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Versatile Ru-based metathesis catalysts designed for both homogeneous and heterogeneous processes

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Abstract

The synthesis of new ruthenium-based catalysts applicable for both homogeneous and heterogeneous metathesis is described. Starting from the Hoveyda-Grubbs first generation (**1**) and the Hoveyda-Grubbs second generation (**2**) catalysts the homogeneous catalysts [RuCl((RO)$_3$Si–C$_3$H$_6$–N(R′)–CO–C$_3$F$_6$–COO)(=CH–*o*-O–*i*Pr–C$_6$H$_4$)(SIMes)] (**4**: R = Et, R′ = H; **5**: R = R′ = Me) (SIMes = 1,3-bis(2,4,6-trimethylphenyl)-4,5-dihydroimidazol-2-ylidene) were prepared by substitution of one chloride ligand with trialkoxysilyl functionalized silver carboxylates (RO)$_3$Si–C$_3$H$_6$–N(R′)–CO–C$_3$F$_6$–COOAg (**3a**: R = Et, R′ = H; **3b**: R = R′ = Me). These homogeneous ruthenium-species are among a few known examples with mixed anionic ligands. Exchange of both chloride ligands afforded the catalysts [Ru((RO)$_3$Si–C$_3$H$_6$–N(R′)–CO–C$_3$F$_6$–COO)(=CH–*o*-O–*i*Pr–C$_6$H$_4$)(SIMes)] (**9**: R = Et, R′ = H; **11**: R = R′ = Me) and [Ru((RO)$_3$Si–C$_3$H$_6$–N(R′)–CO–C$_3$F$_6$–COO)(=CH–*o*-O–*i*Pr–C$_6$H$_4$)(PCy$_3$)] (**8**: R = Et, R′ = H; **10**: R = R′ = Me). The reactivity of the new complexes was tested in homogeneous ring-closing metathesis (RCM) of *N*,*N*-diallyl-*p*-toluenesulfonamide and TONs of up to 5000 were achieved. Heterogeneous catalysts were obtained by reaction of **4**, **5** and **8**–**11** with silica gel (SG-60). The resultant supported catalysts **4a**, **5a**, **8a**–**11a** showed reduced activity compared to their homogenous analogues, but rival the activity of similar heterogeneous systems.

Keywords: Heterogeneous catalysis; Homogeneous catalysis; Metathesis; Ruthenium; Supported catalysts; Silica gel

1. Introduction

Metal-catalyzed olefin metathesis has become established as a powerful tool for carbon–carbon bond formation in organic chemistry [1]. In particular, ruthenium alkylidenes have been of special interest as olefin metathesis catalysts since they possess significant advantages in terms of stability, ease of storage and handling [2]. In recent years there has been an increased demand for supported versions of modern catalysts. Reduction of metal contamination, possibility of catalyst recovery, access to high-throughput chemistry and continuous flow reactors are only some reasons for this interest [3]. There are three general methods for attachment to the solid support: (a) through the alkylidene moiety (**R**), (b) through the permanently bound ancillary ligand (**L**) and (c) through the anionic ligand (**X**) bound directly to the Ru metal [4] (Scheme 1).

The most versatile and widely used method of attachment has been through the alkylidene moiety (**R**), due to the relative ease of their preparation and the several attempts to combine the advantages of homogeneous and heterogeneous catalysts into a single manifold [5]. During the metathesis reaction, the catalyst is released from the solid support, and the active species is solubilized. This is one of the reasons why this type of solid supported catalyst has activities comparable to homogenous catalysts. However, for this method to be viable as a solid support technology, the propagating species must return to the solid support at the end of the sequence, which often is difficult to achieve. Attachment of the catalyst through both the

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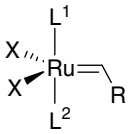


Scheme 1.

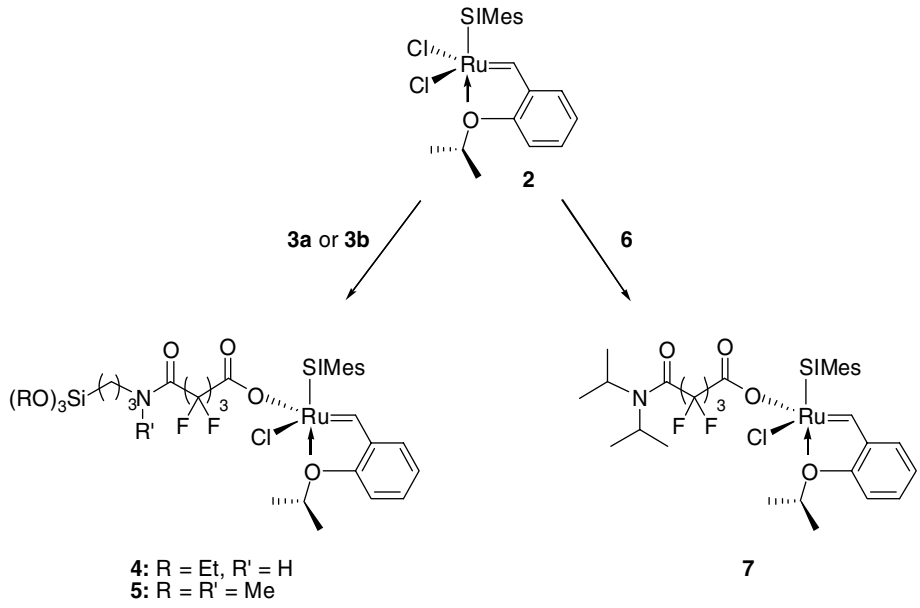
NHC ligand (**L**) [5k,6] and the anionic ligand (**X**) [7–9], avoid the problem of catalysts dissociating and bleeding into the solution phase, because both ligands show little tendency to dissociate from the metal center during metathesis reaction. Buchowicz et al., Nieczpor et al. and Buchmeiser et al. reported the synthesis of various homogeneous and heterogeneous ruthenium-based metathesis catalysts prepared by replacement of one or both chloride ligands by carboxylates resulting in stable systems [8–10]. When using fluorinated carboxylates a dramatic increase in reactivity has been observed. Based on these results we envisaged extending the concept by replacing the chloride ligands in the Hoveyda-Grubbs first and second generation catalysts by electron withdrawing ligands bearing a silyloxygroup; a suitable handle allowing for immobilization on silica gel. We chose trialkoxysilyl-functionalized silver(I) carboxylates as building blocks [11]. In the present work, we achieved for the first time to synthesize and isolate the stable and highly active monosubstituted fluorocarboxylate ruthenium complexes [RuCl($(RO)_3$Si–C_3H_6–N(R′)CO–C_3F_6–COO)(=CH–*o*-O–*i*Pr–C_6H_4)(SIMes)] (**4**: R = Et, R′ = H; **5**: R = R′ = Me). There are few examples of ruthenium complexes with mixed anionic ligands known [6g,8a,8d,9,12], but to the best of our knowledge we are reporting for the first time upon stable and isolatable catalysts based upon this structural motif of synthesizing both mono- and disubstituted fluorocarboxylate ruthenium complexes. We describe herein a direct comparison of stability and reactivity of the mono- and disubstituted catalysts. Furthermore, these novel homogeneous complexes give access to heterogeneous catalysts through the following immobilization step. Silica gel was chosen as the solid support due to the ease of functionalization whilst avoiding the disadvantages of swelling and mechanical destruction associated with other solid-supported systems on organic polymers [13,14]. It should be mentioned that our synthetic sequence provides convenient access to use either the homogeneous or the heterogeneous catalyst, as the immobilization step occurs last in the sequence. Moreover the direct comparison between both homogeneous and heterogeneous species concerning their reactivity and stability has been made possible. We hereby describe the synthesis of mono- and disubstituted homogeneous catalysts by substitution of one or both chlorides in the Hoveyda-Grubbs first (**1**) and second generation (**2**) catalysts. Furthermore, the heterogenization on silica gel is described. In addition the influence of the substitution pattern on the reactivity and stability is compared by RCM reaction of *N*,*N*-diallyl-*p*-toluenesulfonamide.

2. Results and discussion

2.1. Synthesis of the homogeneous Ru complexes

The required trialkoxysilyl-functionalized silver(I) carboxylate $(EtO)_3$Si–C_3H_6–NH–CO–C_3F_6–COOAg (**3a**) and $(MeO)_3$Si–C_3H_6–N(Me)–CO–C_3F_6–COOAg (**3b**) were prepared according to the previously described literature procedure [11]. The two different silver salts (**3a**,**b**) were used to replace one or both chloride ligands in the phosphine-containing [$RuCl_2$(=CH–*o*-O–*i*Pr–C_6H_4)(PCy_3)] (**1**) and the phosphine-free [$RuCl_2$(=CH–*o*-O–*i*Pr–C_6H_4)(SIMes)] (**2**) catalysts. The steric and electronic influences of a different *N*-substituted amide-bond on the synthesis and the activity of the resulting ruthenium complexes was also investigated. As illustrated in Scheme 2, substitution of one of the chloride ligands by reacting 1 equiv of **3a** with 1 equiv of **2** in dichloromethane, at room temperature leads to the formation of the ruthenium complex **4** which contains mixed anionic ligands. After removal of the AgCl by-product, complex **4** was isolated in pure form, as an olive-green powder, in 82% yield. Using **3b**, compound **5** was prepared as a green powder in 85% yield, but also 4% of the disubstituted catalyst **11** (see below) and 4% of catalyst **2** were observed. Complex **5** displays two benzylidene proton signals in the ^{1}H NMR spectrum (Table 1, entry 3). This is a direct consequence of the *Z*/*E*-amide bonds from the ligand. The *Z*/*E* ratio of the ruthenium complex is exactly the same as observed in the NMR of silver salt **3b**.

