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New highly fluorinated dirhodium(II) tetrakis(alkanecarboxylates) as catalysts for carbenoid C–H insertion reactions

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Dedicated to François Mathey at the occasion of his 60th birthday

Abstract

Six highly fluorinated dirhodium(II) tetrakis(alkanecarboxylates) [$Rh_2(OOCR_F)_4$, $R_F = C_7F_{15}$, $CH_2C_6F_{13}$, $CH_2CH_2C_6F_{13}$, $CH_2CH_2C_8F_{17}$, $CH_2CH_2C_{10}F_{21}$, and $CH_2OCH_2CH_2C_{10}F_{21}$] were prepared and characterized. Their suitability as catalysts for intermolecular carbenoid C–H insertion was investigated for the reaction of methyl diazoacetate with hexane. In the frame of fluorous synthesis, only $Rh_2(OOCC_7F_{15})_4$ and $Rh_2(OOCCH_2C_6F_{13})_4$ are interesting, since they are soluble in perfluoro(methylcyclohexane) and catalyze the C–H insertion reaction more effectively than all other catalysts, including $Rh_2(OAc)_4$. The same two catalysts were also used to achieve 1,5-cyclization of an α-diazo-β-keto ester by intramolecular C–H insertion. Unfortunately, deterioration of the catalysts occurs to a significant extent during all reactions, and therefore, the possibilities to recover and reuse them are rather limited. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rhodium complexes; Fluorous synthesis; Diazo compounds

1. Introduction

Dinuclear rhodium complexes (Rh_2L_4) with carboxylate, amidate, and related ligands are highly versatile catalysts for carbene transfer from diazo compounds to a range of substrates via rhodium carbene intermediates [1,2]. These catalysts are not only efficient, but can also be applied to a broad range of carbene transfer reactions, and the choice of an appropriate ligand often allows to influence the chemo-, regio-, and diastereoselectivity of a transformation. One disadvantage of rhodium catalysts is the high price of the metal. In spite of this, efforts to recover the catalysts have rarely been made. One notable exception is Doyle's polyethylene-bound dirhodium(II) pyrrolidin-2-one-5(*S*)-carboxylate [3]. Another possibility is suggested by the recent progress in fluorous phase synthesis. Among other applications, this methodology allows to separate highly fluorinated compounds (reagents, products, catalysts) from a reaction mixture by extraction into perfluorinated solvents, such as perfluoro(methylcyclohexane) (CF_3–C_6F_{11}, PFMC) and FC-75 which themselves are not miscible at room temperature with common organic solvents of low polarity [4]. Along these lines, we have started to investigate the possibility to use highly fluorinated dinuclear rhodium(II) carboxylates as catalysts for carbene transfer reactions and to recover and to reuse them. In a preliminary communication [5], we have shown that dimeric rhodium(II) perfluorooctanoate and rhodium(II) 4-(perfluorohexyl)benzoate [($Rh_2(OOCR)_4$, $R = C_7F_{15}$ and C_6H_4-4-C_6F_{13}, respectively) can be recycled several times with little loss of material and activity in cyclopropanation reactions of alkenes with methyl diazoacetate. In this paper, we look at the performance of several 'fluorous' rhodium(II) alkanecarboxylates in an intermolecular aliphatic C–H insertion reaction with methyl diazoacetate. Transformations of this type are notorious for being not highly efficient even with most rhodium catalysts [1,2,6]. Furthermore, the intramolecular C–H insertion reaction of an α-diazo-β-keto ester is described.

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Table 1
Yields, fluorine content, and solubilities of complexes **2**–**7** [PFMC = perfluoro(methylcyclohexane)]

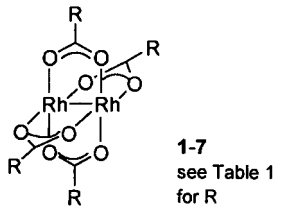
	$Rh_2(OOCR)_4$ R =	Yield (%) method [a]	Fluorine content (%)	Solubility in PFMC
2	C_7F_{15}	77 (A), 32 (B)	61.4	Soluble
3	$CH_2C_6F_{13}$	74 (A)	57.7	Soluble
4	$CH_2CH_2C_6F_{13}$	53 (B)	55.9	Insoluble
5	$CH_2CH_2C_8F_{17}$	57 (B)	59.6	Insoluble
6	$CH_2CH_2C_{10}F_{21}$	68 (B)	62.1	Insoluble
7	$CH_2O(CH_2)_2C_{10}F_{21}$	30 (B)	59.3	Insoluble

r > 30 (B)ca = "D" > > 59.3 > Insoluble
[a] See Scheme 1 for methods A and B.

