Novel Ruthenium(II)$_2$ Carboxylates as Catalysts for Alkene Metathesis

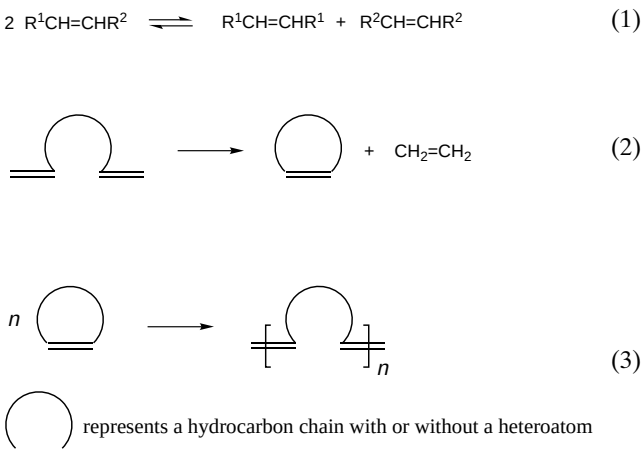
Wlodzimierz Buchowicz,[a] Florent Ingold,[a] Johannes C. Mol,*[a] Martin Lutz,[b] and Anthony L. Spek[b]

Abstract: The reactions of [Ru(=CHR)Cl_2(PCy_3)$_2$] (**1**: R = Ph; **1a**: R = −CH=CPh_2) with silver salts of carboxylic acids afforded new dimeric complexes of the general formula [Ru_2(=CHR)$_2$($R'CO_2$)$_2$(μ-$R'CO_2$)$_2$(PCy_3)$_2$(μ-H_2O)] (**2**: R = Ph, R′ = CF_3; **3**: R = Ph, R′ = C_2F_5; **4**: R = −CH=CPh_2, R′ = CF_3; **5**: R = Ph, R′ = C_6F_5; **6**: R = −CH=CPh_2, R′ = C_6F_5; **7**: R = -CH=CPh_2, R′ = CCl_3) in good yields. With R′ = CF_3, C_2F_5 or CCl_3 these complexes are active catalysts for metathesis of acyclic alkenes, including unsaturated fatty acid esters, as well as for ring closing metathesis. The reactivity of these complexes with bases and weak donor solvents has been studied and their half-life times in several media were determined.

Keywords: alkenes · homogeneous catalysis · metathesis · ruthenium carbenes

Introduction

Alkene metathesis is a powerful method for the cleavage and formation of carbon–carbon double bonds.[1] Various types of olefins, such as acyclic olefins [Eq. (1), R^1 and R^2 = alkyl or H], diolefins [e.g. Eq. (2): ring-closing metathesis, RCM], and cycloolefins [Eq. (3): ring-opening metathesis polymerization, ROMP], undergo metathesis through contact with a suitable catalyst resulting in a wide variety of possible products.



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Since the discovery of well-defined, single-component and efficient metal-carbene catalysts by Schrock and co-workers[2–4] and by Grubbs and co-workers,[5–7] the metathesis reaction can be conveniently carried out in a chemical laboratory at reasonable cost. In particular, the ruthenium carbene complex [Ru(=CHPh)Cl_2(PCy_3)$_2$] (**1**)[6, 7] became a reagent of choice for numerous applications in organic synthesis.[8–10] So far, attempts to improve the catalytic performance of **1** have focused on replacing at least one of the phosphines by nucleophilic N-heterocyclic carbene ligands.[11–18] Attempts to modify the anionic ligands in ruthenium-carbene complexes of the type of **1** are less common.[19–22]

In our group we sought to substitute the chloride ligands in **1** with other anionic groups, such as carboxylates, as a possible route for the development of an immobilised metathesis catalyst. In a preliminary communication the synthesis, properties and metathesis activity of a dimeric complex, namely [Ru_2(=CHPh)$_2$(CF_3CO_2)$_2$(μ-CF_3CO_2)$_2$(PCy_3)$_2$(μ-H_2O)] (**2**), are described.[23] The synthesis of this new type of organometallic dimers has now been extended to other carboxylates (see Scheme 1) and their metathesis activity has been investigated.

Results and Discussion

Synthesis of dimers: All reactions of dimer formation (Scheme 1) were performed at temperatures ranging from −30 °C to 0 °C using hexane as a solvent for **1** or **1a** and THF for the silver salt. Complexes **2**–**7** were isolated as green (R = Ph) or yellow (R = -CH=CPh_2) solids by crystallisation, after filtering off AgCl and [AgClPCy$_3$].[23] Complex **1** also reacts with salts such as AgO_2CCH_3, TlO_2CCH_3 or AgO_3SR (R =

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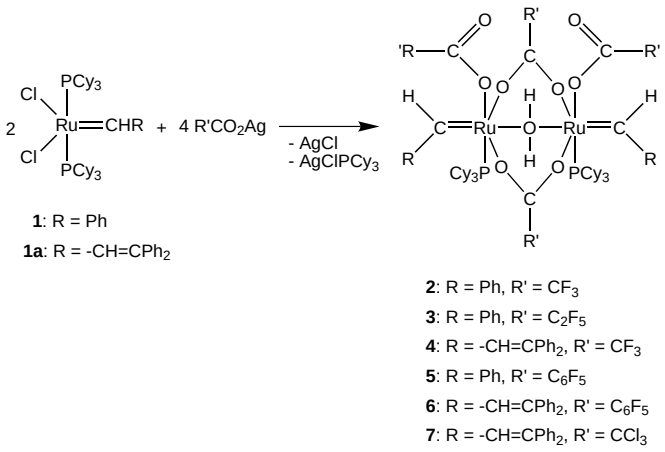


Scheme 1. Synthesis of complexes **2**–**7**: Hexane, THF, −30 to 0 °C.