In contrast, attempts to synthesize the monosubstituted complexes from **1** was achieved with limited success. Only an inseparable 2:1:1 mixture of mono- and disubstituted products as well as **1**, could be isolated. We tentatively attributed this to the increased steric bulk and more basic character of the SIMes ligand in **2** compared to the relatively small PCy_3 ligand in **1** and the difference in donor ability. The electron-withdrawing fluorocarboxylate ligands decrease the electron density at the ruthenium center and should lead to a stronger Ru–Cl bond. As a consequence of this binding, substitution of the second chloride is less favored [8d]. In order to investigate the influence of the alkoxysilyl group on the observed monosubstitution we reacted 1 equiv of **2** with 1 equiv of the alkoxysilyl-free (iPr)$_2$N–CO–C_3F_6–COOAg (**6**) [11] (Scheme 2). Using THF instead of CH_2Cl_2 afforded the olive-green complex **7** in 92% yield, but 4% of the disubstituted catalyst **13** (see below) and 4% of **2** were also isolated. The silyl-free monocarboxylate complex **7** was found to be unstable in solution, especially in chlorinated solvents and disproportionated to **2** and **13.** Indeed, after stirring in $CDCl_3$ for 16 h at room temperature, a mixture of **7** (54%), **2** (21%) and **13** (21%) was obtained. From these results we tentatively attributed the higher stability of **4** and **5** to a stabilizing coordination of the alkoxysilyl-moiety to the ruthenium center. This kind of interaction was also observed for the trialkoxysilyl-functionalized silver(I) carboxylates [11]. However, substitution of both chlorines by



Scheme 2. Synthesis of the homogeneous, monocarboxylated ruthenium catalysts **4**, **5** and **7**.

Table 1
^{1}H and ^{13}C NMR data[a]

Entry	Complex	^{1}H	^{13}C
Phosphine-free ruthenium complexes			
1	**2**	16.52	295.8
2	**4**	17.14	307.4
3	**5**	17.11, 17.09 (t)[b]	306.9
4	**7**	17.06[c]	305.1[c]
5	**9**	17.56	316.6
6	**11**	17.51	316.0
7	**13**	17.54	315.4
Phosphine-containing ruthenium complexes			
8	**1**	17.39 (d)	280.6[d]
9	**8**	18.55 (d)	308.4
10	**10**	18.52 (d)	307.9
11	**12**	18.51 (d)	308.2

[a] Chemical shifts are given in ppm and measured in CD_2Cl_2.
[b] Consists of *Z*/*E* amide-products in the ratio of 1/0.6.
[c] Measured in THF-d_8.
[d] Value taken from Ref. [15].

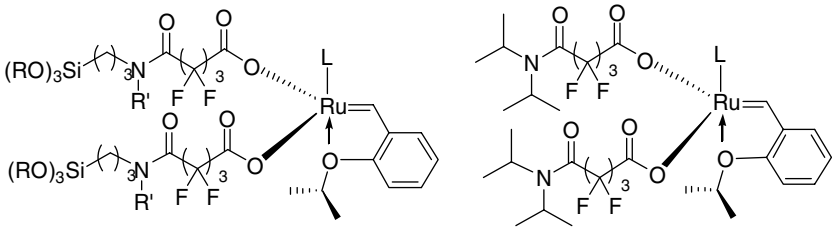
adding 2 equiv of silver carboxylates **3a**, **b** or **6** to 1 equiv of **1** or **2** gave the disubstituted phosphine-containing complexes **8**, **10** and **12** as well as the phosphine-free complexes **9**, **11** and **13**, which were isolated in pure form and in good yields (77–93%) (Scheme 3). Complexes **8**, **10** and **12** represent halide-free Hoveyda-Grubbs first generation complexes. Only a handful of such complexes are known [9].

Formation of the mono- and bis-carboxylate ruthenium complexes was corroborated by a significant low-field shift of the benzylidene ^{1}H NMR and ^{13}C NMR resonances compared to the respective signals for **1** and **2** (Table 1). While monosubstitution shifts the ^{1}H signal of the benzylidene group ca. 0.5 ppm and the ^{13}C signal ca. 10 ppm downfield, in the doubly substituted complexes these signals are even further downfield shifted compare to **1** and **2**, respectively (^{1}H: ca. 1 ppm; ^{13}C: ca. 28 ppm). This suggests a decrease in electron density at the ruthenium center due to the additive effect of the first and second electron-withdrawing fluorocarboxylate ligand (Table 1).

2.2. Synthesis of the heterogeneous Ru complexes

Immobilization of the homogeneous mono- (**4**, **5**) and bis-carboxylate (**8**–**11**) ruthenium catalysts on silica gel was performed via pre-treatment of the silica support prior to the actual immobilization step (Scheme 4). This involved washing the silica successively with methanol, dichloromethane and hexane in order to remove any impurities, and drying at 200 °C under high vacuum for 4 h to achieve thermal desorption of physically adsorbed water molecules from the silica gel surface.

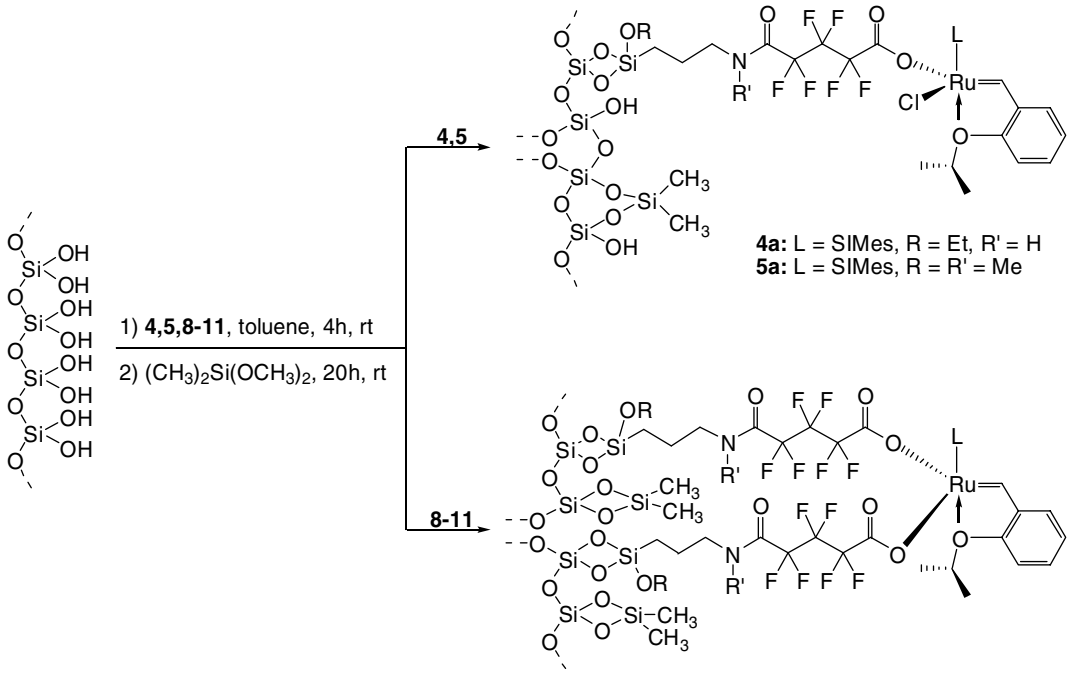
The complexes were attached to the silica surface by adding a solution of the homogeneous monosubstituted Ru-catalysts **4** and **5** and disubstituted Ru-catalysts **8**–**11** in toluene to a silica/toluene suspension and stirring the reaction mixture at room temperature. After heterogenization of the catalysts, the free SiOH-groups were subsequently capped with dimethoxydimethylsilane. The supported catalysts **4a** and **5a** containing mixed anionic ligands were isolated as olive-green solids, and the disubstituted catalysts **8a**–**11a** as light brown solids by filtration and thorough washing with CH_2Cl_2 and hexane. The catalyst loadings were determined by quantitative measurement of the remaining ruthenium in the combined filtrates by GF-AAS. Loadings between 31 and 65 μmol g^{-1} were achieved. The heterogeneous catalysts showed good stability when stored at +4 °C under argon for 4 weeks without any sign of decomposition.



8: L = PCy_3, R = Et, R' = H
9: L = SIMes, R = Et, R' = H
10: L = PCy_3, R = R' = Me
11: L = SIMes, R = R' = Me

12: L = PCy_3
13: L = SIMes

Scheme 3. Homogeneous, chlorine-free, disubstituted ruthenium catalysts **8**–**13**.



