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Synthesis, structure, and metathesis activity of ruthenium carbene complexes containing diphosphines

Piotr Nieczypor [a], Piet W.N.M. van Leeuwen [a], Johannes C. Mol [a,*], Martin Lutz [b], Anthony L. Spek [b]

[a] *Institute of Molecular Chemistry, Faculty of Science, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands*

[b] *Department of Crystal and Structural Chemistry, Bijvoet Center for Biomolecular Research, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands*

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Abstract

A series of ruthenium benzylidene complexes containing diphosphines (xantphos, dppf, $Cy_2P(CH_2)_nPCy_2$ ($n = 5$, 8)) has been prepared, either by phosphine exchange in the ruthenium carbene complex $RuCl_2(=CHPh)(PPh_3)_2$, or in a one-pot two-steps synthesis from $RuCl_2(PPh_3)_3$, phenyldiazomethane, and diphosphine. The complexes have been characterised spectroscopically (NMR, IR, MS) and by X-ray structural analysis. Their catalytic activity in olefin metathesis is also discussed.

Keywords: Alkenes; Carbene complexes; Catalysts; Diphosphines; Metathesis; Ruthenium

1. Introduction

In the past decade an impressive development of olefin metathesis catalysts and their applications has taken place [1], especially after the discovery of ruthenium carbene complexes of the general formula $Ru(=CHR)Cl_2(PR'_3)_2$ [e.g. R = Ph; R′ = Ph (**1a**) or Cy (**1b**)] by Grubbs and co-workers [2]. A wide variety of ligands has been used for the preparation of new analogues of this type of catalyst [3]. Some of these ligands, e.g. *N*-heterocyclic carbenes [3d–g], produce more versatile catalysts for alkene metathesis. In our group, we selectively converted **1b** into a ruthenium carbene dimer that is active in the metathesis of internal alkenes [3h].

Examples of ruthenium carbene complexes containing a diphosphine ligand are scarce. Polystyrene-supported carbenes prepared by Nguyen and Grubbs [4] might be considered as such, although most probably there are several kinds of ruthenium centres present and the exact structure could not be determined. Ruthenium carbene complexes bearing the strained chelating diphosphine bis(di-*tert*-butylphosphino)-methane coordinated in *cis*-fashion to the metal centre have recently been described [5]. The neutral complexes containing this ligand are moderately active catalysts in ring opening metathesis polymerisation (ROMP) of norbornene and cyclooctene [5b]. Their dicationic dinuclear derivatives, obtained by chlorine abstraction, are also good catalysts in ring closing metathesis (RCM) of 1,7-octadiene [5b]. The mechanistic aspects of their catalytic activity are not completely elucidated yet, although it is believed that mononuclear cationic species are the active species.

In order to expand the field of ruthenium carbenes containing diphosphines, we have prepared and structurally characterised ruthenium carbene complexes bearing diphosphines with flexible as well as with rigid backbones. Moreover, we studied their catalytic activity in the metathesis reaction of different kinds of alkenes.

* Corresponding author. Tel.: +31-20-5256490; fax: +31-20-5256456.

E-mail address: jcmol@anorg.chem.uva.nl (J.C. Mol).

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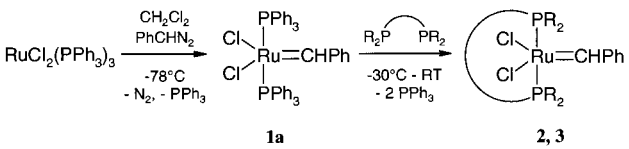
2. Results and discussion

2.1. Synthesis of ruthenium carbene complexes containing diphosphines

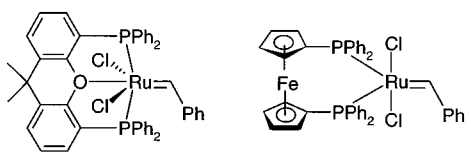
For the preparation of the ruthenium carbene complexes we used two diphosphine ligands with rather rigid backbones, viz. xantphos (9,9-dimethyl-4,5-bis-(diphenylphosphino)xanthene) [6], and dppf (1,1′-bis-(diphenylphosphino)ferrocene). The first ligand has a rather large natural bite angle (calculated value: 111.7° [6]). This could favour *trans* coordination of the phosphines to the ruthenium centre. For dppf the bite angle is much smaller and *cis*-coordination seems to be preferred. Ruthenium benzylidene complexes containing these diphosphines were prepared either by treatment of **1a** with diphosphine that replaces the triphenylphosphines, or in a one-pot two-steps synthetic procedure from $RuCl_2(PPh_3)_3$, phenyldiazomethane and diphosphine (Eq. (1)) in a similar way as described in ref. [2c].



1a **2, 3**

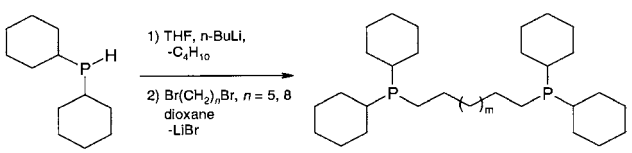
(1)

Via both procedures we obtained the ruthenium carbene complexes **2** and **3** in moderate to good yields (see Section 4). In the solid state, the complexes showed high stability towards oxygen and moisture. When dissolved in dichloromethane complex **2** could even be passed through a short silica gel column.