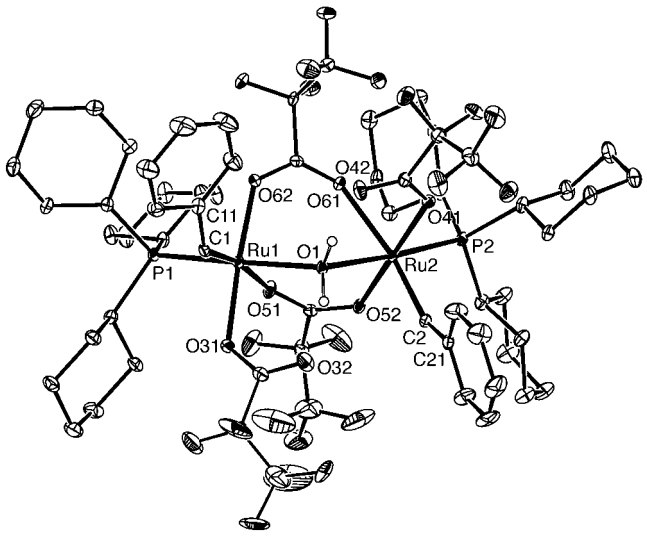


Figure 1. Displacement ellipsoid plot (30% probability level) of compound **3** in the crystal. The hexane solvent molecule and the hydrogen atoms bound to carbons are omitted for clarity. Only one conformation of the disordered pentafluoropropionate ion at O31 is displayed.

Table 1. Selected bond lengths [Å] and angles [°] for **3** with estimated standard deviation in parentheses.

bond length			
Ru1–C1	1.852(4)	Ru2–C2	1.864(4)
Ru1–P1	2.3619(11)	Ru2–P2	2.3383(11)
Ru1–O1	2.184(3)	Ru2–O1	2.227(3)
Ru1–O31	2.103(3)	Ru2–O41	2.088(3)
Ru1–O51	2.248(3)	Ru2–O52	2.089(2)
Ru1–O62	2.075(3)	Ru2–O61	2.276(3)
bond angle			
C1-Ru1-P1	89.28(12)	C2-Ru2-P2	91.16(13)
C1-Ru1-O1	100.17(14)	C2-Ru2-O1	93.12 (14)
P1-Ru1-O1	170.26(8)	P2-Ru2-O1	175.56(7)
C1-Ru1-O31	86.76(15)	C2-Ru2-O41	100.15(14)
C1-Ru1-O51	169.59(15)	C2-Ru2-O52	82.98(14)
C1-Ru1-O62	94.34(15)	C2-Ru2-O61	170.28(14)
O31-Ru1-O51	84.62(11)	O41-Ru2-O61	82.96(10)
O62-Ru1-O51	94.66(11)	O61-Ru2-O52	94.70(10)
Ru1-O1-Ru2	123.05(12)		

CF_3, C_6H_4Me). Despite several attempts with these reagents we could not isolate any organometallic complex under similar experimental conditions. We conclude that the pK_a of the corresponding acid must lie between −7 and +3 to stabilise the carbene ligand.

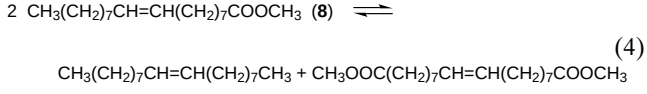
The most noticeable spectroscopic feature for complexes **2**–**7** is the presence of the carbene proton resonance as a doublet (for R = Ph) in the range of $\delta = 20.6-21.1$ ($^3J_{PH} = 5-7$ Hz), or as a doublet of doublets (for R = -CH=CPh$_2$) in the range of $\delta = 19.7-20.2$ ($^3J_{PH} = 5-7$ Hz, $^3J_{HH} = 12$ Hz). The hydrogen atoms of the bridging water molecule are observed as a singlet in the range of $\delta = 11.8-12.6$. ^{31}P NMR spectra of these complexes consist of only one singlet ($\delta = 43.2-46.6$), while ^{19}F NMR spectra contain two sets of peaks in accord with the presence of two different carboxylate ligands.

The IR spectra of complexes **3**–**7** in KBr pellets have the characteristic vibrations of the tricyclohexylphosphine, the carboxylic group and the phenyl ring of the carbene moiety. The solid state structure, with bridging coordination mode of the carboxylates, was destroyed in KBr, because only one unidentate carboxylate stretch is observed at 1651–1696 cm^{-1} for the $\nu_{as}(CO_2)$ and 1381–1202 cm^{-1} for the $\nu_s(CO_2)$.

The mass spectra (FD, MALDI-TOF) contain a molecular peak only in the case of complex **4**; the next fragment observed in its FD mass spectrum is formed by abstraction of the water molecule and two carboxylic groups (similar to the previously reported MALDI-TOF MS of **2**). For complexes **5** and **6** $[M - H_2O]^+$ fragments were detected. Complex **5** shows also fragmentation involving loss of the carbene ligand that is not observed with the other dimers.

The structure of dimer **3** was unambiguously confirmed by X-ray crystallography (Figure 1, Table 1). The molecular structure of **3** closely resembles that of **2**.[23] Ruthenium coordination is distorted octahedral with the two Ru=C(carbene) bond lengths 1.852(4) Å and 1.864(4) Å.

Metathesis activity: Table 2 summarises the catalytic activity of dimers **3**–**7** for the metathesis of internal alkenes, including unsaturated fatty acid esters, such as methyl oleate (**8**) [Eq. (4)]. For comparison, data for the starting compound **1** and the previously described dimer **2** are also shown.



(4)

Within the experimental error, the most active among our new compounds, that is, **3** and **7**, show the same activity as **1**. The vinylalkylidene carbene complex **4** is slightly less efficient than the corresponding benzylidene carbene complex **2**. This can be attributed to a slower initiation step of the bulkier carbene **4**.[7] No correlation is found between the p*K*a of the corresponding acid and the conversion obtained with complexes **2**–**7** since both **3** and **7** display higher activity than **2**. We conclude that both electronic and steric properties of R′ influence the metathesis activity.

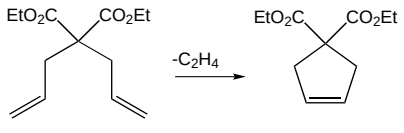
Table 2. Activity of Ru carbenes for the metathesis of alkenes.