4a: L = SIMes, R = Et, R' = H
5a: L = SIMes, R = R' = Me

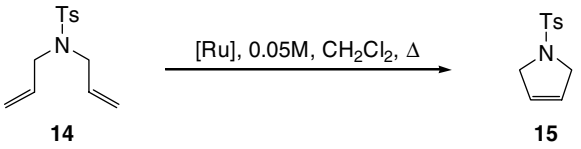
8a: L = PCy_3, R = Et, R' = H
9a: L = SIMes, R = Et, R' = H
10a: L = PCy_3, R = R' = Me
11a: L = SIMes, R = R' = Me

Scheme 4. Immobilization of the complexes **4**, **5** and **8**–**11** onto silica gel.

2.3. Reactivity of homogeneous catalysts in RCM

In order to assess the activities of the complexes **4**, **5** and **8**–**11**, a standard RCM reaction with *N*,*N*-diallyl-*p*-toluenesulfonamide (**14**) was used (Scheme 5).

Turn-over numbers (TONs) rather than yields have emerged as an important method to measure the activity of a catalyst, and have become the preferred indicator for measuring catalyst activity representing the maximum reactivity of a particular system in the chosen solvent [16]. It must be pointed out that only TONs at the same catalyst loading can reasonably be compared. To limit reaction rate to a level useful for comparison, relatively small catalyst loadings were employed. The TONs and conversions that were obtained during the RCM of **14** are shown in Table 2.



14 **15**

Scheme 5.

When comparing the conversions obtained from the different phospine-free catalysts utilizing identical loadings it is clear that the monosubstituted catalyst **4** displays comparable activity to the Hoveyda-Grubbs second generation catalyst (**2**) (Fig. 1). The monosubstituted catalyst **5** also shows high activity, but when compared to **4** and **2** the observed TONs are slightly lower (Fig. 1). TONs of 4860 for **2**, 5050 for **4** and 4490 for **5** were calculated (Table 2,

Table 2
RCM of 14 with the homogeneous Ru-catalysts[a]

Entry		Cat.	Loading 0.01 mol%		Loading 0.02 mol%	
			Conv.[b] (%)	TON	Conv.[b] (%)	TON
Phosphine-free ruthenium complexes						
1	Hoveyda-Grubbs second	**2**	49	4860	66	3300
2	Monocarboxylate complexes	**4**	51	5050	66	3290
3		**5**	45	4490	57	3850
4	Bis-carboxylate complexes	**9**	27	2690	39	1970
5		**11**	19	1870	27	1360
Phosphine-containing ruthenium complexes						
6	Hoveyda-Grubbs first	**1**	76	7600	92	4600
7	Bis-carboxylate complexes	**8**	6	580	41	2060
8		**10**	50	5000	88	4410

[a] Conditions: 0.05 M solution of **14**, solvent CH_2Cl_2, $T = 45$ °C, $t = 14$ h.
[b] Conversions determined by HPLC.

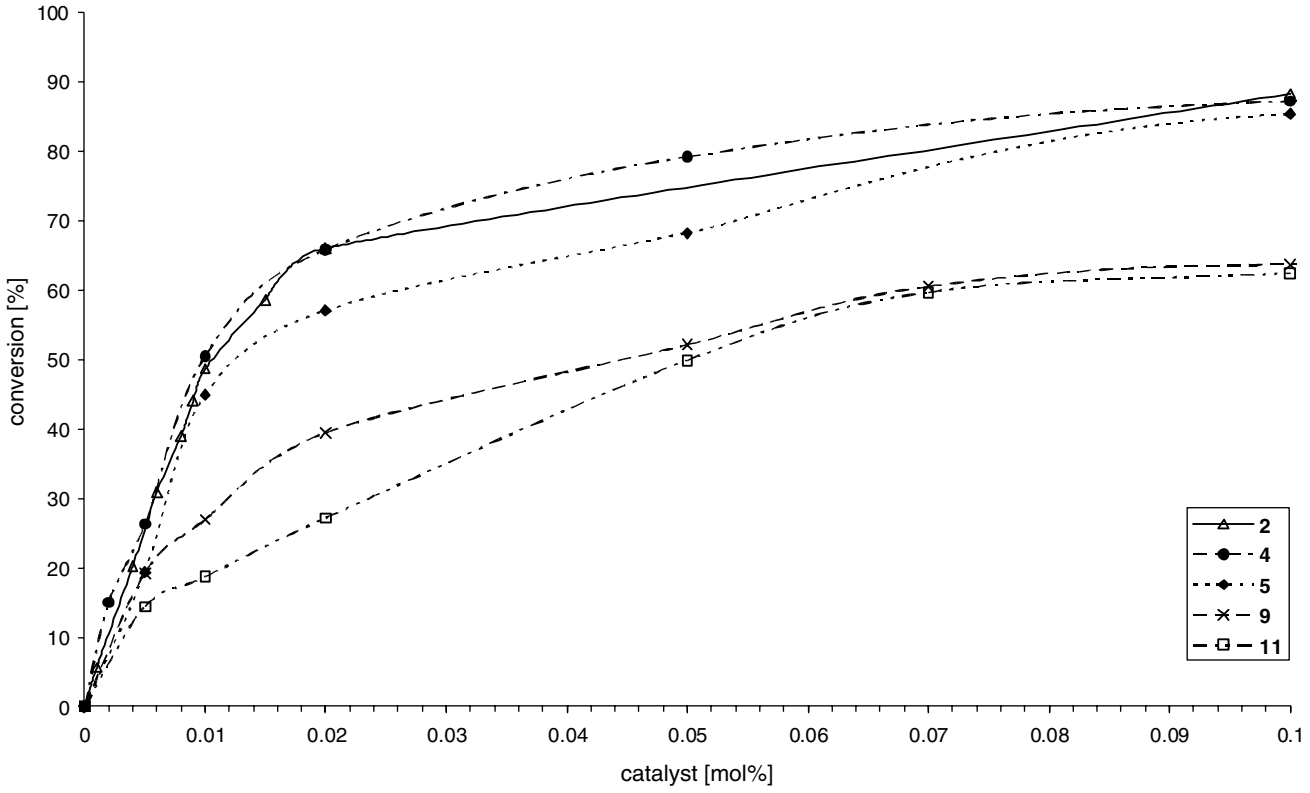


Fig. 1. RCM of **14**: comparison of the conversion as a function of catalyst loading of the homogeneous, phosphine-free, mono- (**4**, **5**) and bis-carboxylate (**9**, **11**) catalysts with **2**.

entries 1–3). However, when both chloride ligands are exchanged the resultant catalysts **9** and **11** clearly show a decreased activity (Fig. 1). Thus, TONs of 2690 for **9** and 1870 for **11** were observed (Table 2, entries 4 and 5). As before catalyst **11** with the disubstituted amide group displayed a slightly decreased activity compared to **9**.

The phosphine-containing disubstituted catalysts **8** and **10** also displayed high activity. Their observed TONs (2060 for **8** and 4410 for **10**) were higher compared to the phosphine-free, disubstituted catalysts **9** and **11** (Table 2, entries 7, 8 and 4, 5). However, compared with the parent Hoveyda-Grubbs first generation catalyst (**1**), the activity is significantly lower (Table 2, entries 6–8). Interestingly, complex **10** with the disubstituted amide group shows higher activity compared to complex **8** with the monosubstituted amide group.

2.4. Reactivity of the supported catalysts

The trend observed for the homogeneous catalyst could also be observed for the supported catalysts. As can be deduced from Table 3, the silica gel bound catalysts contain-

Table 3
RCM of **14** with the supported Ru-catalysts[a]

Entry	Cat.	Loading 0.02 mol%		Loading 0.1 mol%	
		Conv.[b] (%)	TON	Conv.[b] (%)	TON
1	**4a**	13	670	90	900
2	**5a**	13	670	87	870
3	**9a**	10	520	75	750
4	**11a**	24	1170	64	640
5	**8a**	28	1380	85	850
6	**10a**	19	960	88	880

[a] Conditions: 0.05 M solution of **14**, solvent CH_2Cl_2, $T = 45$ °C, $t = 14$ h.
[b] Conversions determined by HPLC.

ing mixed anionic ligands **4a** and **5a** were more active then their disubstituted counterparts **9a** and **11a** (entries 1–4). However, there was not such a marked difference. All supported catalysts displayed considerably lower TONs than their homogeneous counterparts. But compared to similar polymer-bound systems reported by Buchmeiser et al. the silica bound catalysts (**1a**, **5a** and **8a**–**11a**) clearly rival their activity [9]. TONs of between 640 and 900 were achieved.

In order to determine the ruthenium content of the final RCM products due to possible catalyst leaching, GF-AAS measurements were carried out. When the reactions were run using 5 mol% of the complex, ruthenium contamination in the products of 10–186 ppm was observed. This ruthenium residues are in a range detected for other silica supported ruthenium catalysts [5f]. The observed leaching for the both phosphine-containing disubstituted catalysts **8a** and **10a** was the lowest (10 ppm for **8a** and 21 ppm for **10a**). The phosphine-free systems gave ruthenium contamination of 97, 186, 42 and 31 ppm, respectively, for catalysts **4a**, **5a**, **9a** and **11a**. Two observations stand out: first, the leaching from the chloride-free, disubstituted complexes was generally lower and may be due to the double attachment to the solid support and second, the catalysts **5a** and **11a**, containing disubstituted amide groups, displayed higher leaching then **4a** and **9a** with monosubstituted amide bonds.