2 **3**

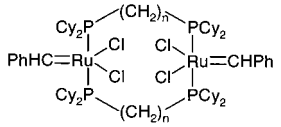
We also prepared two diphosphine ligands in which the phosphorus atoms are connected via a flexible aliphatic chain, viz. 1,5-bis(dicyclohexylphosphino)-pentane (**4a**) and 1,8-bis(dicyclohexylphosphino)octane (**4b**). Good yields were obtained by reaction of the lithium salt of dicyclohexylphosphine with an appropriate dibromoalkane, followed by crystallisation of the product [7] (Eq. (2)).



4a m = 1, **4b** m = 4

(2)

Reaction of **1a** with the flexible ligands **4a** and **4b** according to the above-mentioned procedures afforded pink-coloured products. The yields were moderate, mainly because of the formation of unidentified by-products, which did not contain a carbene moiety. We expected the formation of complexes similar to **2** and **3**, and the initial data (NMR) of the complexes formed were in agreement with our expectations. Both X-ray analysis and molecular weight measurement in solution, however, showed that dimeric structures **5a** and **5b** were formed, in which two ruthenium atoms are bridged by two ligand molecules in μ-fashion (see Section 2.3).



5a n = 5; **5b** n = 8

With the preparation procedures mentioned we did not obtain mononuclear ruthenium carbene complexes, neither with ligands **4a**, **4b** nor with a few other diphosphine ligands [8].

2.2. Reactions with Me_3SiOTf

In attempts to prepare cationic derivatives of the described complexes by chloride abstraction using Me_3SiOTf [5], only occasionally the formation of new ruthenium carbenes species was observed by NMR spectroscopy. Reaction of complexes **5a** and **5b** with 0.5 or 1 molar equivalent of Me_3SiOTf resulted in decomposition of the carbene unit and formation of unidentified products. The reaction of complex **2** with a three molar excess of Me_3SiOTf resulted in a product in which two carbene signals were observed by proton NMR spectroscopy: at 18.95 ppm (t, $J_{PH} = 6.0$ Hz) and 17.12 ppm (t, $J_{PH} = 5.6$ Hz), respectively, in a 1:1 ratio. In the phosphorus spectrum two peaks were present at 46.1 and 42.1 ppm, respectively. Most probably an unsymmetrical dimer was formed, although its structure could not be assigned based on NMR spectra only. Upon treatment with Me_3SiOTf, complex **3** yielded a new carbene species, appearing in proton NMR as triplet at 18.63 ppm (t, $J = 12.3$ Hz), while in phosphorus NMR a singlet was observed at 46.5 ppm. None of these products could be isolated in pure form and therefore crude reaction products were tested for activity in olefin metathesis.

2.3. Structural characterisation

All isolated ruthenium complexes were spectroscopically characterised. The benzylidene proton in complexes **2** and **3**, which bear phenyl groups on the

phosphorus atoms, appeared as triplets. The coupling constant between the carbene proton and the phosphorus atoms of the coordinated phosphine of complex **2** is similar to that of complex **1a** and equal to 7.5 Hz. For complex **3**, this value is 18.3 Hz, which is particularly large due to *cis*-coordination of phosphine moieties. In addition, the signal of the carbene proton is shifted downfield (to 17.2 ppm) compared to other carbene complexes, owing to the electron-withdrawing character of the ferrocene moiety. The carbene signals in **5a** and **5b** showed no P–H coupling, and appeared as singlets around 20 ppm, similar to carbene complex **1b**. The phosphines in these complexes are equivalent and they appeared as singlets in the ^{31}P-NMR spectrum. No relevant changes in the spectra of these complexes could be observed with low-temperature (down to -60°C) NMR studies. Mass spectrometry of dinuclear complexes **5a** and **5b** revealed a fragmentation pathway in which the dimers fall apart into monomeric species with half the weight of the molecular ion. The structures of the carbene ruthenium complexes **2**, **3** and **5a** were confirmed by single-crystal X-ray analysis.

The ruthenium centre in complex **2** is in a distorted octahedral environment; the *cis*-angles vary from 80.54(3)° for O1–Ru–P2 to 102.56(6)° for C1–Ru–P2; the bond lengths are between 1.8645(18) Å for Ru–C1 and 2.4042(4) Å for Ru–Cl1. The Ru–C1 bond distance is somewhat longer with respect to the *p*-chlorophenylcarbene analogue of complex **1b**, which has a bond distance of 1.839 Å [2b]. The P–Ru bond lengths in **2**, viz. 2.3179(4) and 2.3519(4) Å, are quite different. We assume that this difference is a steric consequence of the orientation of the benzylidene group, which breaks the C_s symmetry of the molecule. Compared with complex **5a** (2.4014(4) and 2.4109(4) Å), the Ru–P bond lengths in **2** are shorter, which means that the ligand is more strongly coordinated to the metal. Structure **2** contains an additional Ru–O contact of 2.3314(12) Å. This distance is longer than the usual Ru–O bond length of 2.0–2.2 Å. Therefore we assume that the Ru–O contact in **2** is forced by the phosphorus coordination of the diphosphine. Another indication for the repulsing interaction between Ru and O is the non-planarity of the ligand. The interplanar angle between the aromatic rings of the xanthene backbone is 26.68(9)°; in the free ligand this angle is smaller (~ 14°) [6], Fig. 1.

In the case of complex **3**, Fig. 2, we see another feature. The Ru centre is five-coordinated and the coordination geometry is square pyramidal, distorted towards trigonal bipyramidal, and what is more important, the phosphine moieties and chlorine ligands are no longer *trans*-, but *cis*-coordinated. The Ru–P bonds, viz. 2.2711(6) and 2.3106(6) Å, are even shorter than in complexes **2** and **5a**, while the length of carbene bond (1.860(2) Å) remains basically the same. The ferrocene moiety is essentially undistorted with parallel cyclopentadienyl rings and the phosphine substituents in an eclipsed conformation (torsion angle P1–C8–C13–P2 5.94(11)°).