Catalyst	Substrate	Reaction time [h]	Conversion [%]
2	*trans*-4-decene	4	24[23]
2	methyl oleate[a]	4	36[23]
2	methyl elaidate[b]	4	20[23]
3	*trans*-4-decene	4	33
3	methyl oleate	4	40
3	diethyl diallylmalonate[c]	0.5	30
4	*trans*-4-decene	4	19
4	methyl oleate	4	28
5	*trans*-4-decene	24	0
6	*trans*-4-decene	24	0
7	*trans*-4-decene	4	33
1	*trans*-4-decene	4	36[37]
1	methyl oleate	4	40[37]
1	methyl elaidate	4	36[37]

General reaction conditions except for [c]: 3 mM solution in CH_2Cl_2, molar ratio substrate:catalyst = 550:1, 20 °C. [a] Methyl *cis*-9-octadecenoate. [b] Methyl *trans*-9-octadecenoate. [c] 5 mM solution in CH_2Cl_2, molar ratio substrate:catalyst = 20:1, 20 °C.

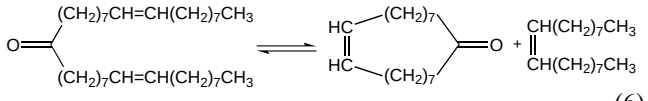
Complexes **5** and **6** do not generate any active species for the metathesis of internal alkenes. The bond order of the carboxylate in **5** and **6** is lower than in all other dimers (see Experimental Section: $\nu_s(CO_2) = 1654$ and $1651\,cm^{-1}$ for **5** and **6**, respectively, instead of $1690 \pm 5\,cm^{-1}$ for **3**, **4** and **7**). Therefore, the oxygen atoms in $C_6F_5CO_2^-$ are less electron rich than in the other halogenated carboxylates $R'CO_2^-$ (with $R' = CF_3$, C_2F_5 and CCl_3). The ruthenium centre has lower electron density in **5** and **6** than in the other dimers and was inert towards olefin metathesis.[24]

RCM of diethyl diallylmalonate (**9**) [Eq. (5)] in the presence of complex **1** (molar ratio substrate:catalyst 20:1) proceeds to 95% conversion in 30 min. Under similar conditions complex **3** gave 30% conversion in 30 min in CH_2Cl_2 and 25% conversion in benzene. The catalyst was not longer active after 30 min. As observed earlier with complex **2**, in a polar solvent such as THF the catalytic activity was dramatically lower (5% conversion after 2 h). Both the ^1H NMR spectrum and GC show that the formation of the cyclopentene needs an initiation time, thereafter the reaction is fast for 15 min and a maximum conversion of 30% is reached within 30 min.



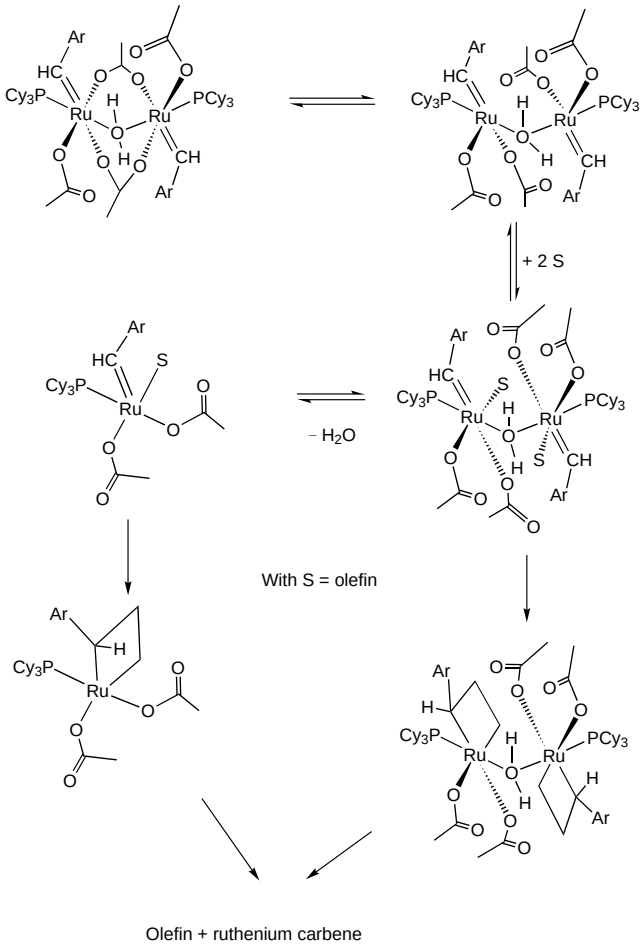
9 (5)

To demonstrate the usefulness of our catalyst for the construction of large rings, RCM of oleon (**10**) using **3** as catalyst was examined. This reaction afforded a 1.2:1 *trans*/*cis* mixture of 9-cycloheptadecen-1-one (**11**) [Eq. (6)]. The *cis* isomer of **11** is civetone, an important base material in the perfume industry.



10 **11** (6)

An associative mechanism of alkene metathesis is not possible with dimers **2**–**7** because the ruthenium centre is already six-coordinated. The first elemental reaction must be a dissociation of one ligand: the bridging coordination mode of the carboxylate is easily broken as shown in Scheme 2. This reaction generates a water-bridged complex, which may form a ruthenium metallacycle or, as observed in experiments with donor solvents (see below), the water is removed from the metal to form a 16-electron, five-coordinate (monomeric) complex. Intermediates of this type have been postulated by Grubbs and co-workers in the catalytic cycle involving complex **1**.[20] Moreover, a ruthenium carbene complex with one tricyclophosphine ligand was isolated from a reaction of **1** with a substituted cyclobutene.[25]



Scheme 2. Proposed mechanism of the reaction of complexes **2**–**4** and **7** with olefins or weak donor ligands.