3. Conclusion

In summary, we have developed a new strategy for synthesizing ruthenium catalysts which can be used both homogeneously or supported on silica. The advantage of performing the chloride exchange before the immobilization step avoids the problem of separation the insoluble silver chloride from the insoluble silica-bound catalysts. The synthesis of the homogeneous complexes take place by selective exchange of one or both chloride ligands with partially fluorinated trialkoxysilyl-containing silver(I) carboxylates. The homogenous monoexchanged complexes rivaled the reactivity of the parent Hoveyda-Grubbs catalyst, whereas a loss of reactivity was observed for the chloride-free disubstituted complexes. The silica-supported derivatives were obtained by facile reaction with silica gel. They are catalytically active and displayed an increased activity to similar polymer-bound systems. However, only when compared to their homogeneous counterparts their activity is reduced. Further investigations of activity as well as immobilization strategies in order to reduce ruthenium leaching is in progress.

4. Experimental

4.1. General information

NMR data were recorded using a Bruker DPX 250 Advance, Bruker AMX 300 or Bruker DRX 500 Advance. The spectra are referenced using the signals of the residual solvent as internal standards. Fourier transform IR spectroscopy on KBr pellets were performed with a Bruker Equinox 55 FT–IR instrument. ATR spectra were recorded using Perkin–Elmer Spectrometer 881. Elemental analyses were measured by a Vario EL. Ruthenium-content was measured by GF-AAS ($\lambda = 240.272$ nm) by a SpectrAA 880Z with Zeeman background correction. Synthesis of the catalysts was performed under an argon atmosphere by standard Schlenk techniques or in an Argon-mediated dry-box (Labmaster 130, Mbraun, Germany) unless stated otherwise. Solvents were dried before use, employing standard drying agents [17]. $[RuCl_2(=CH\text{–}o\text{-}O\text{–}i\text{Pr}\text{–}C_6H_4)(PCy_3)]$ (**1**) was purchase from Aldrich, silica gel 60 was purchased from Merck. $[RuCl_2(=CH\text{–}o\text{-}O\text{–}i\text{Pr}\text{–}C_6H_4)(SIMes)]$ (**2**) [18], $(EtO)_3Si\text{–}C_3H_6\text{–}NH\text{–}CO\text{–}C_3F_6\text{–}COOAg$ (**3a**) [11] and $(MeO)_3Si\text{–}C_3H_6\text{–}N(Me)\text{–}CO\text{–}C_3F_6\text{–}COOAg$ (**3b**) [11] were prepared according to the literature. All other commercially available chemicals were used as received without further purification.

4.2. Synthesis

4.2.1. $[RuCl((EtO)_3Si\text{–}C_3H_6\text{–}NH\text{–}CO\text{–}C_3F_6\text{–}COO)(=CH\text{–}o\text{-}O\text{–}iPr\text{–}C_6H_4)(SIMes)]$ (4)

A solution of **3a** (100.4 mg, 159.6 μmol, 1 equiv) in dry CH_2Cl_2 (40 ml) was slowly added to a stirred solution of **2** (100.0 mg, 159.6 μmol, 1 equiv) in dry CH_2Cl_2 (10 ml). While stirring was continued for 60 min, the color of the reaction mixture changed from green to olive green and a white, disperse precipitate formed. The precipitate was filtered off and the filtrate was evaporated to dryness. The residue was dissolved in CH_2Cl_2 (2 ml) and *n*-hexane (6 ml) added. A white precipitation formed that was filtered off. Removal of the solvent and drying under high vacuum afforded 135.3 mg (130.9 μmol, 82.0%) of a olive green powder. ^1H NMR (250 MHz, CD_2Cl_2): δ 17.14 (s, 1H, C*H*=Ar), 7.48 (dt, $J = 7.8$ Hz, 1.8 Hz, 1H, aromat. C*H*), 7.17, 7.07 (s, 4H, mes.-C*H*), 7.02 (dd, $J = 7.5$ Hz, 1.8 Hz, 1H, aromat. C*H*), 6.94 (t, $J = 7.1$ Hz, 1H, aromat. C*H*), 6.76 (br s, 1H, N*H*), 6.76 (d, $J = 8.3$ Hz, 1H, aromat. C*H*), 4.69 (septet, $J = 6.1$ Hz, 1H, *i*Pr–C*H*), 4.14 (s, 4H, imidazol-CH_2), 3.80 (q, $J = 7.0$ Hz, 6H, Si–OCH_2), 3.20 (q, $J = 6.7$ Hz, 2H, CH_2NH), 2.46 (s, 6H, mes.-*o*-CH_3),

2.43 (s, 6H, mes.-*p*-CH_3), 2.25 (s, 6H, mes.-*o*-CH_3), 1.57 (m, 2H, Si—CH_2–CH_2), 1.21 (t, $J = 7.0$ Hz, 9H, Si–OCH_2–CH_3), 1.02 (d, $J = 6.1$ Hz, 3H, *i*Pr–CH_3), 0.98 (m, 3H, *i*Pr–CH_3), 0.57 (t, $J = 8.0$ Hz, 2H, SiCH_2). ^{19}F NMR (235 MHz, CD_2Cl_2): δ −124.5, −124.3 (2s, 2F, CF_2), −119.7, −119.4 (2t, 2F, CF_2CONH), −115.1, −114.8 (dt, t, 2F, CF_2COORu). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 307.4 (*C*H=Ar), 210.7 (imidazol-*C*N), 161.3 (*C*OO), 158.7 (*C*ONH), 153.4 (aromat. *C*), 144.6 (aromat. *C*), 139.6 (mes.-*p*-*C*), 139.5, 139.1 (mes.-*o*-*C*), 135.7 (mes.-*C*–N), 130.3 (aromat. *C*), 129.9 (mes.-*C*H), 123.0 (aromat. *C*), 122.7 (aromat. *C*), 112.7 (aromat. *C*), 111.3 (*C*F_2CONH), 109.7 (*C*F_2COORu), 108.1 (*C*F_2), 75.6 (*i*Pr–*C*H), 58.9 (SiO*C*H_2), 51.9 (imidazol-*C*H_2), 42.5 (*C*H_2NH), 22.7 (Si–CH_2–*C*H_2), 21.3 (mes.-*p*-*C*H_3), 20.5 (*i*Pr–*C*H_3), 19.2 (br s, mes.-*o*-*C*H_3), 18.7 (mes.-*o*-*C*H_3), 18.5 (Si–OCH_2–*C*H_3), 8.0 (Si–*C*H_2). IR (KBr): *v* 3072 (w), 2976 (m), 2925 (m), 2895 (w), 1772 (w), 1717 (vs), 1700 (vs), 1592 (w), 1577 (w), 1540 (m), 1482 (m), 1455 (m), 1399 (w), 1387 (m), 1377 (w), 1355 (w), 1297 (w), 1266 (s), 1215 (w), 1157 (vs), 1113 (s), 1100 (s), 1078 (s), 1038 (w), 940 (m), 851 (w), 841 (m), 798 (m), 749 (m). Anal. Calc. for $C_{45}H_{60}ClF_6N_3O_7RuSi_2$: C, 52.29; H, 5.85; N, 4.07. Found: C, 52.2; H, 5.9; N, 4.0%.

4.2.2. *[RuCl((MeO)$_3$Si–C$_3$H$_6$–N(Me)–CO– C$_3$F$_6$–COO)(=CH–o-O–iPr–C$_6$H$_4$)(SIMes)] (5)*