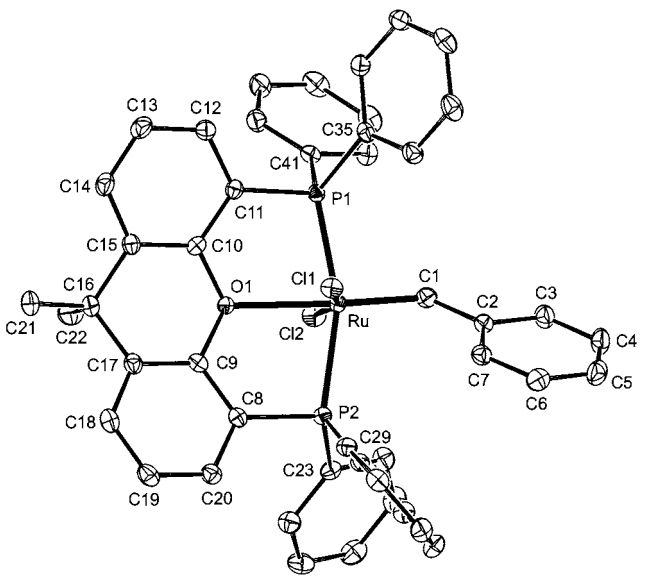


Fig. 1. Displacement ellipsoid plot of **2** drawn at the 50% probability level. Hydrogen atoms and the dichloromethane solvent molecule are omitted for clarity. Relevant bond distances (Å) and angles (°): Ru–P1 2.3179(4), Ru–P2 2.3519(4), Ru–Cl1 2.4042(4), Ru–Cl2 2.3797(4), Ru–C1 1.8645(18), Ru–O 2.3314(12), Cl1–Ru–P1 87.089(15), Cl1–Ru–P2 88.467(15), Cl1–Ru–Cl2 165.145(16), Cl1–Ru–C1 101.05(6), P1–Ru–C1 96.41(6), P1–Ru–P2 161.021(17), Cl2–Ru–P1 88.603(16), Cl2–Ru–P2 91.025(16), Cl2–Ru–C1 93.55(6), P2–Ru–C1 102.56(6), C1–Ru–O 175.90(6).

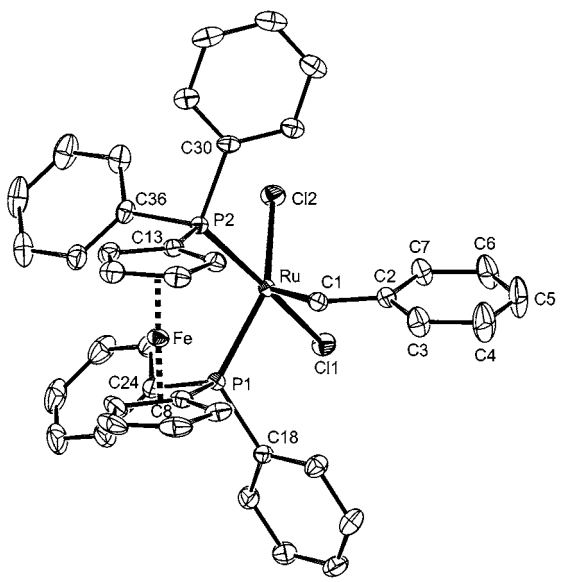


Fig. 2. Displacement ellipsoid plot of **3** drawn at the 50% probability level. Hydrogen atoms and the dichloromethane solvent molecules are omitted for clarity. Relevant bond distances (Å) and angles (°): Ru–P1 2.2711(6), Ru–P2 2.3106(6), Ru–Cl1 2.4075(6), Ru–Cl2 2.3974(6), Ru–C1 1.860(2), Cl1–Ru–P1 87.28(2), Cl1–Ru–P2 167.30(2), Cl1–Ru–Cl2 87.02(2), Cl1–Ru–C1 101.92(7), P1–Ru–C1 88.81(7), P1–Ru–P2 95.37(2), Cl2–Ru–P1 146.80(2), Cl2–Ru–P2 83.97(2), Cl2–Ru–C1 124.35(7), C1–Ru–P2 90.57(7).

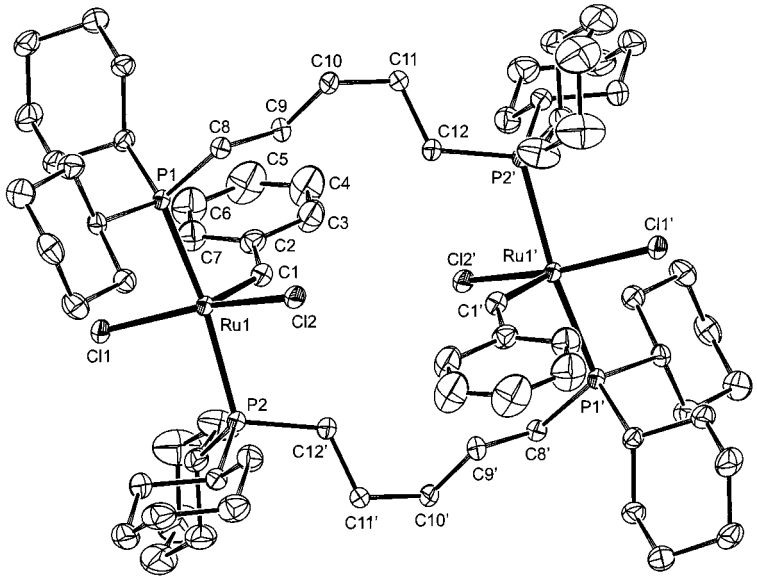
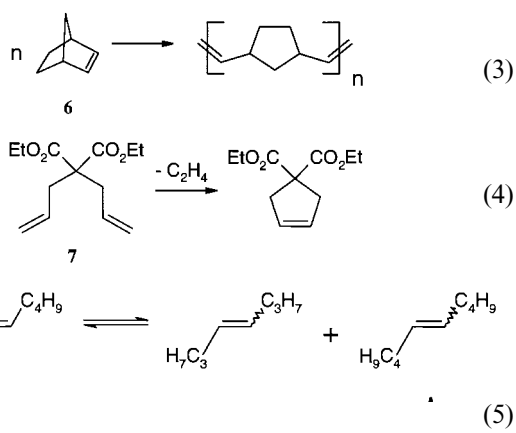