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Reactions of 3 and 5 with weak σ donor ligands: In the course of our studies of the metathesis activity we became interested in the stability of these dimers towards bases and weak donor solvents (Table 3). In contrast to **1**,[7] dimer **3** is not stable in a protic solvent such as methanol and has a half-life time of 36 h at 20 °C. Pyridine reacted as well with complex **3** to form a neutral species with the phosphine and the carboxylate coordinated to the ruthenium centre. The carbene ligand was substituted by pyridine and a yellow crystalline product was isolated by slow diffusion of hexane into the toluene solution. A bidentate organic molecule (1,2-dimethoxyethane, DME) also substitutes the water molecule in complex **5**. The ^{1}H NMR spectrum of the resulting material showed that the carbene and the water ligands were removed from the ruthenium centre. Nonequivalent phosphorous atoms were found in the corresponding ^{31}P NMR spectrum; a small coupling constant $^2J_{PP} = 46$ Hz suggests a *cis* geometry at the ruthenium atom. Complex **3** was stable for days in a mixture of hexane/THF (26:1) or hexane/Et_2O (25:1). Fast decomposition of the carbene ligand was observed in $CHCl_3$ (see Table 3).

Table 3. Half-life time of complexes **2**, **3** and **5** in selected donor solvents at 20 °C.

Complex	Solvent	Half-life time [h]	Concentration [mmol L^{-1}]
2	Py	< 1	1.5
2	CH_2Cl_2	7	1.5
2	THF	120	2.3
3	Py	< 1	3.4
3	$CHCl_3$	< 1	1.9
3	MeOH	36	3.1
3	Et_2O	216	0.8
3	THF	100	0.06
5	CH_2Cl_2	9	1.3
5	DME	9	1.2

The substitution of the water and the carbene ligand by bases or weak donor solvents may follow a similar route as shown for the alkene metathesis in Scheme 2: the weakest ruthenium–ligand bond is broken with formation of a vacant site, which then becomes occupied by an electron rich atom.

Conclusion

New dimeric ruthenium carbene complexes of the general formula $[Ru_2(=CHR)_2(R'CO_2)_2(\mu\text{-}R'CO_2)_2(PCy_3)_2(\mu\text{-}H_2O)]$ have been obtained in high yields by reacting $[Ru(=CHR)Cl_2(PCy_3)_2]$ with silver salts of carboxylic acids. The synthetically useful scope of this reaction has been established, showing that the carbene ligand is stable only with strongly electron-withdrawing carboxylates. The same procedure can be used to prepare immobilised ruthenium carbenes.

The new compounds were tested for their catalytic activity for the metathesis of alkenes. With $R' = CF_3$, C_2F_5 or CCl_3 these complexes are highly active for the metathesis of linear olefins and for ring-closing metathesis. Reactions of dimers **2**, **3** and **5** with weak donor ligands were also studied and were found to follow the same scheme as the olefins.

Experimental Section

General aspects: All manipulations were carried out under an atmosphere of purified nitrogen using standard Schlenk techniques. All solvents were purified by standard procedures prior to use (hexane, THF and DME were distilled from sodium/benzophenone). Compound **1** was prepared according to the literature;[7] compound **1a** was synthesised from **1** and 1,1-diphenyl-1,3-butadiene[26] by a modified literature procedure.[7] CF_3CO_2Ag (Merck) and $C_2F_5CO_2Ag$ (Aldrich) were used as received; $C_6F_5CO_2Ag$[27] and CCl_3CO_2Ag[28] were prepared from the corresponding acid and $AgNO_3$ according to the literature. Dimer **2** was prepared as described earlier.[23] Alkenes (Fluka) and diethyl diallylmalonate (Aldrich) were purified by passing through activated alumina and distillation. NMR spectra were acquired using a Bruker AMX-300 spectrometer at room temperature. Mass spectra were measured with a JEOL JMS SX/SX102A mass spectrometer.

$[Ru_2(=CHPh)_2(C_2F_5CO_2)_2(\mu\text{-}C_2F_5CO_2)_2(PCy_3)_2(\mu\text{-}H_2O)]$ (3): A solution of $C_2F_5CO_2Ag$ (231.4 mg, 0.854 mmol) in THF (7 mL) was added to a solution of **1** (346.8 mg, 0.412 mmol) in hexane (180 mL) at −30 °C in 20 min. Formation of a white precipitate and a change of colour from purple to light-green followed. The mixture was stirred for another 60 min at −20 °C and then filtered. The filtrate was evaporated to dryness to yield a green solid. This solid was extracted with hexane (3 × 5 mL) at −78 °C to give a green solution and an insoluble residue. This solution was reduced in volume to 5 mL and placed at −80 °C overnight. Green crystals of **3** were formed which were separated from the mother liquor at −78 °C and dried under vacuum for several hours (202.9 mg, 57 %). ^{1}H NMR (CD_2Cl_2): $\delta =$ 20.61 (d, $^3J_{PH} = 5.1$ Hz, Ru=CH), 11.84 (s, H_2O), 8.08 (d, $^3J_{HH} = 8.1$ Hz, *o*-H of Ph), 7.75 (t, $^3J_{HH} = 7.3$ Hz, *p*-H of Ph), 7.41 (t, $^3J_{HH} = 7.7$ Hz, *m*-H of Ph), 2.02–0.86 (m, PCy_3 and C_6H_{14}); ^{31}P NMR (C_6D_6): $\delta = 43.52$ (s); ^{19}F NMR (CD_2Cl_2): $\delta = -80.67$ (s), −81.64 (s), −116.49 (s), −116.54 (s), 118.30 (s); IR (KBr): $\tilde{\nu} =$ 3047 vw (CH), 3007 vw (CH), 2932 w (CH_2), 2854 w (CH_2), 1690 vs $(CO_2)_a$, 1448 m (CH_2), 1266 m, 1202 s $(CO_2)_s$, 1147 s, 726 m (CF_3), 515 cm^{-1} w; FD-MS: *m*/*z* (%): 1390 (60), 668 (100), 280 (5) $[PCy_3]^+$; elemental analysis calcd (%) for $C_{62}H_{80}F_{20}O_9P_2Ru_2 \times C_6H_{14}$ (1698.5): C 48.1, H 5.57; found: C 48.9, H 5.79.[29]