Compound **5** was prepared in analogous manner to the synthesis of **4** from **2** (101.7 mg, 162.3 μmol, 1 equiv) and **3b** (84.8 mg, 162.3 μmol, 1 equiv). Yield: 135.5 mg (134.8 μmol, 83.0%) olive green powder (purity: 92% **5**, 4% **11**, 4% **2**). ^{1}H NMR (250 MHz, CD_2Cl_2): δ 17.11 (s, 1H, *E*-C*H*=Ar), 17.09 (t, J(F,H) = 2.1 Hz, 1H, *Z*-C*H*=Ar), 7.46 (dt, $J = 7.7$ Hz, 1H, aromat. C*H*), 7.16, 7.07 (2s, 4H, mes.-C*H*), 7.02 (dd, $J = 7.6$ Hz, 1.8 Hz, 1H, aromat. C*H*), 6.93 (t, $J = 7.3$ Hz, 1H, aromat. C*H*), 6.75 (d, $J = 8.4$ Hz, 1H, aromat. C*H*), 4.68 (septet, $J = 6.1$ Hz, 1H, *Z*-*i*Pr–C*H*), 4.68 (septet, $J = 5.9$ Hz, 1H, *E*-*i*Pr–C*H*), 4.14 (s, 4H, imidazol-CH_2), 3.54, 3.42 (2 s, 9H, Si–OCH_3), 3.28 (m, 2H, CH_2N(CH_3)), 2.91 (s, 3H, *E*-N(CH_3)), 2.89 (t, J(F,H) = 2.2 Hz, 3H, *Z*-N(CH_3)), 2.43 (s, 6H, mes.-*p*-CH_3), 2.45, 2.27 (2 s, 12H, mes.-*o*-CH_3), 1.63 (m, 2H, Si–CH_2–CH_2), 1.02 (d, $J = 6.1$ Hz, 6H, *Z*-*i*Pr–CH_3), 0.99 (d, $J = 5.9$ Hz, 6H, *E*-*i*Pr–CH_3), 0.55 (2t, $J = 8.3$ Hz, 2H, SiCH_2). ^{19}F NMR (235 MHz, CD_2Cl_2): δ −122.1, −122.0, −122.0, −121.9 (4s, 2F, CF_2), −115.3, −115.0, −114.9, −114.6 (4t, 2F, CF_2CONH), −112.0, −111.7, −111.4, −111.3 (4t, 2F, CF_2COORu). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 306.9 (*C*H=Ar), 210.9 (imidazol-*C*N), 161.1 (*C*OORu), 158.5 (*C*ON(Me)), 153.4 (aromat. *C*), 144.6 (aromat. *C*), 139.6 (mes.-*o*-*C*), 139.4 (mes.-*p*-*C*), 135.9 (mes.-*C*–N), 130.0 (aromat. *C*), 129.9 (2s, mes.-*C*H), 123.9 (aromat. C), 122.7 (aromat. C), 112.6 (aromat. C), 111.6 (*C*F_2CON(Me)), 111.6 (*C*F_2COORu), 108.3 (*C*F_2), 75.6 (*i*Pr–*C*H), 52.4 (*C*H_2N(Me)), 51.9 (imidazol-*C*H_2), 50.8 (O*C*H_3), 35.5 (N*C*H_3), 21.1 (mes.-*p*-*C*H_3), 20.6 (*i*Pr–*C*H_3), 20.1 (Si–CH_2–*C*H_2), 19.2, 18.7 (2s, mes.-*o*-*C*H_3), 6.6, 6.4 (2s, Si–*C*H_2). IR (ATR): *v* 2964 (m), 2942 (m), 2923 (m), 2842 (w), 1781 (w), 1694 (vs), 1680 (vs), 1607 (w), 1592 (w), 1577 (w), 1482 (m), 1454 (m), 1399 (w), 1386 (w), 1377 (w), 1353 (w), 1293 (w), 1263 (vs), 1214 (w), 1157 (vs), 1113 (s), 1090 (vs), 1035 (m), 939 (m), 878 (w), 853 (w), 841 (w), 817 (m), 798 (m), 750 (m).

4.2.3. *[RuCl(iPr)$_2$N–CO–C$_3$F$_6$–COO)(=CH–o-O–iPr–C$_6$H$_4$)(SIMes)] (7)*

A solution of **6** (17.2 mg, 39.9 μmol, 1 equiv) in dry THF (5 ml) was slowly added to a stirred solution of **2** (25.0 mg, 39.9 mmol, 1 equiv) in THF (5 ml). While stirring was continued for 60 min, in dark, the color of the reaction mixture changed from green to olive-green and a white precipitate formed. The precipitate was filtered off and the filtrate was filtered through Celite. Drying in vacuo provided a olive-green powder. Yield: 33.5 mg (36.7 μmol, 91.9%) olive-green powder (purity: 92% **7**, 4% **13**, 4% **2**). ^{1}H NMR (250 MHz, THF-d_8): δ 17.06 (s, 1H, C*H*=Ar), 7.37 (dt, $J = 7.8$ Hz, 1.3 Hz, 1H, aromat. C*H*), 7.13, 7.03 (2 s, 4H, mes.-C*H*), 6.91 (dd, $J = 7.7$ Hz, 1.3 Hz, 1H, aromat. C*H*), 6.83 (d, 1H, aromat. C*H*), 6.82 (m, 1H, aromat. C*H*), 4.74 (septet, $J = 6.6$ Hz, 1H, *i*Pr–C*H*(=CH–*o*-O–*i*Pr–C$_6$H$_4$)), 4.15 (m, 2H, imidazol-CH_2), 4.08 (septet, $J = 6.6$ Hz, 1H, *i*Pr–C*H*), 3.49 (septet, $J = 6.7$ Hz, 1H, *i*Pr–C*H*), 2.49 (s, 6H, mes.-*o*-CH_3), 2.40 (s, 6H, mes.-*p*-CH_3), 2.26 (s, 6H, mes.-*o*-CH_3), 1.32 (m, 6H, *i*Pr–CH_3), 1.23 (d, $J = 5.9$ Hz, 3H, *i*Pr–CH_3(=CH–*o*-O–*i*Pr–C$_6$H$_4$)), 1.06 (d, $J = 6.6$ Hz, 6H, *i*Pr–CH_3), 1.04 (d, $J = 5.9$ Hz, 3H, *i*Pr–CH_3(=CH–*o*-*i*Pr–C$_6$H$_4$)). ^{19}F NMR (235 MHz, THF-d_8): δ −123.6 (2s, 2F, CF_2), −116.3 (t, $J = 10.7$ Hz, 1F, CF_2COORu), −116.1 (t, $J = 10.0$ Hz, 1F, CF_2COORu), −113.4(t), −112.8(t) (td, J(F,F) = 278.5, 10.0 Hz, 1F, CF_2CON), −111.9(t), −111.3(t) (td, J(F,F) = 278.7, 10.6 Hz, 1F, CF_2CON). ^{13}C NMR (75.5 MHz, THF-d_8): δ 305.1 (*C*H=Ar), 212.5 (imidazol-*C*N), 161.1 (*C*OORu), 157.5 (*C*ONH), 154.3 (aromat. *C*), 145.4 (aromat. *C*), 140.5, 140.3 (mes.-*o*-*C*), 139.6 (mes.-*p*-*C*), 130.7 (aromat. *C*), 130.6, 130.4 (mes.-*C*H), 130.3 (aromat. C*H*), 123.6 (aromat. *C*), 122.8 (aromat. *C*), 113.3 (aromat. *C*), 75.9 (*i*Pr–*C*H(=CH–*o*-O–*i*Pr–C$_6$H$_4$)), 51.9 (imidazol-*C*H_2), 49.5 (*i*Pr–*C*H), 48.3 (*i*Pr–*C*H), 21.5 (*i*Pr–*C*H_3), 21.5 (*i*Pr–*C*H(=CH–*o*-O–*i*Pr–C$_6$H$_4$)), 21.1 (mes.-*p*-*C*H_3), 20.8 (mes.*o*-CH_3), 20.3 (*i*Pr–CH_3), 19.3 (mes.-*o*-*C*H_3). IR (ATR): *v* 2969 (m), 2924 (s), 2854 (m), 2735 (w), 1695 (vs), 1677 (vs), 1607 (w), 1592 (w), 1577 (w), 1478 (m), 1454 (m), 1398 (w), 1377 (m), 1339 (w), 1263 (s), 1214 (w), 1156 (vs), 1114 (m), 1099 (w), 1049 (w), 1025 (m), 940 (m), 893 (w), 876 (w), 852 (w), 842 (w), 798 (m), 748 (m).

4.2.4. *[Ru((EtO)$_3$Si–C$_3$H$_6$–NH–CO–C$_3$F$_6$–COO)$_2$(=CH–o-O–iPr–C$_6$H$_4$)(PCy$_3$)] (8)*

A solution of **3a** (214.7 mg, 341.3 μmol, 2.05 equiv) in dry CH_2Cl_2 (40 ml) was slowly added to a stirred solution of **1** (100.0 mg, 166.5 μmol, 1 equiv) in CH_2Cl_2 (10 ml). While stirring was continued for 60 min, the color of the

