which only monodentate ligands are present. Additionally, dissociation of phosphines or arene moieties from the metal center occurs [5]. The resulting free coordination sites are occupied by solvent or monomer molecules, which may displace each other in equilibrium processes. This labile coordination sphere lacks rigid elements that are necessary to control the catalytic process.

With respect to the ROMP of norbornene as model system for metathesis reactions, three activation patterns for the structurally related [$RuCl_2(\eta^1{:}\eta^6\text{-}PR_2R')$] were pursued in order to vary the number of available coordination sites and therefore, the steric bulk at the catalytic center (Fig. 4). The species A, B, C depicted represent structural principles, not real molecules. In solution, such fragments would be stabilized either by coordinating solvent

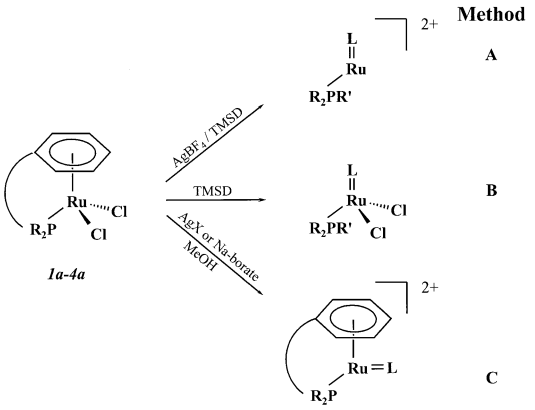

Fig. 4. Activation methods for $(\eta^1{:}\eta^6)$-phosphinoarene ruthenium(II) dichloride complexes (L = carbene) and correlated ruthenium fragments.

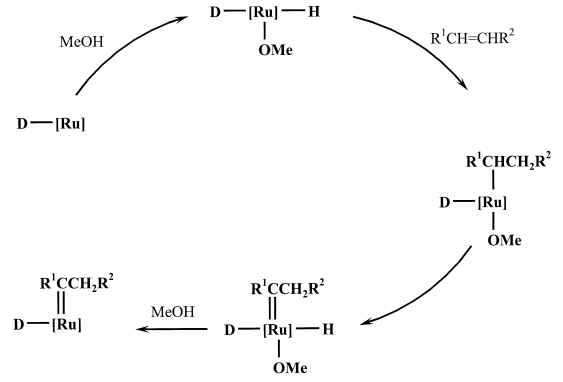

Fig. 5. Hypothetical pathway for the formation of carbene species in the presence of methanol (method C; D = phosphine).

molecules or monomer, which would prevent a coordinative unsaturation.

Abstraction of the chlorine moieties by reaction with silver(I) salts AgX ($X = BF_4, SbF_6$) or sodium - tetrakis - [3,5-bis - (trifluoromethyl)phenyl] borate ($NaB(Ar_f)_4$ (Ar_f = 3,5 - $(CF_3)_2$-C_6H_3)) cleanly produced the dicationic complexes $[Ru(\eta^1{:}\eta^6\text{-}PR_2R')]^{2+}$, as was confirmed by ^1H and ^{31}P NMR.[2] The subsequent addition of TMSD (Fig. 4, method A) to form initial carbene species led to polymerization active complexes,[3] but in these cases, a decoordination of the arene moiety was observed.[4] Analogous results occurred if the ruthenium dichlorides were exposed to TMSD (Fig. 4, method B). If methanol was introduced after the chlorine abstraction step, we also observed the formation of polynorbornene — what implies the generation of a carbene species (Fig. 4, method C). Here, carbenes can be speculated to be produced by oxidative addition of methanol to ruthenium(II) species, alkene insertion into the Ru—H bond, H elimination to the carbene species, followed by reductive elimination of methanol (Fig. 5) [27]. This procedure would yield carbene complexes with coordinated arene moiety and one coordination site left [26]. In contrast, method A produces four and method B