$[Ru_2(=CH\text{-}CH=CPh_2)_2(CF_3CO_2)_2(\mu\text{-}CF_3CO_2)_2(PCy_3)_2(\mu\text{-}H_2O)]$ (4): Compound **4** was obtained in a similar way as described for **3** from **1a** (132.5 mg, 0.143 mmol) and CF_3CO_2Ag (63.3 mg, 0.287 mmol) at 0 °C. Filtration and removal of the volatiles yielded a yellow solid (125 mg, 54 %). Microcrystalline **4** was obtained from hexane at −78 °C. ^{1}H NMR (CD_2Cl_2): $\delta =$ 19.75 (dd, $^3J_{PH} = 5.7$ Hz, $^3J_{HH} = 12.3$ Hz, Ru=C*H*-CH=CPh_2), 11.79 (s, H_2O), 8.45 (d, $^3J_{HH} = 13.2$ Hz, Ru=CH-C*H*=CPh_2), 7.70 (d, $^3J_{HH} = 7.5$ Hz), 7.55–7.45 (m), 7.37–7.27 (m), all Ph, 2.0–0.80 (m, PCy_3, C_6H_{14}); ^{13}C NMR (C_6D_6): $\delta = 318.0$ (d, $^2J_{PC} = 14$ Hz, Ru=*C*H-CH=CPh_2), 170.6 (q, $^2J_{CF} =$ 38 Hz, *C*O_2CF_3), 167.2 (q, $^2J_{CF} = 38$ Hz, *C*O_2CF_3), 142.5 (d, $^3J_{PC} = 2.2$ Hz, Ru=CH-*C*H=CPh_2), 114.9 (q, $^1J_{CF} = 289$ Hz, CO_2CF_3), 114.6 (q, $^1J_{CF} =$ 289 Hz, CO_2CF_3), 35.60 (d, $^1J_{CP} = 21$ Hz), 31.53 (s), 28.48 (t, $J_{CP} = 10$ Hz), 26.84 (d, $J_{CP} = 5.1$ Hz); ^{31}P NMR (C_6D_6): $\delta = 45.72$ (s); ^{19}F NMR (CD_2Cl_2): $\delta = -74.00$ (s), −74.35 (s); IR (KBr): $\tilde{\nu} =$ 3053 w (CH), 3007 vw (CH), 2930 s (CH_2), 2852 ms (CH_2), 1689 vs $(CO_2)_a$, 1512 m (C=C), 1489 mw (C=C), 1446 m (CH_2), 1262 s $(CO_2)_s$, 1202 s, 1175 ms, 1147 ms, 1105 ms, 1025 w, 849 w, 801 ms (CF_3), 726 m, 700 m, 515 cm^{-1} w; FD-MS: *m*/*z* (%): 1617 (30) $[M]^+$, 1373 (10) $[Ru_2(=CH\text{-}CH=CPh_2)_2(CF_3CO_2)_2(PCy_3)_2]^+$, 1231 (10), 1092 (11), 670 (100), 384 (17), 280 (5) $[PCy_3]^+$; MALDI-TOF MS: *m*/*z* (%): 670 (100), 281 (10) $[HPCy_3]^+$; elemental analysis calcd (%) for $C_{74}H_{92}F_{12}O_9P_2Ru_2 \times 0.5\,C_6H_{14}$ (1660.6): C 55.6, H 5.96; found: C 55.6, H 5.87.

$[Ru_2(=CHPh)_2(C_6F_5CO_2)_2(\mu\text{-}C_6F_5CO_2)_2(PCy_3)_2(\mu\text{-}H_2O)]$ (5): Compound **5** was obtained in a similar way as described for **3** from **1** (155.2 mg, 0.189 mmol) and $C_6F_5CO_2Ag$ (129.5 mg, 0.406 mmol) at −20 °C. The stirring at this temperature was maintained for additional 4 h. The green solid obtained after filtration and solvents removal was washed with hexane

at $-78\,^{\circ}C$ (3×2 mL) and dried under vacuum for several hours (145.2 mg, 85%). ^1H NMR (CD_2Cl_2): $\delta=21.06$ (d, $^3J_{PH}=7.2$ Hz, Ru=CH), 12.96 (s, H_2O), 8.35 (d, $^3J_{HH}=8.4$ Hz, *o*-H of Ph), 7.78 (t, $^3J_{HH}=7.5$ Hz, *p*-H of Ph), 7.52 (t, $^3J_{HH}=7.3$ Hz, *m*-H of Ph), 2.0–1.0 (m, PCy_3), 0.8–0.6 (m, C_6H_{14}); ^{31}P NMR (C_6D_6): $\delta=43.20$ (s); ^{19}F NMR (C_6D_6): $\delta=-141.6$ (m), -144.3 (m), -155.9 (dd, $^3J_{FF}=22$ Hz), -156.1 (dd, $^3J_{FF}=22$ Hz), -162.7– -162.9 (m); IR (KBr): $\tilde{\nu}=$ 3049 vw (CH), 3003 vw (CH), 2931 s (CH_2), 2854 m (CH_2), 1654 vs $(CO_2)_a$, 1521 m (C=C), 1496 ms (C=C), 1449 mw (CH_2), 1383 s $(CO_2)_s$, 1264 w, 1107 m, 994 m, 933 w, 747 m, 514 cm^{-1} w; FD-MS: *m*/*z* (%): 1787 (16) $[Ru_2(=CHPh)_2(C_6F_5CO_2)_4(PCy_3)_2]^+$, 1762 (24) $[Ru_2(=CHPh)(C_6F_5CO_2)_4(PCy_3)_2]^+$, 1697 (35), 1608 (30) $[Ru_2(C_6F_5CO_2)_4(PCy_3)_2]^+$, 1579 (29), 1350 (33), 894 (100), 667 (35), 280 (92) $[PCy_3]^+$; elemental analysis calcd (%) for $C_{78}H_{80}F_{20}O_9P_2Ru_2\times0.5C_6H_{14}$ (1848.63): C 52.63, H 4.74; found: C 52.13, H 4.89.