2. Results and discussion

2.1. Preparation and characterization of rhodium complexes **2**–**7**

As a rule of thumb, a compound with a good solubility in a perfluorinated solvent should have a fluorine content of ca. 60% or higher. This requirement is fulfilled by dirhodium(II) tetrakis(perfluorooctanoate) (**2**, 61.4% F). However, it is clear that the four strongly electron-withdrawing ligands affect the electronic properties of the rhodium core of the complex and enhance its electrophilicity. In fact, the related rhodium perfluorobutyrate [$Rh_2(pfb)_4$] has been used in diazo decomposition and carbene transfer reactions when a much more electrophilic catalyst than the standard catalyst $Rh_2(OAc)_4$ was needed [1,7], and it is also known for its high π-coordination of olefins [8].

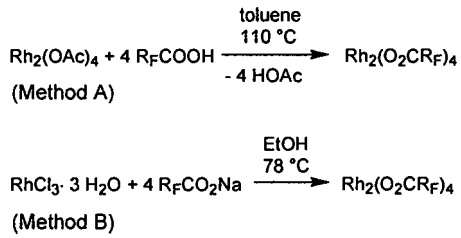


(Formula 1)

In order to create fluorous rhodium catalysts that still resemble $Rh_2(OAc)_4$ in their electronic properties, we prepared complexes **3**–**7** (Table 1) where spacer groups [CH_2, $(CH_2)_2$ and $(CH_2)_2OCH_2$] have been introduced to isolate the metal atoms from the strongly electron-withdrawing perfluoroalkyl segments of the ligands. The spacer concept has been widely used in the design of compounds bearing long perfluoroalkyl chains [4,9–11].

Complexes **2** and **3** were prepared from $Rh_2(OAc)_4$ (**1**) by exchange of the acetate ligands (Scheme 1, method A). By reaction of $Rh_2(OAc)_4$ with four equivalents of perfluorooctanoic acid and (perfluorohexyl)acetic acid, respectively, in boiling toluene and with azeotropic removal of the liberated acetic acid, the complexes were obtained in good yields (77 and 74%). Complexes **4**–**7** were prepared from the sodium salts of the corresponding acids and rhodium(III) chloride hydrate in refluxing ethanol according to a standard procedure [12] (Scheme 1, method B). The moderate yields (Table 1) are due at least in part to the formation of elemental rhodium under the reaction conditions, in particular in the case of **7**. While **2** was also obtained by method B in modest yield, the ligand exchange method A was not suited to prepare **4**, probably, because the pK_a value of 3-(perfluorohexyl)propionic acid was not sufficiently low. We found it difficult to remove the last solvent traces from the complexes. In particular, toluene could not be removed completely even by heating the complexes at 60 °C/1 mbar for 12 h. While, complexes **4**–**7** are green microcrystalline solids, **2** and **3** were obtained as dark-green, waxy materials which were not easy to isolate from the reaction vessel. However, they formed solid purple bis(acetonitrile) complexes on exposure to CH_3CN which could be handled conveniently and from which the solvent-free complexes could be recovered by treatment at 60 °C/1 mbar for 5 h.

Complexes **2** and **3** are soluble in PFMC, but unfortunately with respect to fluorous synthesis, **4**–**7** are completely insoluble in PFMC, in spite of the fact that their fluorine content is between 55.8% (**4**) and 62.1% (**6**). It appears that due to the presence of the spacer groups, the perfluoroalkyl segments do no longer shield the polar carboxylate moieties efficiently enough to prevent repulsive interactions between the latter and the perfluorinated solvent molecules. It should be kept in mind that the fluorous rhodium carboxylates presented here differ from most other fluorous catalysts by their polar carboxylate head groups; typically, fluorous cata-



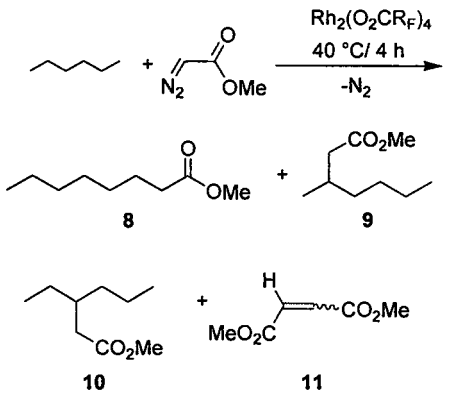
Scheme 1.