Fig. 3. Displacement ellipsoid plot of **5a** drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry operation: $1.5-x$, $1.5-y$, $1-z$. Relevant bond distances (Å) and angles (°): Ru–P1 2.4014(4), Ru–P2 2.4109(4), Ru–Cl1 2.3885(4), Ru–Cl2 2.4060(4), Ru–C1 1.8392(17), Cl1–Ru–P1 89.585(13), Cl1–Ru–P2 88.234(14), Cl1–Ru–Cl2 163.144(15), Cl1–Ru–C1 107.93(5), P1–Ru–C1 97.83(5), P1–Ru–P2 168.721(14), Cl2–Ru–P1 90.875(13), Cl2–Ru–P2 88.034(14), Cl2–Ru–C1 88.70(5), C1–Ru–P2 93.37(5).

Complex **5a** is a centrosymmetric dimer with the Ru atoms five-coordinated. The coordination geometries around the metal centres in **5a** are nearly undistorted square pyramidal with phosphine moieties in *trans* positions. The bond lengths and angles are comparable to those observed in *p*-chlorophenyl analogue of **1b** [2b], Fig. 3.

2.4. Metathesis activity of ruthenium carbenes bearing diphosphines

Table 1 shows the catalytic activity of the complexes in ROMP of norbornene (Eq. (3)), RCM of diethyl diallylmalonate (Eq. (4)) and self-metathesis of *trans*-4-decene (Eq. (5)) at room temperature (see Section 4). For comparison some literature data are also given.



Complex **2** showed no activity in metathesis, in contrast to internal oxygen–ruthenium chelate complexes [9] and Schiff-base-substituted ruthenium carbenes [3b]. This inactivity is most probably due to the fact that a ruthenium–oxygen interaction is present in this complex along with two coordinated phosphorus atoms, so the ligand is tridentate (see Section 2.3) and it is strongly coordinated to the metal. The ruthenium atom is then six-coordinated without a vacant coordination site, which makes the coordination of any substrate impossible. Complex **3**, which contains a dppf ligand having phenyl substituents on phosphorus atoms, is only active in the ROMP of norbornene, but less than complex **1a**.

Table 1
Metathesis activity of the ruthenium complexes **3**, **5a**, and **5b** [a]

Catalyst	Alkene	Alkene:catalyst molar ratio	Time (h)	Conversion (%)
3	6	100	4 (24)	43 (99 [b])
3	7	20	no activity	
5a	7	20	4 (24)	25 (77)
5a	8	100	48	2
5b	7	20	4 (24)	33 (85)
5b	8	100	48	3
1a	6	100	1	99 [c]
1b	7	20	1	100
1b	8	550	4	36 [d]

[a] Reactions conditions: room temperature, solvent CH_2Cl_2; catalyst concentration for ROMP of **6**: 6.0 mM, for RCM of **7**: 0.01 M, for self-metathesis of **8**: 2.0 (or 3.0 for **1b**) mM.
[b] Isolated yield 86%.
[c] Isolated yield 95% (Ref. [2c]).
[d] Ref. [18].

The dinuclear species with cyclohexyl moieties on the phosphorus atoms, **5a** and **5b**, show activity towards RCM, although lower than **1b**. They are only slightly active in metathesis of *trans*-4-decene after prolonged reaction time.

The catalytic properties of all of the described complexes can be explained by considering the accepted mechanism of the metathesis reaction [10]. The dissociation of one of the phosphine moieties is required in the initial steps of the reaction. The chelating effect of the bidentate ligand slows down this process. The uncoordinated arm of the ligand can exert some steric bulkiness in the ruthenium coordination sphere making the approach of the olefin more difficult.

The new ruthenium carbene species observed in the products of chlorine abstraction reactions with Me_3SiOTf from complexes **2** and **3** were not active in metathesis.

3. Conclusions

Ruthenium carbene complexes containing diphosphines could be synthesised by either phosphine substitution in complex **1a** or in a one-pot two-steps synthetic procedure from $RuCl_2(PPh_3)_3$, phenyldiazomethane and an appropriate phosphine. Using diphosphines with rigid backbones mononuclear complexes were formed, whereas with ligands with flexible aliphatic chain dinuclear complexes were obtained. These complexes are stable to air and moisture, but they show lower catalytic activity in ROMP of norbornene and RCM of diethyl diallylmalonate than complexes **1a** and **1b**, respectively. This can be attributed to a detrimental effect of the chelating of the ligand, while also steric effects can contribute to a lower activity. Our observations are in agreement with the mechanism for the metathesis reaction.