$[Ru_2(=CH\text{-}CH=CPh_2)_2(C_6F_5CO_2)_2(\mu\text{-}C_6F_5CO_2)_2(PCy_3)_2(\mu\text{-}H_2O)]$ (6): Compound **6** was obtained in a similar way as described for **3** from **1a** (123.2 mg, 0.133 mmol) and $C_6F_5CO_2Ag$ (85.5 mg, 0.268 mmol) at $-20\,^{\circ}C$. Compound **6** (84.4 mg, 63%) was isolated as yellow, micro-crystalline solid from hexane at $-80\,^{\circ}C$. ^1H NMR (CD_2Cl_2): $\delta=20.22$ (dd, $^3J_{PH}=7.8$ Hz, $^3J_{HH}=12.6$ Hz, Ru=C*H*-CH=CPh_2), 12.61 (s, H_2O), 8.63 (d, $^3J_{HH}=12.6$ Hz, Ru=CH-C*H*=CPh_2), 7.63 (d, $^3J_{HH}=6.9$ Hz, Ph), 7.46–7.15 (m, Ph), 1.86–1.04 (m, PCy_3), 0.85–0.60 (m, C_6H_{14}); ^{13}C NMR (C_6D_6): $\delta=317.9$ (d, $^2J_{PC}=16$ Hz, Ru=*C*H-CH=CPh_2), 171.8 (m, *C*O_2CF_3), 167.5 (m, *C*O_2CF_3), 141.4 (d, $^3J_{PC}=2.0$ Hz, Ru=CH-*C*H=CPh_2), 36.03 (d, $^1J_{CP}=20$ Hz), 31.53 (s), 28.48 (m), 26.84 (s); ^{31}P NMR (C_6D_6): $\delta=43.85$ (s); ^{19}F NMR (CD_2Cl_2): $\delta=-139.5$ (m), -141.5 (m), -155.0 (t, $J_{FF}=21$ Hz), -155.3 (t, $J_{FF}=19$ Hz), -161.6 (m), -162.0 (m); IR (KBr): $\tilde{\nu}=$ 3033 vw (CH), 3007 vw (CH), 2928 s (CH_2), 2853 mw (CH_2), 1651 vs $(CO_2)_a$, 1520 ms (C=C), 1496 s (C=C), 1446 w (CH_2), 1381 $(CO_2)_s$ s, 1263 w, 1106 m, 993 s, 746 m, 533 cm^{-1} w; FD-MS: *m*/*z* (%): 1992 (37) $[Ru_2(=CH\text{-}CH=CPh_2)_2(C_6F_5CO_2)_4(PCy_3)_2]^+$, 1624 (55), 996 (100), 667 (65), 280 (28) $[PCy_3]^+$; elemental analysis calcd (%) for $C_{94}H_{92}F_{20}O_9P_2Ru_2\times C_6H_{14}$ (2096.0): C 57.3, H 5.10; found: C 57.6, H 5.19.

$[Ru_2(=CH\text{-}CH=CPh_2)_2(CCl_3CO_2)_2(\mu\text{-}CCl_3CO_2)_2(PCy_3)_2(\mu\text{-}H_2O)]$ (7): Compound **7** was prepared in a similar way as described for **3** from **1a** (81.5 mg, 0.088 mmol) and about two equivalents of CCl_3CO_2Ag (50 mg, 0.18 mmol) at $-30\,^{\circ}C$. Stirring was continued for 2 h while the temperature was slowly raised to $-10\,^{\circ}C$. Filtration and solvents removal under vacuum yielded a yellow solid (14 mg, 40%). ^1H NMR (CD_2Cl_2): $\delta=20.11$ (dd, $^3J_{PH}=6.0$ Hz, $^3J_{HH}=12.6$ Hz, Ru=C*H*-CH=CPh_2), 12.06 (s, H_2O), 8.48 (d, $^3J_{HH}=12.6$ Hz, Ru=CH-C*H*=CPh_2), 7.68 (d, $^3J_{HH}=7.8$ Hz), 7.59 (d, $^3J_{HH}=7.5$ Hz), 7.51 (t, $^3J_{HH}=7.1$ Hz), 7.42 (q, $^3J_{HH}=6.6$ Hz), 7.31–7.21 (m), all Ph, 2.09–1.08 (m), PCy_3; ^{31}P NMR (CD_2Cl_2): $\delta=46.65$ (s); IR (KBr): $\tilde{\nu}=$ 3039 vw (CH), 3011 vw (CH), 2928 s (CH_2), 2851 m (CH_2), 1683 s $(CO_2)_a$, 1512 mw (C=C), 1489 m (C=C) 1445 m (CH_2), 1338 ms $(CO_2)_s$, 1262 m, 1089 m, 1028 m, 846 m, 804 m, 740 m, 679 m, 515 cm^{-1} w; FD-MS: *m*/*z* (%): 384 (100), 296 (25), 208 (15); elemental analysis calcd (%) for $C_{74}H_{92}Cl_{12}O_9P_2Ru_2\times C_6H_{14}$ (1887.1): C 50.54, H 5.62; found: C 51.05, H 5.75.

Oleon (pentatriaconta-9,26-dien-18-one) (10): Ketone **10** (oleon) was obtained from methyl oleate (methyl *cis*-9-octadecenoate) as described by McMurry et al.[30]

Reactions of 3 and 5 with donor solvents

*Reaction of **3** with MeOH*: Complex **3** (5 mg, 3.1×10^{-3} mmol) was dissolved in 1 mL of a 1:1 mixture of solvents CD_3OD/C_6D_6 at room temperature. A dark purple colour was formed over a period of 72 h. ^{31}P NMR (CD_3OD/C_6D_6): $\delta=55.03$ (s); ^1H NMR (CD_3OD/C_6D_6): $\delta=2.09$–1.08 (m), PCy_3.