[2] To a solution of 6.3×10^{-2} mmol $[RuCl_2(\eta^1{:}\eta^6\text{-(PDCyPE)})]$ (**2a**) in 1 ml $CDCl_3$ 19.0×10^{-2} mmol $AgBF_4$ were added under argon and stirred for 10 min. After the removal of AgCl by filtration, a ^1H and ^{31}P NMR spectrum were recorded. Selected spectroscopic data: ^1H NMR δ ($CDCl_3$): 6.54 ppm (m, 2H, Ar), 6.12 ppm (m, 1H, Ar), 5.54 ppm (m, 2H, Ar). ^{31}P NMR δ ($CDCl_3$): 78.7 ppm. Absorptions in the region of 5.0–6.8 ppm are especially typical for coordinated arene moieties [20]. The complete abstraction of chlorine is obvious from the appearance of a single resonance in the ^{31}P NMR spectrum at 78.7 ppm (dichloro complex: 70.4 ppm).

[3] The formation of carbene species upon the addition of TMSD was concluded from the obvious polymerization activity of the ruthenium complexes after this treatment, (see also Ref. [5]). NMR investigations to ascertain this assumption need to be done.

[4] In some cases, the release of the arene moiety plays a crucial role for generating the catalytic species.

Table 5
Polymerization results of complexes **1a**, **2a**, **4a**

Complex	Method of Activation	% *trans*[a]	Activity [10^3 $g_{polymer}$ / mol^2 h]	t_p
1a	A	59	909	14 h
1a	B	61	163	14 h
1a	C	80	3	14 h
2a	A	61	9690	8 min
2a	B	74	4381	10 min
2a	C	87	65	10 h
4a	A	55	1558	20 min
4a	B	61	2	10 min
4a	C	85	33	14 h

[a]According to the integrated ^1H NMR spectra of the formed poly(norbornene)s.

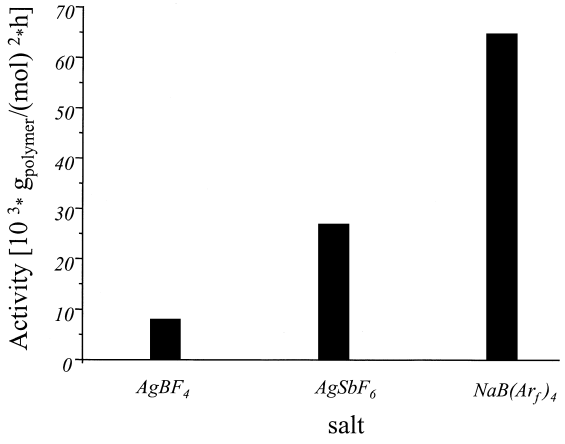

Fig. 6. Influence of the counter ion on the polymerization activity.

two unoccupied sites ready for monomer coordination (Fig. 4).

A comparison of the polymerization activities obtained within a set of active species suggests that a high number of available coordination sites is connected to an increased rate of monomer conversion (Table 5).

Additionally, polymerization activity seems to be governed by the nucleophilicity of the counter ion (Fig. 6). Weakly coordinating counter ions, for instance $B(Ar_f)_4$, show a reduced tendency to interact with the metal center and, hence, do not prevent monomer coordination as strongly as BF_4. The influence of counter anion on the activity and the selectivity of ruthenium metathesis catalysts was recently described by Picquet et al. [26] who performed metathesis experiments with ruthenium allenylidene complexes.

In correlation with a decrease in the number of free coordination sites, the *cis/trans* ratio of the formed poly(norbornene)s with complex **2a** increases from 61% (method A) up to 74% (method B) and then to 87% (method C), reflecting the interdependence of steric interaction and control over the orientation of monomer insertion (*cis/trans* selectivity) (Table 5).

These results suggest that the use of a rigid ligand framework may provide a tool to influence the microstructure of ROMP polymers. Further effort, though, will be required to decide if these findings can be developed into a principle for the control of the regioselectivity of olefin metathesis reactions by the design of the ligand sphere.

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