4. Experimental

All manipulations were performed using standard Schlenk-tube techniques under an atmosphere of purified nitrogen. All solvents were purified by standard procedures [11]. $RuCl_2(PPh_3)_3$ [12], $Ru(=CHPh)Cl_2(PPh_3)_2$ [2c], xantphos [6] and phenyldiazomethane solution [13] were prepared according to literature procedures. Dicyclohexylphosphine (Strem), *n*-butyllithium solution in hexane (Acros), and dppf (Aldrich) were used as received. Norbornene (Acros) was purified by sublimation; diethyl diallylmalonate (Aldrich) and *trans*-4-decene (Fluka) were purified by passing through activated alumina and distillation. Decane, 1,5-dibromopentane (Merck), and 1,8-dibromooctane (Merck) were purified by distillation. All reagents were degassed through three continuous freeze-pump-thaw cycles. NMR spectra were measured with a Varian Mercury 300 spectrometer (at room temperature (r.t.)). Mass spectra were measured with a Jeol JMS SX/SX102A mass spectrometer. GC analyses were performed on a Carlo Erba 8000^{Top} GC using a DB-5 (J&W Scientific) column. The determinations of the molecular weight in solution were done on Hewlett–Packard 302B vapour pressure osmometer.

4.1. Synthesis of 1,5-bis(dicyclohexylphosphino)pentane (**4a**) and 1,8-bis(dicyclohexyl-phosphino)octane (**4b**)

Both compounds were synthesised by reaction of dicyclohexylphosphine lithium salt (prepared by a slightly modified literature procedure [7a]) and an appropriate dibromoalkane, according to a modified literature procedure [7b].

4.1.1. Preparation of **4b**

n-Butyllithium (4.6 ml, 2.4 M) in hexanes (~ 11 mmol) was added to a solution of dicyclohexylphosphine (2.03 ml, 10.1 mmol) in diethyl ether (20 ml) at r.t. The reaction mixture was stirred for 10 min during which time a yellow precipitate of phosphine lithium salt was formed. The supernatant was taken out via cannula filtration and the solid was washed twice with ether (2×10 ml). Next, freshly distilled 1,4-dioxane (20 ml) was added causing dissolution of a certain amount of the salt. 1,8-Dibromooctane (0.86 ml, 4.67 mmol) was added drop wise via a syringe. An immediate reaction occurred with dissolution of the solid and warming of the reaction mixture. It was refluxed for 10 min and formation of a white precipitate of a $LiBr \times C_4H_8O_2$ complex was observed. The precipitate was filtered off on a G4 filter, washed with ether and discarded. The combined solutions were then concentrated under vacuum and the formed white oil was dissolved in dry hot ethanol (15 ml). The solution was left overnight at 0°C for crystallisation. Next the crystallisation procedure was repeated. A white solid (1.84 g, yield 81%) was obtained. ^{1}H-NMR (C_6D_6): δ (ppm) 2.00–1.05 (*m*). $^{13}C\{^1H\}$-NMR (C_6D_6): δ (ppm) 34.39 (d, $J = 14.7$ Hz), 32.40 (d, $J = 11.0$ Hz), 31.23 (d, $J = 14.6$ Hz), 30.25 (s), 29.85 (d, $J = 8.2$ Hz), 29.52 (d, $J = 20.8$ Hz), 28.08 (pseudo t, $J_{app} = 3.7$ Hz), 27.37 (s), 22.44 (d, $J = 18.3$ Hz). $^{31}P\{^1H\}$-NMR (C_6D_6): δ (ppm) -4.85 (s). FAB-MS: m/z (rel. intensity,%): 507 ($[M + H]^+$, 80), 506 ($[M]^+$, 18), 505 ($[M - H]^+$, 50), 423 ($[M - Cy]^+$, 100), 341 ($[M - 2Cy + H]^+$, 25), 309 (73), 267 (10), 225 (13), 130 (15), 115 (20), 78 (40), 76 (32), 55 (50), 41 (20).

*4.1.2. Data for **4a***

Starting from 2.02 ml (10.1 mmol) of dicyclohexylphosphine and 1,5-dibromopentane (0.68 ml, 0.50 mmol), a white solid was obtained with a yield of 65% (1.36 g). ^{1}H-NMR (C_6D_6): δ (ppm) 2.05–1.10 (m). ^{13}C{^{1}H}-NMR (C_6D_6): δ (ppm) 34.31 (d, $J = 14.6$ Hz), 31.18 (d, $J = 14.6$ Hz), 29.77 (d, $J = 8.5$ Hz), 29.21 (d, $J = 19.6$ Hz), 28.08 (pseudo t, $J_{app} = 3.8$ Hz), 27.32 (s), 22.25 (d, $J = 18.3$ Hz); ^{31}P{^{1}H}-NMR (C_6D_6): δ (ppm) -4.82 (s). FAB-MS: m/z (rel. intensity,%): 465 ([M + H]$^+$, 85), 464 ([M]$^+$, 10), 463 ([M $-$ H]$^+$, 45), 381 ([M $-$ Cy]$^+$, 100), 299 ([M $-$ 2Cy + H]$^+$, 30), 267 (88), 153 (15), 83 (35), 81 (25), 41 (15). Anal. Calc. for $C_{29}H_{54}P_2$: C, 74.96; H, 11.71. Found: C, 74.69; H, 11.78%.