*Reaction of **3** with NC_5H_5*: Complex **3** (20 mg, 1.2×10^{-2} mmol) was dissolved in hexane (5 mL) at room temperature. The green colour turned slowly to yellow after pyridine (25×10^{-3} mL) was added. Yellow crystals were obtained by slow diffusion of hexane into toluene. ^{31}P NMR (NC_5D_5): $\delta=26.10$ (s); ^1H NMR (NC_5D_5): $\delta=8.34$ (m, 2H, ortho-RuNC_5H_5), 7.58 (m, 2H, meta-RuNC_5H_5), 7.2 (m, 1H, para-RuNC_5H_5), 2.09–1.08 (m), PCy_3; molar conductimetry: $\Lambda_M<2\ cm^{-2}Ohm^{-1}mmol^{-1}$.

*Reaction of **5** with DME*: Complex **5** (25 mg, 1.4×10^{-3} mmol) was dissolved in hexane (10 mL) at room temperature. The addition of DME (50×10^{-3} mL) was monitored by ^{31}P NMR. The dimer carbene complex decomposed when new phosphorus absorption appeared. This process needed 18 h to be completed. The half-life of complex **5** was 9 h. The solvents were evaporated and the residue was dissolved in CD_2Cl_2. ^{31}P NMR (CD_2Cl_2): $\delta=51.87$ s, 48.30 (d, $J_{PP}=46$ Hz), 42.91 (d, $J_{PP}=46$ Hz); ^1H NMR (CD_2Cl_2): $\delta=7.53$ (m, 1H), 7.33 (m, 2H), 7.2 (m, 2H), 2.09–1.08 (m, 43H, 1PCy_3/1DME).

*Reaction of **3** with THF*: Complex **3** (0.50 mg, 2.8×10^{-5} mmol) was dissolved in C_6D_6 (0.5 mL) and THF (1×10^{-3} mL) was added at room temperature. The reaction was followed by ^{31}P NMR and ^1H NMR. The half-life of complex **3** was 100 h.

*Reaction of **3** with Et_2O*: Complex **3** (7 mg, 3.9×10^{-4} mmol) was dissolved in C_6D_6 (0.5 mL) and Et_2O (1×10^{-3} mL) was added at room temperature. After stirring this solution for nine days, the ^{31}P NMR and ^1H NMR spectra of the reaction mixture were identical to those of the starting material, that is no reaction took place.

X-ray crystal structure of 3: Crystals of **3** suitable for an X-ray diffraction experiment were grown by cooling a concentrated solution in *n*-hexane to $-22\,^{\circ}C$. A green crystal of $0.45\times0.15\times0.06$ mm^3 was mounted on a glass capillary on a Nonius KappaCCD diffractometer at a temperature of 150 K (rotating anode, $Mo_{K\alpha}$ radiation, $\lambda=0.71073$ Å). The unit cell determination was performed with the program DIRAX[31] and lead to a triclinic cell with $a=13.6727(10)$, $b=13.8344(10)$, $c=21.3117(10)$ Å, $\alpha=94.061(10)$, $\beta=91.494(10)$, $\gamma=110.258(10)^{\circ}$, $V=3766.8(4)$ Å^3. It turned out that the crystal was non-merohedrically twinned with a twofold rotation around $hkl=(001)$ as twin operation. The intensities were evaluated separately for the two twin domains using the program EVAL14.[32] The structure was solved with automated Patterson methods[33] based on the non-overlapping reflections of the first twin domain. The structure was refined against F^2 with a HKLF5 twin refinement[34] based on the non-merged reflections of both domains using the program SHELXL97[35] up to a resolution of $(\sin\theta\lambda)_{max}=0.59$ Å^{-1}. Formula: $C_{62}H_{80}F_{20}O_9P_2Ru_2\times0.8C_6H_{14}$, $Fw=1682.28$, space group $P\bar{1}$ (No. 2), $Z=2$, $\rho=1.483$ g cm^{-3}, $\mu=0.54$ mm^{-1}.

Non hydrogen atoms were refined freely with anisotropic displacement parameters, hydrogen atoms were refined as rigid groups. The partially occupied hexane solvent molecule was refined with isotropic displacement parameters. One of the pentafluoropropanate ligands was refined with a disorder model. The drawing, structure calculations, and checking for higher symmetry were performed with the program PLATON.[36] The final *R* values were obtained as $R1$ $(I>2\sigma(I))=0.0709$ and $wR2$ $(I>2\sigma(I))=0.1482$; $R1$ (all refl.) $=0.0960$ and $wR2$ (all refl.) $=0.1654$. GoF $=1.138$.

Crystallographic data (excluding structure factors) for structure **3** in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-151150. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

Metathesis experiments: The glassware used in these experiments was dried for several hours at $120\,^{\circ}C$ and cooled down to the reaction temperature under nitrogen. In a typical experiment, *trans*-4-decene (0.62 mL, 3.27 mmol) was added to a solution of complex **3** (9.5 mg, 5.94×10^{-3} mmol) in CH_2Cl_2 (2.0 mL). The resulting solution was vigorously stirred. The progress of the metathesis reaction was monitored by sampling through a septum at suitable time intervals. The catalyst in these samples was immediately quenched with an excess of ethyl vinyl ether. The samples were analysed by GC (Carlo Erba 8000^{Top}) on a DB-5 (J&W Scientific) column.

For the ring-closing metathesis of diethyl diallylmalonate (**9**), neat diethyl diallylmalonate (35 mg, 0.15 mmol) was added at room temperature to a stirred solution of dimer **3** (12 mg, 7.2×10^{-3} mmol) in CH_2Cl_2 (1.5 mL). The colour of the reaction mixture turned yellow, the mixture was kept under a nitrogen pressure of 1.015 bar. The progress of the reaction was followed in the same way as described above.