reaction mixture changed from brown to violet and a white, disperse precipitate formed. The precipitate was filtered off and the filtrate was evaporated to dryness. The residue was dissolved in CH_2Cl_2 (2 ml) and *n*-hexane (6 ml) added. A white precipitation formed that was filtered off. Removal of the solvent and drying under high vacuum afforded 181.8 mg (128.5 μmol, 77.2%) of a ruby colored powder. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 18.55 (d, J(P,H) = 5.9 Hz, 1H, C*H*=Ar), 7.85 (dd, J = 7.5 Hz, 1.4 Hz, 1H, aromat. C*H*), 7.68 (dt, J = 7.2 Hz, 1.4 Hz, 1H, aromat. C*H*), 7.25 (t, J = 7.4 Hz, 1H, aromat. C*H*), 7.06 (d, J = 8.4 Hz, 1H, aromat. C*H*), 6.81 (t, J(F,H) = 4.9 Hz, 2H, N*H*), 4.96 (septet, J = 6.2 Hz, 1H, *i*Pr–C*H*), 3.80 (q, J = 7.0 Hz, 12H, Si–OCH_2), 3.26 (q, J = 6.6 Hz, 4H, CH_2NH), 2.10–1.26 (33H, PCy_3), 1.63 (m, 4H, SiCH$_2$–CH_2), 1.46 (d, J = 6.2 Hz, 6H, *i*Pr–CH_3), 1.20 (t, J = 7.0 Hz, 18H, Si–OCH$_2$–CH_3), 0.59 (t, J = 8.2 Hz, 4H, SiCH_2). ^{31}P NMR (250 MHz, CD_2Cl_2): δ 57.6. ^{19}F NMR (235 MHz, CD_2Cl_2): −123.8 (s, 4F, CF_2), −120.0 (m, 4F, CF_2CON), −115.4 (m, 4F, CF_2CORu). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 308.4 (*C*H=Ar), 163.9 (t, J(C,F) = 26.6 Hz, *C*OO), 158.6 (t, J(C,F) = 25.7 Hz, *C*ONH), 155.2 (aromat. *C*), 144.6 (aromat. *C*), 131.5 (aromat. *C*), 124.3 (aromat. *C*), 123.5 (aromat. *C*), 113.5 (aromat. *C*), 111.3 (*C*F_2CONH), 109.8 (*C*F_2COORu), 108.0 (*C*F_2), 77.0 (*i*Pr–*C*H), 58.9 (Si–O*C*H$_2$), 42.5 (*C*H$_2$NH), 34.7 (d, PCy$_3$CH), 29.6 (PCy$_3$CH$_2$), 28.0 (d, PCy$_3$CH$_2$), 26.7 (PCy$_3$CH$_2$), 22.7 (Si–CH$_2$–*C*H$_2$), 21.3 (*i*Pr–*C*H$_3$), 18.5 (Si–OCH$_2$–*C*H$_3$), 8.0 (Si–*C*H$_2$). IR (KBr): ν 3077 (w), 2976 (m), 2934 (m), 2856 (w), 1777 (w), 1707 (vs), 1634 (m), 1592 (w), 1579 (s), 1546 (m), 1478 (m), 1454 (m), 1392 (m), 1378 (m), 1302 (m), 1270 (s), 1249 (m), 1163 (vs), 1115 (s), 1100 (s), 1079 (s), 942 (m), 929 (w), 890 (w), 844 (w), 801 (m), 748 (m). Anal. Calc. for $C_{56}H_{89}F_{12}N_2O_{13}PRuSi_2$: C, 47.55; H, 6.34; N, 1.98. Found: C, 47.4; H, 6.3; N, 2.1%.

4.2.5. [Ru((EtO)$_3$Si–C$_3$H$_6$–NH–CO–C$_3$F$_6$–COO)$_2$(=CH–*o*-O–*i*Pr–C$_6$H$_4$)(SIMes)] (9)

Compound **9** was prepared analogously to **8** using **2** (100.0 mg, 159.6 μmol, 1 equiv) and **3a** (210.8 mg, 335.2 μmol, 2.1 equiv) as starting materials. Yield: 174.2 mg (120.9 μmol, 75.8%) violet powder. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 17.56 (s, 1H, C*H*=Ar), 7.40 (dt, J = 7.8, 1.7 Hz, 1H, aromat. C*H*), 7.17 (s, 4H, mes.-C*H*), 7.09 (dd, J = 7.5 Hz, 1.7 Hz, 1H, aromat. C*H*), 6.98 (t, J = 7.3 Hz, 1H, aromat. C*H*), 6.75 (t, J(F,H) = 5.1 Hz, 1H, N*H*), 6.67 (d, J = 8.4 Hz, 1H, aromat. C*H*), 4.56 (septet, J = 6.1 Hz, 1H, *i*Pr–C*H*), 4.12 (s, 4H, imidazol-CH_2), 3.80 (q, J = 7.0 Hz, 12H, Si–OCH_2), 3.22 (q, J = 6.6 Hz, 4H, CH_2NH), 2.46 (s, 6H, mes.-*p*-CH_3), 2.26 (s, 12H, mes.-*o*-CH_3), 1.58 (m, 4H, Si–CH$_2$–CH_2), 1.21 (t, J = 7.0 Hz, 18H, Si–OCH$_2$–CH_3), 0.96 (d, J = 6.1 Hz, 6H, *i*Pr–CH_3), 0.57 (t, J = 8.0 Hz, 4H, SiCH_2). ^{19}F NMR (235 MHz, CD_2Cl_2): δ −126.0, −126.1 (2s, 4F, CF_2), −121.5, −121.4 (2t, 4F, CF_2CONH), −116.7, −116.7 (2t, 4F, CF_2COORu). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 316.6 (*C*H=Ar), 209.8 (imidazol-*C*N), 161.2 (*C*OORu), 158.6 (*C*ONH), 154.0 (aromat. *C*), 143.8 (aromat. *C*), 139.9 (mes.-*o*-*C*), 139.5 (mes.-*p*-*C*), 135.5 (mes.-*C*–N), 130.4 (aromat. *C*), 130.0 (mes.-*C*H), 123.8 (aromat. *C*), 122.7 (aromat. *C*), 111.7 (aromat. *C*), 111.1 (*C*F_2CONH), 109.7 (*C*F_2COORu), 108.1 (*C*F_2), 75.3 (*i*Pr–*C*H), 58.8 (Si–O*C*H$_2$), 51.9 (imidazol-*C*H$_2$), 42.5 (*C*H$_2$NH), 22.6 (Si–CH$_2$–*C*H$_2$), 21.3 (mes.-*p*-*C*H$_3$), 20.4 (*i*Pr–*C*H$_3$), 18.5 (Si–OCH$_2$–*C*H$_3$), 18.1 (mes.-*o*-*C*H$_3$), 7.9 (Si–*C*H$_2$). IR (KBr): ν 3083 (w), 2977 (m), 2927 (m), 2896 (w), 1705 (vs), 1595 (w), 1580 (w), 1545 (m), 1485 (m), 1456 (m), 1390 (m), 1378 (m), 1355 (w), 1269 (s), 1163 (vs), 1114 (s), 1100 (s), 1077 (s), 941 (m), 915 (w), 842 (w), 797 (m), 750 (m). Anal. Calc. for $C_{59}H_{82}F_{12}N_4O_{13}RuSi_2$: C, 49.19; H, 5.74; N, 3.89. Found: C, 49.1; H, 5.8; N, 3.8%.

4.2.6. [Ru((MeO)$_3$Si–C$_3$H$_6$–N(Me)–CO–C$_3$F$_6$–COO)$_2$(=CH–*o*-O–*i*Pr–C$_6$H$_4$)(PCy$_3$)] (10)

Compound **10** was prepared analogously to **8** using **1** (100.8 mg, 167.8 μmol, 1 equiv) and **3b** (184.0 mg, 352.4 μmol, 2.1 equiv) as starting materials. Yield: 153.5 mg (112.9 μmol, 67.2%) ruby colored powder. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 18.52 (d, J(P,H) = 5.9 Hz, 1H, C*H*=Ar), 7.84 (dd, J = 7.5 Hz, 1.5 Hz, 1H, aromat. C*H*), 7.67 (dt, J = 7.9 Hz, 1.4 Hz, 1H, aromat. C*H*), 7.24 (t, J = 7.4 Hz, 1H, aromat. C*H*), 7.07 (d, J = 8.5 Hz, 1H, aromat. C*H*), 4.96 (septet, J = 6.1 Hz, 1H, *i*Pr–C*H*), 3.53 (s, 18H, Si–OCH_3), 3.34 (t, J = 7.6 Hz, 4H, CH_2N(Me)), 3.03 (t, 6H, J(F,H) = 2.0 Hz, *Z*-NCH_3), 2.93 (s, 6H, *E*-NCH_3), 2.11–1.28 (33H, PCy_3), 1.65 (m, 4H, SiCH$_2$–CH_2), 1.46 (d, J = 6.2 Hz, 6H, *i*Pr–CH_3), 0.56 (t, J = 8.4 Hz, 4H, SiCH_2). ^{31}P NMR (250 MHz, CD_2Cl_2): δ 56.9. ^{19}F NMR (235 MHz, CD_2Cl_2): δ −121.5 (s, 4F, *E*-CF_2), −121.4 (s, 4F, *Z*-CF_2), −115.1 (t, J(F,F) = 11.5 Hz, 4F, *Z*-CF_2CON(Me)), −114.9 (t, J(F,F) = 12.4 Hz, 4F, *E*-CF_2CON(Me)), −111.7 (t, J(F,F) = 12.0 Hz, 4F, *Z*-CF_2COORu), −111.2 (t, J(F,F) = 12.3 Hz, 4F, *E*-CF_2COORu). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 307.9 (*C*H=Ar), 164.1 (*C*OORu), 158.4 (*C*ON(Me)), 155.2 (aromat. *C*), 144.6 (aromat. *C*), 131.4 (aromat. *C*), 124.3 (aromat. *C*), 123.5 (aromat. *C*), 113.6 (aromat. *C*), 111.6 (*C*F_2CON(Me)), 111.6 (*C*F_2COORu), 108.3 (*C*F_2), 77.2 (*i*Pr–*C*H), 53.1 (*C*H$_2$N(Me)), 50.7 (O*C*H$_3$), 35.5 (N*C*H$_3$), 34.7 (d, PCy$_3$*C*H), 29.6 (PCy$_3$*C*H$_2$), 28.0 (d, PCy$_3$*C*H$_2$), 26.7 (PCy$_3$*C*H$_2$), 22.3 (Si–CH$_2$–*C*H$_2$), 21.3 (*i*Pr–*C*H$_3$), 6.5 (Si–*C*H$_2$). IR (KBr): ν 3074 (w), 2928 (s), 2854 (m), 1786 (w), 1704 (s), 1681 (vs), 1632 (m), 1591 (m), 1579 (w), 1479 (m), 1454 (m), 1414 (m), 1393 (w), 1380 (w), 1354 (m), 1316 (w), 1296 (w), 1262 (s), 1164 (s), 1093 (vs), 1042 (s), 929 (m), 889 (w), 819 (m), 803 (m), 749 (m). Anal. Calc. for $C_{52}H_{81}F_{12}N_2O_{13}PRuSi_2$: C, 45.98; H, 6.01; N, 2.06. Found: C, 46.1; H, 6.1; N, 2.0%.