4.2. Synthesis of ruthenium carbene complexes bearing diphosphines

*4.2.1. Ru(=CHPh)Cl$_2$(xantphos) (**2**)*

Complex **1a** (0.256 g, 0.325 mmol) was dissolved in CH_2Cl_2 (20 ml) and the solution was cooled down to -78°C. The xantphos ligand (0.171 g, 0.295 mmol) was added as a solution in CH_2Cl_2 (5 ml) via a syringe. The reaction mixture was stirred for 15 min at -78°C, then allowed to warm to r.t. and stirred for 2 h. The mixture was then concentrated and a green precipitate was formed upon addition of pentane (20 ml). The brownish liquor was discarded and the solid was washed with pentane. It was redissolved in CH_2Cl_2 and reprecipitated. The reaction yielded 0.23 g (92%) of a green microcrystalline solid. ^{1}H-NMR (CD_2Cl_2): δ (ppm) 19.08 (t, $J_{PH} = 7.5$ Hz; 1H, Ru=C*H*Ph); 7.92 (d, $J_{HH} = 7.6$ Hz; 2H, C*H* of xanthene); 7.78 (d, $J_{HH} = 7.5$ Hz; 2H, C*H* of xanthene); 7.59 $-$ 7.23 (m, 25 H, 5 × Ph); 7.08 (t, $J_{HH} = 7.5$ Hz; 2H, C*H* of xanthene); 1.82 (s, 6H, CH_3). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ (ppm) 320.59 (t, $J = 10.6$ Hz, Ru=*C*HPh), 155.62 (t, $J = 4.0$ Hz), 154.39 (t, $J = 7.3$ Hz), 135.45, 134.91 (t, $J = 5.5$ Hz), 132.68, 131.41 (d, $J = 45$ Hz), 131.18 (d, $J = 46$ Hz), 131.09 (d, $J = 47$ Hz), 130.22, 129.17, 128.02 (t, $J = 4.9$ Hz), 125.37, 123.31 (t, $J = 18.9$ Hz), 35.19 (*C*(CH$_3$)$_2$), 33.52 (*C*H$_3$). ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ (ppm) 36.26 (s). IR (KBr): (cm^{-1}) 3056 (m), 2953 (w), 2918 (w), 1481 (w), 1436 (s), 1399 (vs), 1260 (w), 1213 (m), 1194 (m), 1094 (m), 877 (w), 743 (m), 693 (s), 522 (s), 505 (m). FD-MS: m/z (rel. intensity,%): 840 ([M]$^+$, 100), 820 (15), 611 (5), 353 (97); isotopic pattern for [$C_{46}H_{38}Cl_2OP_2Ru$]$^+$: m/z (Calc. intensity, Found intensity): 834 (10, 20), 835 (5, 12), 836 (11, 24), 837 (28, 44), 838 (39, 59), 839 (62, 80), 840 (100, 100), 841 (66, 82), 842 (96, 95), 843 (45, 63), 844 (40, 61), 845 (16, 28), 846 (7, 28), 847 (2, 17), 848 (1, 6). Anal. Calc. for $C_{46}H_{38}Cl_2OP_2Ru$: C, 65.71; H, 4.56. Found: C, 64.92; H, 4.69%.

*4.2.2. Ru(=CHPh)Cl$_2$(dppf) (**3**)*

To a cooled -78°C solution of **1a** (0.235 g, 0.30 mmol) in CH_2Cl_2 (30 ml), a solution of dppf (0.166 g, 0.30 mmol) in CH_2Cl_2 (5 ml) was added via a syringe. The reaction mixture was stirred for 20 min at -78°C. It was allowed to warm to r.t., and the colour of the mixture changed to brown. After 1 h most of the solvent was evaporated and a greenish solid was precipitated with pentane (25 ml). The orange solution was discarded and the solid was washed a few times with pentane, reprecipitated twice from CH_2Cl_2 and then dried under vacuum. 0.123 g (50%) of a green–brown microcrystalline product was obtained. ^{1}H-NMR (CD_2Cl_2): δ (ppm) 17.20 (t, $J_{PH} = 18.3$ Hz; 1H, Ru=C*H*Ph); 8.66 (d, $J_{HH} = 7.7$ Hz; 2H, *o*-CH_{arom}); 7.92–6.95 (m, 23H, CH_{arom}); 4.78, 4.60, 4.48, 4.37 (4 × s, 4 × 2H, C*H* of Cp). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ (ppm) 303.06 (t, $J = 17.4$ Hz, Ru=*C*HPh), 151.06, 136.21 (t, $J = 5.1$ Hz) 133.70 (t, $J = 4.9$ Hz), 133.38, 131.40 (2C), 130.03 (2C), 128.39 (t, $J = 4.9$ Hz), 127.75 (t, $J = 5.2$ Hz), 75.16 (4C), 73.33 (2C, t, $J = 3.6$ Hz), 70.14 (2C). ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ (ppm) 51.95 (s). IR (KBr): (cm^{-1}) 3054 (m), 1482 (m), 1434 (s), 1249 (m), 1178 (m), 1161 (m), 1094 (s), 1038 (m), 874 (w), 826 (w), 744 (s), 693 (s), 631 (w), 562 (m), 511 (s), 476 (m). FD-MS: m/z (rel. intensity,%): 816 ([M]$^+$, 100), 780 (20), 726 (5), 689 (5), 586 (10), 554 (8); isotopic pattern for [$C_{41}H_{34}Cl_2FeP_2Ru$]$^+$: m/z (Calc. intensity, Found intensity): 808 (1, 2), 809 (0.5, 1), 810 (10, 18), 811 (6, 14), 812 (13, 15), 813 (31, 32), 814 (43, 45), 815 (63, 75), 816 (100, 100), 817 (63, 67), 818 (92, 92), 819 (41, 51), 820 (38, 41), 821 (14, 23), 822 (7, 12), 823 (2, 4). Anal. Calc. for $C_{41}H_{34}Cl_2FeP_2Ru \times CH_2Cl_2$: C, 55.98; H, 4.08. Found: C, 55.96; H, 4.02%.