Table 2
Distribution of catalysts **2** and **3** in the two-phase system PFMC – organic solvent, determined gravimetrically

	$K = c_{PFMC}/c_{Solv}$			
	Et_2O	CH_2Cl_2	Hexane	Toluene
2	4.9	18.7	29.4	18.9
3	0.6	8.5	28.7	25.7

Table 3
Characteristic IR absorptions of complexes **1**–**7**

	$Rh_2(OOCR)_4$ R =	IR (KBr, cm^{-1})		
		$\nu(CO)_{asym}$	$\nu(CO)_{sym}$	$\nu(CF)$
1	CH_3	1577	1413/1428	–
2	C_7F_{15}	1663	1424	1207/1244
3	$CH_2C_6F_{13}$	1611	1414/1428	1206/1241
4	$CH_2CH_2C_6F_{13}$	1579	1422/1444	1188/1249
5	$CH_2CH_2C_8F_{17}$	1575	1422/1445	1147/1206
6	$CH_2CH_2C_{10}F_{21}$	1581	1421/1443	1104/1263
7	$CH_2O(CH_2)_2C_{10}F_{21}$	1599	1414	1146/1242



Scheme 2.

lysts contain phosphane or amine ligands with perfluoroalkyl segments but no other polar function. Low solubility in perfluorocarbons was also noticed for related highly fluorinated cobalt(II) [13] and manganese(II) [14] carboxylates.

Complexes **2** and **3** are also soluble at ambient temperature in organic media such as THF and diethyl ether (good solubility), dichloromethane, chloroform (intermediate), and toluene (low). In the two-phase systems PFMC–organic solvent, with the exception of PFMC–hexane, a leaching into the organic phase can be noticed visually by the green color of the latter. As Table 2 shows, the distribution coefficients of mixtures with hexane, toluene and CH_2Cl_2 are sufficiently far on the side of PFMC to allow an efficient extraction of the catalysts into the perfluorocarbon solvent.

As expected due to their D_{4h} symmetry, **2**–**6** have very simple ^{1}H-NMR spectra. As already noted by Brunner for other rhodium(II) carboxylate complexes [15], the resonances of the alkyl protons of the carboxylate ligand in **3**–**6** show a high-field shift compared with the free carboxylic acids ($\Delta\delta \approx 0.2$ ppm). The ^{19}F-NMR spectra of the complexes are remarkably similar for complexes with the same length of the perfluorinated chain. The IR spectra of the complexes (Table 3) exhibit three characteristic absorptions in the ranges 1575–1663, 1414–1445, and 1104–1263 cm^{-1}, corresponding to the antisymmetric and symmetric stretching modes of the carboxylate ligands [12] and the C–F stretching vibrations. The ν_{asym}(OOCR) vibration is a good indicator for the electron-withdrawing effect of the fluorinated alkyl chain [12]. The comparison with $Rh_2(OAc)_4$ suggests that the $(CH_2)_2$ and $CH_2O(CH_2)_2$ spacers are sufficient to suppress the electronic influence of the perfluoroalkyl segments on the Rh–Rh core of the complex.

Since, we did not characterize **2**–**7** by elemental analysis, we verified the absence of any starting material by IR and NMR spectroscopy. In addition, the complexes were characterized by laser desorption time-of-flight mass spectrometry (positive ion mode). For **2**–**5**, main peaks corresponding to the units Rh_2L_4 and Rh_2L_5 could be observed, while complexes **6** and **7**, yielded only unspecific particle patterns.