For the ring-closing metathesis of oleon (**10**), a solution of **10** (780 mg, 1.52 mmol) in CH_2Cl_2 (100 mL) and a solution of catalyst **3** (134 mg, 0.0788 mmol, 5 mol%) in hexane (100 mL) were added simultaneously to CH_2Cl_2 (100 mL). The resulting mixture was vigorously stirred at room temperature. The progress of the reaction was followed in the same way as described above. The formation of the macrocyclic product **11** [see Eq. (6)] was confirmed by GC/MS. The *trans*/*cis* ratio was measured on a CP-Sil 88 column.

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[1] K. J. Ivin, J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, **1997**.
[2] R. R. Schrock, J. S. Murdzek, G. C. Bazan, J. Robbins, M. DiMare, M. O'Regan, *J. Am. Chem. Soc.* **1990**, *112*, 3875.
[3] G. C. Bazan, E. Khosravi, R. R. Schrock, W. J. Feast, V. C. Gibson, M. B. O'Regan, J. K. Thomas, W. M. Davis, *J. Am. Chem. Soc.* **1990**, *112*, 8378.
[4] G. C. Bazan, J. H. Oskam, H-N. Cho, L. Y. Park, R. R. Schrock, *J. Am. Chem. Soc*. **1991**, *113*, 6899.
[5] S. T. Nguyen, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc*. **1993**, *115*, 9858.
[6] P. Schwab, M. B. France, J. W. Ziller, R. H. Grubbs, *Angew. Chem.* **1995**, *107*, 2179; *Angew. Chem. Int. Ed. Engl*. **1995**, *34*, 2039.
[7] P. Schwab, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc*. **1996**, *118*, 100.
[8] M. Schuster, S. Blechert, *Angew. Chem.* **1997**, *109*, 2124; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2037.
[9] R. H. Grubbs, S. Chang, *Tetrahedron* **1998**, *54*, 4413.
[10] *Alkene Metathesis in Organic Synthesis* (Ed.: A. Fürstner), Springer, Berlin, **1998**.
[11] T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem.* **1998**, *110*, 2631; *Angew. Chem. Int. Ed.* **1998**, *37*, 2490.
[12] M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett*. **1999**, *40*, 2247.
[13] J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc*. **1999**, *121*, 2674.
[14] L. Ackermann, A. Fürstner, T. Weskamp, F. J. Kohl, W. A. Herrmann, *Tetrahedron Lett*. **1999**, *40*, 4787.
[15] T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem.* **1999**, *111*, 2573; *Angew. Chem. Int. Ed.* **1999**, *38*, 2416.
[16] M. Scholl, S. Ding, C. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953.
[17] J. Huang, H-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 5375.
[18] a) L. Jafarpour, E. D. Stevens, S. P. Nolan, *J. Organomet. Chem*. **2000**, *606*, 49; b) L. Jafarpour, S. P. Nolan, *Organometallics* **2000**, *19*, 2055.
[19] Z. Wu, S. T. Nguyen, R. H. Grubbs, J. W. Ziller, *J. Am. Chem. Soc.* **1995**, *117*, 5503.
[20] E. L. Dias, S. T. Nguyen, R. H. Grubbs, *J. Am. Chem. Soc.* **1997**, *119*, 3887.
[21] S. Chang, L. Jones II, C. Wang, L. M. Henling, R. H. Grubbs, *Organometallics* **1998**, *17*, 3460.
[22] S. M. Hansen, M. A. O. Volland, F. Rominger, F. Eisenträger, P. Hofmann, *Angew. Chem.* **1999**, *111*, 1360; *Angew. Chem. Int. Ed.* **1999**, *38*, 1273.
[23] W.Buchowicz, J. C. Mol, M. Lutz, A. L. Spek, *J. Organomet. Chem*. **1999**, *588*, 205.
[24] This interpretation is in contrast to the findings of Chen and co-workers (C. Adlhart, C. Hinderling, H. Baumann, P. Chen, *J. Am. Chem. Soc.* **2000**, *122*, 8204), who observed that in the gas phase increasing electron deficiency at the Ru centre enhances the activity. However, in their work only the metathesis step was investigated, that is a reaction of a Ru carbene with 1-butene after dissociation of one phosphine ligand. We interpret our data in terms of the carboxylates affecting the initial ligand dissociation. See also C. Adlhart, M. A. O. Volland, P. Hofmann, P. Chen, *Helv. Chim. Acta* **2000**, *83*, 3306.
[25] J. A. Tallarico, P. J. Bonitatebus, M. L. Snapper, *J. Am. Chem. Soc.* **1997**, *119*, 7157.
[26] J. J. Eisch, G. R. Husk, *J. Org. Chem*. **1966**, *31*, 589.
[27] P. Sartori, M. Weidenbruch, *Chem. Ber*. **1967**, *100*, 3016.
[28] G. Wulff, G. Röhle, W. Krüger, *Chem. Ber.* **1972**, *105*, 1097.
[29] Complexes **3**–**7** crystallise with variable amounts of solvent (hexane). Therefore correct elemental analyses could not obtained in some cases.
[30] J. E. McMurry, M. P. Fleming, K. L.Kees, L. R. Krepski, *J. Org. Chem.* **1978**, *43*, 3255.
[31] A. J. M. Duisenberg, *J. Appl. Crystallogr.* **1992**, *25*, 92.
[32] A. J. M. Duisenberg, Ph.D. thesis, Utrecht University (The Netherlands), **1998**.
[33] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P.Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, *The DIRDIF97 program system*, *Technical Report of the Crystallography Laboratory*, University of Nijmegen, The Netherlands, **1997**.
[34] R. Herbst-Irmer, G. M. Sheldrick, *Acta Crystallogr. Sect. B* **1998**, *54*, 443.
[35] G. M. Sheldrick, *SHELXL97. Program for crystal structure refinement*, University of Göttingen, Germany, **1997**.
[36] A. L. Spek, *PLATON. A multipurpose crystallographic tool*, Utrecht University, The Netherlands, **2000**.
[37] W. Buchowicz, J. C. Mol, *J. Mol. Catal*. **1999**, *148*, 97.

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