*4.2.3. Cl$_2$(PhHC=)Ru[μ-(Cy$_2$P(CH$_2$)$_8$PCy$_2$)]$_2$Ru-(=CHPh)Cl$_2$ (**5b**)*

$RuCl_2(PPh_3)_3$ (1.44 g, 1.50 mmol) was dissolved in CH_2Cl_2 (50 ml) and the solution was cooled to -50°C. The cooled to 0°C solution of phenyldiazomethane ($\sim$2 molar excess) was added via a polyethylene cannula over 10 min. Then the mixture was allowed to warm up to -30°C and then 1.1 molar excess (0.88 g) of diphosphine **4b** was added. The reaction mixture was allowed to warm up to r.t. and stirred for the next 30 min. Next, most of the solvent was evaporated leaving a dark-red oil. Ethanol (30 ml) was added and the mixture was vigorously stirred. A dark-red precipitate was formed, which was separated from the liquor, redissolved and reprecipitated with ethanol. The red–pink solid thus obtained was washed with cooled CH_2Cl_2 (10 ml) and dried, giving a pink solid. The remaining liquor was concentrated to a few millilitres and left overnight at -20°C. The crystallised dark-pink solid was filtered, washed with cold CH_2Cl_2 and dried. The yield of the product was 0.392 g (34%).

^{1}H-NMR (CD_2Cl_2): δ (ppm) 20.00 (s, 1H, Ru=C*H*Ph); 8.52 (d, $J_{HH} = 7.8$ Hz; 2H, *o*-CH_{arom}); 7.84 (t, $J_{HH} = 7.5$ Hz; 1H, *p*-CH_{arom}); 7.56 (t, $J_{HH} = 7.8$ Hz; 2H, *m*-CH_{arom}); 2.40–0.63 (m, 60H, all CH_{alif}). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ (ppm) 297.6 (Ru=*C*HPh), 155.9, 131.1, 130.8, 130.0, 33.0 (m), 30.2, 29.7, 29.3, 28.1 (pseudo t, $J_{app} = 6.4$ Hz), 26.9, 26.1, 25.3, 18.4. ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ (ppm) 33.46 (s). IR (KBr): (cm^{-1}) 3060 (w), 2927 (vs), 2851 (s), 1903 (w), 1446 (m), 1243 (w), 1173 (w), 1117 (w), 1005 (w), 892 (w), 851 (w), 743 (m), 689 (w), 515 (w). FD-MS: *m*/*z* (rel. intensity,%) 1536 ([M]$^+$, 66), 768 ([M/2]$^+$, 74), 638 (55), 507 (100, [$Cy_2P(CH_2)_8PCy_2$]$^+$), 254 (61). Anal. Calc. for $C_{78}H_{132}Cl_4P_4Ru_2$: C, 60.92; H, 8.65. Found: C, 60.35; H, 8.70%. Molecular weight determination in CH_2Cl_2 showed the complex to be dimeric in the solution.

4.2.4. $Cl_2(PhHC=)Ru[\mu$-$(Cy_2P(CH_2)_5PCy_2)]_2Ru$-$(=CHPh)Cl_2$ (**5a**)

The reaction was carried out as described for **5b**, starting from 1.218 g (1.25 mmol) of $RuCl_2(PPh_3)_3$, phenyldiazomethane solution ($\sim$2 molar excess) and 0.660 g (1.40 mmol) of diphosphine **4a**. A pink–brown solid was isolated (0.290 g, 32% yield) upon repeated precipitation from CH_2Cl_2 solution using ethanol. ^{1}H-NMR (CD_2Cl_2): δ (ppm) 19.89 (s, 1H, Ru=C*H*Ph); 8.52 (d, $J_{HH} = 7.7$ Hz; 2H, *o*-CH_{arom}); 7.60 (t, $J_{HH} = 7.2$ Hz; 1H, *p*-CH_{arom}); 7.36 (t, $J_{HH} = 7.6$ Hz; 2H, *m*-CH_{arom}); 2.40–0.83 (m, 54H, all CH_{alif}). ^{13}C{^{1}H}-NMR (CD_2Cl_2): δ (ppm) 296.9 (Ru=*C*HPh), 153.1, 130.3, 129.8, 129.2, 34.1, 33.0 (pseudo t), 29.3 (d, $J = 17.2$ Hz), 27.9, 26.9, 24.5, 18.7. ^{31}P{^{1}H}-NMR (CD_2Cl_2): δ (ppm) 30.40 (s). IR (KBr): (cm^{-1}) 3057 (w), 2926 (vs), 2850 (vs), 2108 (w), 1933 (w), 1901 (w), 1446 (s), 1329 (w), 1262 (m), 1241 (m), 1173 (m), 1026 (m), 1005 (m), 891 (m), 850 (m), 818 (m), 742 (m), 690 (m), 515 (w). FD-MS: *m*/*z* (rel. intensity,%) 1453 ([M–H]$^+$, 12), 1249 (30), 727 ([M/2]$^+$, 22), 637 (85), 599 (100), 572 (54), 481 (27), 258 (23). Anal. Calc. for $C_{72}H_{120}Cl_4P_4Ru_2$: C, 59.49; H, 8.32. Found: C, 58.90; H, 8.27%. Molecular weight determination in CH_2Cl_2 showed the complex to be dimeric in the solution.