4.2.7. [Ru((MeO)$_3$Si–C$_3$H$_6$–N(Me)–CO–C$_3$F$_6$–COO)$_2$(=CH–*o*-O–*i*Pr–C$_6$H$_4$)(SIMes)] (11)

Compound **11** was prepared analogously to **8** using **2** (100.2 mg, 159.9 μmol, 1 equiv) and **3b** (185.8 mg, 355.8

μmol, 2.1 equiv) as starting materials. Yield: 205.4 mg (157.7 μmol, 92.8%) violet powder. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 17.51 (s, 1H, C*H*=Ar), 7.38 (dt, $J = 7.8$, 1.6 Hz, 1H, aromat. C*H*), 7.17 (s, 4H, aromat. mes.-C*H*), 7.08 (dd, $J = 7.5$, 1.5 Hz, 1H, aromat. C*H*), 6.96 (t, $J = 7.4$ Hz, 1H, aromat. C*H*), 6.66 (d, $J = 8.3$ Hz, 1H, aromat. C*H*), 4.55 (septet, $J = 6.0$ Hz, 1H, *i*Pr–C*H*), 4.12 (s, 4H, imidazol-CH_2), 3.54 (18H, Si–OCH_2), 3.28 (m, 4H, CH_2N(CH$_3$)), 2.91 (br s, 6H, N(CH_3)), 2.45 (s, 6H, mes.-*p*-CH_3), 2.27 (s, 12H, mes.-*o*-CH_3), 1.63 (m, 4H, Si–CH$_2$–CH_2), 0.97 (d, $J = 6.1$ Hz, 6H, *i*Pr–CH_3), 0.55 (t, $J = 8.4$ Hz, 4H, SiCH_2). ^{19}F NMR (235 MHz, CD_2Cl_2): δ −122.0 (m, 4F, CF_2), −115.2 (t, J(F,F) = 11.2 Hz, 2F, *Z*-CF_2COORu), −115.0 (m, 1F, *Z*-CF_2COORu), −114.9 (t, J(F,F) = 11.6 Hz, 4F, *E*-CF_2COORu), −114.5 (q, J(F,F) = 11.3 Hz, 1F, *Z*-CF_2COORu), −111.9 (t, J(F,F) = 11.2 Hz, 2F, *Z*-CF_2CON(Me)), −111.7 (t, J(F,F) = 10.7 Hz, 2F, *Z*-CF_2CON(Me)), −111.4 (t, J(F,F) = 11.9 Hz, 2F, *E*-CF_2CON(Me)), −111.3 (t, J(F,F) = 11.8 Hz, 2F, *E*-CF_2CON(Me)). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 316.0 (*C*H=Ar), 210.3 (imidazol-*C*N), 161.1 (*C*OORu), 158.5 (*C*ON(Me)), 154.0 (aromat. *C*), 143.9 (aromat. *C*), 139.9 (mes.-*o*-*C*), 139.5 (mes.-*p*-*C*), 135.2 (mes.-C–N), 130.3 (aromat. *C*), 130.0 (mes.-*C*H), 123.9 (aromat. C), 122.7 (aromat. C), 111.7 (aromat. C), 112.1 (*C*F$_2$CON(Me)), 111.0 (*C*F$_2$COORu), 108.4 (*C*F$_2$), 75.3 (*i*Pr–*C*H), 53.1 (*C*H$_2$N-(Me)) 52.4 (imidazol-*C*H$_2$), 50.8 (O*C*H$_3$), 35.5 (N*C*H$_3$), 22.3 (Si–CH$_2$–*C*H$_2$), 21.3 (mes.-*p*-*C*H$_3$), 20.5 (*i*Pr–*C*H$_3$), 18.2 (mes.-*o*-*C*H$_3$), 6.6 (Si–*C*H$_2$). IR (KBr): *ν* 3075 (w), 2945 (m), 2922 (m), 2845 (w), 1705 (m), 1678 (m), 1610 (w), 1595 (w), 1580 (w), 1548 (m), 1485 (m), 1455 (m), 1378 (m), 1352 (w), 1266 (s), 1162 (s), 1073 (vs), 942 (m), 879 (w), 842 (w), 823 (m), 796 (m), 748 (m). Anal. Calc. for $C_{55}H_{74}F_{12}N_4O_{13}RuSi_2$: C, 47.70; H, 5.39; N, 4.04. Found: C, 47.8; H, 5.5; N, 3.9%.

4.2.8. [Ru((*i*Pr)$_2$)$_2$N–CO–C$_3$F$_6$–COO)$_2$(=CH–*o*-O–*i*Pr–C$_6$H$_4$)(PCy$_3$)] (**12**)

Compound **12** was prepared analogously to **8** using **1** (10.5 mg, 17.5 μmol, 1 equiv) and **6** (16.5 mg, 38.4 μmol, 2.1 equiv) as starting materials. Yield: 18.1 mg (15.4 μmol, 87.9%) crimson powder. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 18.51 (d, J(P,H) = 5.9 Hz, 1H, C*H*=Ar), 7.84 (dd, $J = 7.5$, 1.6 Hz, 1H, aromat. C*H*), 7.67 (dt, $J = 7.9$ Hz, 1.5 Hz, 1H, aromat. C*H*), 7.24 (t, $J = 7.4$ Hz, 1H, aromat. C*H*), 7.07 (d, $J = 8.4$ Hz, 1H, aromat. C*H*), 4.96 (dseptet, $J = 6.3$, 1.2 Hz, 1H, *i*Pr–C*H*(=CH–*o*-O–*i*Pr–C$_6$H$_4$)), 4.22 (septet, $J = 6.5$ Hz, 2H, *i*Pr–C*H*), 3.51 (septet, $J = 6.8$ Hz, 2H, *i*Pr–C*H*), 2.11–1.21 (33H, PCy$_3$), 1.46 (d, $J = 6.3$ Hz, 6H, *i*Pr–CH_3(=CH–*o*-O–*i*Pr–C$_6$H$_4$)), 1.37 (d, $J = 6.8$ Hz, 12H, *i*Pr–C*H*), 1.16 (d, $J = 6.5$ Hz, 12H, *i*Pr–C*H*). ^{31}P NMR (250 MHz, CD_2Cl_2): δ 57.9. ^{19}F NMR (235 MHz, CD_2Cl_2): δ −122.0 (s, 4F, CF_2), −115.8 (t, J(F,F) = 11.2 Hz, 4F, CF_2COORu), −111.6 (t, J(F,F) = 11.8 Hz, 4F, CF_2CON). ^{13}C NMR (75.5 MHz, CD_2Cl_2): δ 308.2 (*C*H=Ar), 164.4 (*C*OORu), 157.2 (*C*ON), 155.4 (aromat. *C*), 144.8 (aromat. *C*), 131.3 (aromat. *C*), 124.3 (aromat. *C*), 122.4 (aromat. *C*), 113.8 (aromat. *C*), 111.9 (*C*F$_2$COORu), 111.5 (*C*F$_2$), 108.2 (*C*F$_2$CON), 77.2 (*i*Pr–*C*H(=CH–*o*-O–*i*Pr–C$_6$H$_4$)), 49.1 (*i*Pr–*C*H), 48.1 (*i*Pr–*C*H), 34.6 (d, J(P,C) = 24.2 Hz, PCy$_3$CH), 29.6 (PCy$_3$CH$_2$), 28.0 (d, J(P,C) = 10.5 Hz, PCy$_3$CH$_2$), 26.7 (PCy$_3$CH$_2$), 21.3 (*i*Pr–*C*H(=CH–*o*-O–*i*Pr–C$_6$H$_4$)), 20.7 (*i*Pr–*C*H$_3$), 19.9 (*i*Pr–*C*H). IR (KBr): *ν* 2971 (w), 2933 (s), 2856 (m), 1705 (s), 1679 (vs), 1633 (m), 1591 (w), 1579 (w), 1477 (m), 1448 (m), 1391 (w), 1380 (m), 1339 (m), 1302 (w), 1262 (m), 1246 (w), 1209 (m), 1159 (vs), 1115 (s), 1099 (w), 1051 (m), 1026 (m), 929 (m), 893 (w), 873 (w), 850 (w), 827 (w), 801 (m), 749 (m). Anal. Calc. for $C_{50}H_{73}F_{12}N_2O_7PRu$: C, 51.14; H, 6.27; N, 2.39. Found: C, 51.0; H, 6.3; N, 2.3%.