2.2. Catalytic intermolecular C–H insertion with methyl diazoacetate

Intermolecular C–H insertion into alkanes by diazoacetate esters is significantly more effective with dirhodium(II) tetrakis(trifluoroacetate) than with simple rhodium alkanoates such as $Rh_2(OAc)_4$ and Rh_2(octanoate)$_4$ [6,16]. Hence, we investigated the intermolecular C–H insertion into hexane by methyl diazoacetate with catalysts **2**–**4**, **7**, and $Rh_2(OAc)_4$ (**1**) in order to disclose the effect of the spacer groups (Scheme 2). The reactions were carried out in a large excess of hexane to reduce the extent of dimerization and oligomerization of the carbenes. In the case of **2** and **3**, a small volume of PFMC was added to the hexane kept at 40 °C; at this temperature, the two liquids form a homogeneous phase in which the catalyst is completely soluble. Yields and product distributions were determined by GC (see Section 4). The results are listed in Table 4. They confirm the earlier observations (see above) that the more electrophilic catalysts (**2** and **3**) are also more effective at C–H insertion. The uneffectiveness of $Rh_2(OAc)_4$, **4**, and **7** can be attributed to both their similarly low electrophilicity and their insolubility in the reaction medium. The selectivity of the insertion reaction is not influenced markedly by the catalysts used in this study, and it is also rather similar

Table 4
Products and yields of the reaction of methyl diazoacetate with hexane catalyzed by **1**–**7**

	Catalyst $Rh_2(OOCR)_4$ R =	Yield (%)				Relative yield of insertion
		8	**9**	**10**	**11** ($E+Z$)	C-1/C-2/C-3
1	CH_3	0.3	2.8	1.1	24.9	1/14.0/5.5
2	C_7F_{15}	2.5	26.0	12.3	8.8	1/15.6/7.4
	[a]	0.4	5.7	2.9	20.6	
3	$CH_2C_6F_{13}$	2.6	24.9	11.9	8.7	1/14.4/6.9
4	$CH_2CH_2C_6F_{13}$	<0.2	2.2	1.0	19.9	
7	$CH_2O(CH_2)_2C_{10}F_{21}$	≈ 0.2	2.6	0.8	14.9	

[a] Yields of a second reaction cycle in which the amount of catalyst recovered from the first cycle was used.

to other rhodium carboxylate catalysts such as $Rh_2(OOCCF_3)_4$ and Rh_2(octanoate)$_4$ [1,16].

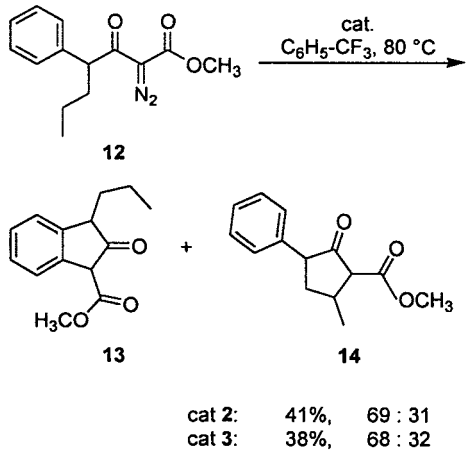
We have also checked whether the catalysts can be recovered and reused. In the case of the insoluble complexes **4**, **7**, and $Rh_2(OAc)_4$, green sticky solids were obtained at the end of the reaction, which are a mixture of catalyst (IR) and organic material consisting most likely of carbene oligomers (based on the very broad NMR absorptions in the range for COOMe protons). Obviously, efforts to recover the catalysts from these mixtures are not meaningful. A color change of catalysts **2** and **3** from green to olive-yellow at the end of the reaction indicated at least a partial alteration. In the case of **2**, only 32% of the catalyst could be recovered by extraction into the fluorinated solvent (i.e. by phase separation of the hexane–PFMC mixture at -18 °C). When this material was applied to a second cycle of the C–H insertion reaction with the same concentration of diazoacetate as before, a strong decrease of the insertion reaction and a simultaneous increase of carbene dimer formation was noted. This result can be attributed to the lower concentration of catalyst in the second cycle; we know from other experiments that carbene dimer formation becomes more important when the catalyst drops below a certain threshold.

2.3. Intramolecular C–H insertion

As a test case for an intramolecular C–H insertion, we looked at the reaction of α-diazo-β-keto ester **12** catalyzed by **2** and **3**, respectively, in benzotrifluoride as solvent (Scheme 3). In line with previous studies using $Rh_2(OAc)_4$ [17] and other rhodium catalysts [18], both the aromatic C–H insertion product **13** and the methylene insertion product **14** were formed. The preference for **13** is higher than in the case of $Rh_2(OAc)_4$ (54:46 mixture) but a bit lower than in the case of $Rh_2(O_2CCF_3)_4$ [18]. We observed, however, that catalysis by **2** and **3** required harsher conditions than with all other rhodium catalysts reported so far and that the combined yield of insertion was lower. Furthermore, none of the two catalysts could be recovered by extraction into PFMC at the end of the reaction. Complex formation of the highly electrophilic catalysts with the β-diketonate moieties of **13** and **14** — either at the open coordination site of the rhodium atoms or by exchange of the bridging ligands under the forcing reaction conditions — could explain both the deactivation of the catalysts and the loss of solubility in fluorous solvents.