4.2.5. Treatment of **2**, **3**, **5a**, and **5b** with Me_3SiOTf

The experiments were carried out as described in reference [5b], usually with three molar excess of the trimethylsilyl triflate added to a CH_2Cl_2 solution of ruthenium complex at -78°C. The reaction mixture was stirred for 1 h at r.t. The product was isolated by repeated precipitation from CH_2Cl_2 solution using pentane.

4.3. Metathesis experiments

4.3.1. ROMP of norbornene [2b]

In a typical experiment, a stock mixture of norbornene and decane as internal standard for GC analysis was used. An aliquot of this solution (116 mg of norbornene, 1.23 mmol) was added via a syringe to the solution of ruthenium compound **3** (9.5 mg, 12.1 μmol) in CH_2Cl_2 (2 ml) at r.t. The resulting concentration of catalyst and norbornene were 0.006 M (1 equivalent) and 0.60 M (100 equivalents), respectively. The viscous mixture was stirred for 24 h, while occasionally samples were taken and analysed by GC. Next, the mixture was exposed to air and CH_2Cl_2 (4 ml), with traces of ethyl vinyl ether to quench the reaction, was added. The mixture was stirred for another 20 min, filtered through a short column of silica gel and poured into vigorously stirred methanol. A white, tacky polymer precipitated, which was washed several times with MeOH and dried under vacuum; yield 98 mg (86%).

4.3.2. RCM of diethyl diallylmalonate

In a typical experiment the diene (0.120 ml, 0.50 mmol) was added to 12.5 μmol (19.2 mg; 5 mol% of carbene moiety) of the ruthenium catalyst **5b** in CH_2Cl_2 (2.5 ml) at r.t. The progress of the reaction was followed by GC.

4.3.3. Self-metathesis of trans-4-decene

In a typical experiment *trans*-4-decene (0.19 ml, 1.0 mmol) was added to a solution of **5a** (7.1 mg, 4.9 μmol, 1 mol% of carbene moiety) in CH_2Cl_2 (2.5 ml) at r.t. The resulting solution was stirred vigorously. The progress of the metathesis reaction was followed by GC.

4.4. X-ray structure determinations

Crystals of complexes **2** and **3** suitable for X-ray study were grown from mixture of *n*-hexane–CH_2Cl_2 (1/1 v/v) at 2°C and in case of complex **5a** from CH_2Cl_2. X-ray intensities were measured on a Nonius KappaCCD diffractometer with rotating anode ($\lambda =$ 0.71073 Å) at a temperature of 150(2) K. Structures **2** and **5a** were solved with automated Patterson methods (DIRDIF 97) [14]; structure **3** was solved with direct methods (SIR 97) [15]. The structures were refined with SHELXL 97 [16] against F^2 of all reflections. Structure **5a** contains large voids (2571.8 Å^3/unit cell) filled with disordered CH_2Cl_2 molecules. Their contribution to the structure factors was secured by back-Fourier transformation (program PLATON [17], CALC SQUEEZE, 615 e^-/unit cell). Structure calculations, structure drawings and checking for higher symmetries were performed with the PLATON package [17]. Further information about the crystal structure determinations is given in Table 2.

Table 2
Summary of data for the crystal structure analysis of **2**, **3**, and **5a**

	2	**3**	**5a**
Formula	$C_{46}H_{38}Cl_2OP_2Ru{\cdot}CH_2Cl_2$	$C_{41}H_{34}Cl_2FeP_2Ru{\cdot}2CH_2Cl_2$	$C_{72}H_{120}Cl_4P_4Ru_2$ + solvent
Formula weight	925.60	986.29	1453.50 [a]
Crystal colour	Green	Brown	Red
Crystal size	$0.48\times0.15\times0.15$	$0.51\times0.27\times0.18$	$0.30\times0.30\times0.12$
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$ (No. 2)	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a (Å)	11.0320(2)	13.9971(1)	24.2122(3)
b (Å)	11.1015(2)	14.6922(1)	27.8321(4)
c (Å)	17.7959(3)	20.0647(1)	14.3627(2)
α (°)	89.7781(9)	90	90
β (°)	81.1990(10)	98.6868(4)	109.2424(7)
γ (°)	70.8813(10)	90	90
V (Å^3)	2032.54(6)	4078.94(5)	9138.0(2)
Z	2	4	4
ρ (g cm^{-3})	1.512	1.606	1.057 [a]
μ (mm^{-1})	0.765	1.229	0.549 [a]
Absorbance corrections	PLATON (MULABS)	PLATON (MULABS)	PLATON (MULABS)
Transmission	0.82–0.90	0.70–0.81	0.87–0.93
Reflections collected/unique	47590/9233	87477/9342	53789/10470
Parameters/restraints	502/0	514/0	374/0
R_1, wR_2 ($I>2\sigma(I)$)	0.0275, 0.0649	0.0314/0.0803	0.0283/0.0746
R_1, wR_2 (all reflections)	0.0347, 0.0678	0.0360/0.0832	0.0333/0.0768
S	1.067	1.030	1.047
e-Density (min./max.)	−0.88/0.39	−1.17/1.73	−1.39/0.37

[a] The contribution of the disordered solvent was not taken into account for the calculation of formula weight, ρ, and μ (see text in Section 4).

5. Supplementary data

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 147 124 (**2**), 147 125 (**3**), and 147 126 (**5a**). Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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