4.2.9. [Ru((*i*Pr)$_2$)$_2$N–CO–C$_3$F$_6$–COO)$_2$(=CH–*o*-O–*i*Pr–C$_6$H$_4$)(SIMes)] (**13**)

Compound **13** was prepared analogously to **7** using **2** (34.2 mg, 54.6 μmol, 1 equiv) and **6** (51.6 mg, 120.0 μmol, 2.2 equiv) as starting materials. While stirring was continued for 60 min, the color of the reaction mixture changed from green to pink and a white, disperse precipitate formed. The precipitate was filtered off and the filtrated was concentrated in vacuo. The solid was redissolved in CH_2Cl_2 and passed over a short pad of silica. Elution with CH_2Cl_2 removed **2** and **11** as a green band from the column. The following addition of ethyl acetate/*n*-hexane (1/2) supply a violet band. The solvent was evaporated and the resulting solid was dried under vacuum to give 31.8 mg violet powder (26.5 μmol, 48.6%). ^{1}H NMR (250 MHz, THF-d_8): δ 17.54 (s, 1H, C*H*=Ar), 7.28 (dt, $J = 7.0$ Hz, 1.7 Hz, 1H, aromat. C*H*), 7.14 (s, 4H, mes.-C*H*), 6.97 (dd, $J = 7.5$, 1.6 Hz, 1H, aromat. C*H*), 6.83 (t, $J = 7.0$ Hz, 1H, aromat. C*H*), 6.72 (d, $J = 8.3$ Hz, 1H, aromat. C*H*), 4.63 (septet, $J = 6.1$ Hz, 1H, *i*Pr–C*H*(=CH–*o*-O–*i*Pr–C$_6$H$_4$)), 4.14 (s, 4H, imidazol-CH_2), 4.08 (septet, $J = 6.7$ Hz, 2H, *i*Pr–C*H*), 3.49 (septet, $J = 6.7$ Hz, 2H, *i*Pr–C*H*), 2.43 (s, 6H, mes.-*p*-CH_3), 2.30 (s, 12H, mes.-*o*-CH_3), 1.33 (d, $J = 6.7$ Hz, 12H, *i*Pr–CH_3), 1.07 (t, $J = 5.5$ Hz, 12H, *i*Pr–CH_3), 1.00 (d, $J = 6.1$ Hz, 6H, *i*Pr–CH_3(=CH–*o*-O–*i*Pr–C$_6$H$_4$)). ^{19}F NMR (235 MHz, THF-d_8): δ −120.3, −120.2 (2s, 4F, CF_2), −112.9 (m, 4F, CF_2COORu), −109.3 (t, J(F,F) = 11.1 Hz, 2F, CF_2CON), −108.7 (t, J(F,F) = 10.7 Hz, 2F, CF_2CON). ^{13}C NMR (75.5 MHz, THF-d_8): δ 315.4 (*C*H=Ar), 211.2 (imidazol-*C*N), 161.0 (*C*OORu), 157.4 (*C*ONH), 154.5 (aromat. *C*), 144.1 (aromat. *C*), 140.0 (mes.-*o*-*C*), 139.9 (mes.-*p*-*C*), 136.9 (mes.-C–N), 130.5 (aromat. *C*), 130.1 (mes.-*C*H), 124.1 (aromat. *C*), 122.3 (aromat. *C*), 112.1 (*C*F$_2$COORu), 111.9 (aromat. *C*), 111.1 (*C*F$_2$), 108.7 (*C*F$_2$CON), 75.3 (*i*Pr–*C*H(=CH–*o*-O–*i*Pr–C$_6$H$_4$)), 51.9 (imidazol-*C*H$_2$), 48.9, 47.8 (*i*Pr–*C*H), 21.0 (mes.-*p*-*C*H$_3$), 20.5 (*i*Pr–*C*H$_3$), 20.3 (*i*Pr–*C*H(=CH–*o*-O–*i*Pr–C$_6$H$_4$)), 19.8 (*i*Pr–*C*H), 18.3 (mes.-*o*-*C*H$_3$). IR (KBr): *ν* 2966 (m), 2924 (m), 2854 (w), 1705 (s), 1679 (vs), 1595 (w), 1580 (w), 1484 (m), 1456 (m), 1446 (m), 1400 (m), 1379 (m), 1338 (m), 1263 (vs), 1211 (m), 1157 (vs), 1114 (s), 1099

(m), 1049 (m), 1022 (s), 941 (m), 894 (w), 877 (w), 852 (w), 843 (w), 797 (s), 748 (m). Anal. Calc. for $C_{53}H_{66}F_{12}N_4O_7Ru$: C, 53.04; H, 5.54; N, 4.67. Found: C, 53.1; H, 5.5; N, 4.7%.

4.3. General procedure for heterogenization on silica gel 60

The silica gel (SG-60) was washed successively with MeOH, CH_2Cl_2 and *n*-hexane. After dehydration for 4 h at 200 °C in vacuo, SG-60 (200–400 mg) was suspended in dry toluene and a solution of homogeneous catalysts in toluene was added. The resulting suspension was stirred at room temperature for 4 h. Dimethoxydimethylsilane was added dropwise and stirring was continued for additional 20 h. The product was isolated by filtration and washed with CH_2Cl_2 and *n*-hexane. Drying in vacuo over night afforded the product.

4.3.1. [RuCl([SG]–C_3H_6–NH–CO–C_3F_6–COO)(=CH–o-O–iPr–C_6H_4)(SIMes)] (**4a**)

Starting with **4** (44.8 mg, 30.9 μmol) in 6 ml toluene, SG-60 (433.5 mg) in 6 ml toluene and dimethoxydimethyl silane (139.0 μl, 996.9 μmol), **4a** was obtained as olive green solid. Ru content 31.5 μmol g^{-1}, corresponding to 32.6 mg catalysts g^{-1}.

4.3.2. [RuCl([SG]–C_3H_6–N(Me)–CO–C_3F_6–COO)(=CH–o-O–iPr–C_6H_4)(SIMes)] (**5a**)

Starting with **5** (43.6 mg, 43.4 μmol) in 6 ml toluene, SG-60 (433.8 mg) in 6 ml toluene and dimethoxydimethyl silane (139.1 μl, 998.0 μmol), **5a** was obtained as olive green solid. Ru content 47.4 μmol g^{-1}, corresponding to 47.6 mg catalysts g^{-1}.

4.3.3. [Ru([SG]–C_3H_6–NH–CO–C_3F_6–COO)$_2$(=CH–o-O–iPr–C_6H_4)(PCy_3)] (**8a**)

Starting with **8** (25.0 mg, 17.7 μmol) in 3 ml toluene, SG-60 (176.9 mg) in 3 ml toluene and dimethoxydimethyl silane (56.8 μl, 407.0 μmol), **8a** was obtained as light brown solid. Ru content 32.8 μmol g^{-1}, corresponding to 46.4 mg catalysts g^{-1}.

4.3.4. [Ru([SG]–C_3H_6–NH–CO–C_3F_6–COO)$_2$(=CH–o-O–iPr–C_6H_4)(SIMes)] (**9a**)

Starting with **9** (44.5 mg, 39.6 μmol) in 6 ml toluene, SG-60 (308.9 mg) in 6 ml toluene and dimethoxydimethyl silane (99.0 μl, 710.5 μmol), **9a** was obtained as light brown solid. Ru content 65.4 μmol g^{-1}, corresponding to 94.3 mg catalysts g^{-1}.

4.3.5. [Ru([SG]–C_3H_6–N(Me)–CO–C_3F_6–COO)$_2$(=CH–o-O–iPr–C_6H_4)(PCy_3)] (**10a**)

Starting with **10** (67.6 mg, 49.8 μmol) in 9 ml toluene, SG-60 (478.1 mg) in 9 ml toluene and dimethoxydimethyl silane (153.3 μl, 1.1 mmol), **10a** was obtained as light brown solid. Ru content 38.8 μmol g^{-1}, corresponding to 52.6 mg catalysts g^{-1}.

4.3.6. [Ru([SG]–C_3H_6–N(Me)–CO–C_3F_6–COO)$_2$(=CH–o-O–iPr–C_6H_4)(SIMes)] (**11a**)

Starting with **11** (52.9 mg, 38.2 μmol) in 6 ml toluene, SG-60 (382.6 mg) in 6 ml toluene and dimethoxydimethyl silane (124.7 μl, 894.5 μmol), **11a** was obtained as light brown solid. Ru content 58.9 μmol g^{-1}, corresponding to 81.6 mg catalysts g^{-1}.

4.3.7. Leaching tests

For the determination of the arisen Leachings, the metathesis samples with 5 mol% catalyst were used. The suspensions were filtered and the filtrate were evaporated to dryness. The investigation of the ruthenium quantities took place by GF-AAS.

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