3. Conclusion

This study has revealed that the applicability of the concept of fluorous synthesis to rhodium-catalyzed carbene transfer reactions is limited. The widely used catalyst $Rh_2(OAc)_4$ can be made fluorous by replacing the acetate ligands with alkanecarboxylate ligands bearing long perfluoroalkyl segments (C_6F_{13}, C_8F_{17}, $C_{10}F_{21}$). In order to suppress the electron-withdrawing effect of the latter on the Rh–Rh core of the complex, at least two methylene groups are required as spacers between these segments and the carboxylate head group. However, only catalysts **2** and **3**, i.e. those without a spacer or with only one methylene spacer are soluble in the perfluorinated solvent PFMC, this solubility being a



Scheme 3.

prerequisite for recovery of the catalyst. Thus, there is the dilemma that those catalysts, which are electronically similar to rhodium acetate (**5**–**7**), cannot be used under homogeneous catalysis conditions and are, therefore, not suited for the intermolecular C–H insertion into alkanes. On the other hand, the soluble and more electrophilic catalysts **2** and **3** promote the C–H insertion into hexane with methyl diazoacetate in a combined yield of ca. 40% but are altered and deactivated in the course of the reaction and can be recovered only to a low extent (ca. 30%) by extraction into PFMC. In combination with our earlier studies on cyclopropanation of alkenes and of toluene with methyl diazoacetate [5], it can be concluded that high recovery of catalyst **2** can only be expected (a) if the carbene transfer reaction is sufficiently fast to prevent the formation of carbene dimers or oligomers which appear to deactivate the catalyst or (b) if the catalysts are not too electrophilic, in order to prevent product inhibition to occur. We are now investigating rhodium (perfluoroalkyl)benzoates, which appear to qualify better for fluorous synthesis due to their higher and more selective solubility in fluorous phases.

4. Experimental

All reactions were carried out under argon. Analytical grade solvents were used. The petroleum ether used had a boiling point range of 30–50 °C. Flash chromatography was performed on silica gel (Merck silica gel 60 (0.040–0.063 mm). NMR spectra were recorded on an Bruker AMX 400 instrument (^{1}H: 400.1 MHz; ^{13}C: 100.6 MHz; ^{19}F: 376 MHz). Internal standards were used [^{1}H: TMS or THF-d_8 ($\delta = 1.73$ and 3.58); ^{19}F: CF_2Cl–$CFCl_2$ ($\delta = -68$ and -73 ppm). IR spectra were recorded on Perkin–Elmer 883 and Bruker Vector 22 spectrometers. LD mass spectra were obtained with a Bruker Reflex III instrument. GC analyses were performed on a Varian 3800 instrument. (1*H*,1*H*,2*H*,2*H*-perfluorododecyl)oxyacetic acid [19], 2-(perfluorohexyl)acetic acid [20], 3-(perfluorohexyl)propionic acid [21], 3-(perfluorooctyl)propionic acid [21] and 3-(perfluorodecyl)propionic acid [21] were prepared according to literature procedures.

4.1. Preparation of the dirhodium tetrakis(alkanecarboxylates)

4.1.1. Tetrakis(μ-perfluorooctanoato-O:O′) dirhodium (2)

A solution of perfluorooctanoic acid (112 mg, 0.27 mmol) in toluene (15 ml) was placed in a reaction vessel equipped with a dropping funnel and a Dean-Stark trap and was heated at 100 °C. A solution of $Rh_2(OAc)_4$ (30.0 mg, 0.07 mmol) in EtOH (15 ml) was added within 10 min. After the ethanol had distilled off, the temperature was raised to 110 °C. In order to remove the acetic acid liberated in the ligand exchange reaction, four portions of toluene (4 × 10 ml) were added subsequently and were allowed to distill off each time. The mixture was refluxed during 11 h, then about half of the solvent was removed. By cooling to 4 °C a dark green, a waxy solid separated which was dissolved in hot 1,1,2-trichlorotrifluoroethane–toluene (1:1). On cooling, complex **2** separated again as a waxy solid, which was subjected to flash column chromatography [silica gel, petroleum ether–pentane (7:3)] to remove traces of acid. Yield: 97 mg (77%). Treatment of the dark green waxy product with acetonitrile yielded the bis(acetonitrile) complex **2** × $(CH_3CN)_2$ as a pink solid, melting point (m.p.) 71 °C, which was more convenient to handle and from which the solvent-free complex **2** could be regenerated by heating at 60 °C 1 mbar for 5 h. $R_f = 0.89$ (petroleum ether–ether, 7:3). ^{19}F-NMR ($CDCl_3$): $\delta = -81.64$ (m, 12 F, CF_3), -117.11 (m, 8 F), -122.92 (m, 8 F), -123.55 (m, 8 F), -124.31 (m, 16 F), -127.77 (m, 8 F). IR (KBr): $\nu = 2314$ (w), 1739 (w), 1663 (s), 1424 (m), 1365 (m), 1319 (w), 1244 (s), 1207 (s), 1148 (s), 1018 (m), 669 (m) cm^{-1}. MS (LD-TOF): $m/z = 1857.7$ (Rh_2L_4), 2268.2 (Rh_2L_5); Calc. 1856.7, 2270.6. $C_{32}F_{60}O_8Rh_2$ ($M = 1856.7$ g mol^{-1}).

4.1.2. Tetrakis[μ-2-(perfluorohexyl)acetato-O:O′] dirhodium, $Rh_2(OOCCH_2C_6F_{13})_4$ (3)

The complex was prepared and purified analogously to **2**, described above, from 41.2 mg (0.11 mmol) (perfluorohexyl)acetic acid in toluene (25 ml) and $Rh_2(OAc)_4$ in ethanol (12 ml). Yield: 35 mg (74%) of a waxy material. Treatment with acetonitrile yields an adduct **3** × $(CH_3CN)_2$ as a pink solid, m.p. 73 °C, which is more convenient to handle and from which the original complex **3** can be regenerated as described for **2**. $R_f = 0.59$ (petroleum ether–ether, 7:3). ^{1}H-NMR ($CDCl_3$–THF-d_8): $\delta = 3.17$ (t, 8 H, ^3J(H,F) = 17.9 Hz, CH_2). ^{19}F-NMR ($CDCl_3$–THF-d_8): $\delta = -82.15$ (m, 12 F, CF_3), -113.34 (m, 8 F), -123.01 (m, 8 F), -124.04 (m, 8 F), -124.26 (m, 8 F), -127.34 (m, 8 F). IR (KBr): $\nu = 2961$ (m), 1719 (m), 1611 (s), 1428 (s), 1414 (s), 1365 (m), 1317 (m), 1241(s), 1206 (s), 1145 (s), 1123 (m), 1064 (m), 748 (m), 738 (m), 709 (m), 683 (m) cm^{-1}. MS (LD-TOF): $m/z = 1712.8$ (Rh_2L_4), 2089.6 (Rh_2L_5); Calc. 1712.7, 2090.7. $C_{32}H_8F_{52}O_8Rh_2$ ($M = 1712.7$ g mol^{-1}).

4.1.3. Tetrakis[μ-3-(perfluorohexyl)propionato-O:O′] dirhodium, $Rh_2(OOCCH_2CH_2C_6F_{13}]_4$ (4)

A solution of 3-(perfluorohexyl)propionic acid (80.0 mg, 0.20 mmol) and sodium hydroxide (8.2 mg, 0.20 mmol) in ethanol (15 ml) was added to a stirred solution of $RhCl_3 \cdot 3H_2O$ (13.4 mg, 0.05 mmol) in refluxing ethanol (5 ml). The color of the solution changed from

red to yellow and yellow brown. A green solid precipitated, leaving a colorless mother liquor. The solid was isolated by filtration, dissolved in hot EtOH, and filtered hot to remove traces of a grey powder (rhodium). The solution was concentrated and cooled at 4 °C to furnish the complex **4** together with a small amount of sodium 3-(perfluorohexyl)propionate. Recrystallization from THF yielded pure **4** as a pale green microcrystalline solid; m.p. > 280 °C; yield: 24 mg (53%). $R_f = 0.31$ (petroleum ether–ether, 7:3). ^{1}H-NMR (CD_3OD–1,1,2-trichlorotrifluoroethane): $\delta = 2.40$–2.48 (m, 16 H, $(CH_2)_2$). ^{19}F-NMR (CD_3OD–1,1,2-trichlorotrifluoroethane): $\delta = -82.10$ (t, 12 F, $^3J = 10.3$ Hz, CF_3), -115.73 (m, 8 F, CF_2), -122.59 (m, 8 F, CF_2), -123.59 (m, 8 F, CF_2), -124.38 (m, 8 F, CF_2), -126.99 (m, 8 F, CF_2). IR (KBr): $\nu = 2966$ (w), 1579 (s), 1534 (m), 1444 (s), 1422, 1375, 1366, 1300 (all m), 1249, 1211, 1188 (all s), 1138 (s), 1120, 1107, 1039, 1077 (all m), 703, 651, 641 (all m) cm^{-1}. MS (LD-TOF): $m/z = 1768.8$ (Rh_2L_4), 2159.8 (Rh_2L_5); Calc. 1768.8, 2159.8. $C_{36}H_{16}F_{52}O_8Rh_2$ ($M = 1768.8$ g mol^{-1}).

4.1.4. Tetrakis[μ-3-(perfluorooctyl)propionato-O:O′] dirhodium, $Rh_2(OOCCH_2CH_2C_8F_{17})_4$ (5)

The complex was prepared analogously to **4**, described above, from 3-(perfluorooctyl)propionic acid (90.0 mg, 0.18 mmol), sodium hydroxide (7.3 mg, 0.18 mmol) and $RhCl_3 \cdot 3H_2O$ (12 mg, 0.46 mmol). M.p. > 220 °C; yield: 28 mg (57%). $R_f = 0.4$ (petroleum ether–ether, 7:3). ^{1}H-NMR ([d_8] THF–1,1,2-trichlorotrifluoroethane): $\delta = 2.23$–2.34 (m, 8 H, H_β), 2.38–2.41 (t, 8 H, $^3J = 6.7$ Hz, H_α). ^{19}F-NMR (THF-d_8–1,1,2-trichlorotrifluoroethane): $\delta = -82.32$ (t, 12 F, $^3J = 10.3$ Hz, CF_3), -116.07 (m, 8 F, CF_2), -122.4 (m, 8 F, CF_2), -122.94 (m, 16 F, CF_2), -123.78 (m, 8 F, CF_2), -124.72 (m, 8 F, CF_2), -127.30 (m, 8 F, CF_2). IR (KBr): $\nu = 2944$ (w), 1575 (s), 1445, 1422, 1372, 1335 (all m), 1206, 1147, 1107 (all s), 705 (m), 660 (m) cm^{-1}. MS (LD-TOF): $m/z = 2169.9$ (Rh_2L_4); Calc. 2169.3. $C_{44}H_{16}F_{68}O_8Rh_2$ ($M = 2169.3$ g mol^{-1}).

4.1.5. Tetrakis[μ-3-(perfluorodecyl)propionato-O:O′] dirhodium, $Rh_2(OOCCH_2CH_2C_{10}F_{21})_4$ (6)

The complex was prepared analogously to **4**, described above, from 3-(perfluorodecyl)propionic acid (60.0 mg, 0.10 mmol), sodium hydroxide (4 mg, 0.10 mmol), and $RhCl_3 \cdot 3H_2O$ (6.7 mg, 0.025 mmol). Pale green microcrystals were obtained by crystallization from hot ethanol; m.p. > 220 °C; yield: 22 mg (68%). Due to the insolubility in common solvents at room temperature (r.t.), no NMR spectra could be recorded. IR (KBr): $\nu = 3434$ (m), 1581(s), 1443 (m), 1421 (m), 1376 (m), 1346 (m), 1213 (s), 1152 (s), 1108 (m), 664 (m), 644 (m) cm^{-1}. $C_{52}H_{16}F_{84}O_8Rh_2$ ($M = 2570.4$ g mol^{-1}).

4.1.6. Tetrakis[μ-(1H,1H,2H,2H-perfluorododecyloxy)-acetato-O:O′] dirhodium (7)

The complex was prepared analogously to **4**, described above, from 2-(1*H*,1*H*,2*H*,2*H*-perfluorododecyloxy)acetic acid (61.0 mg, 0.10 mmol), sodium hydroxide (4 mg, 0.10 mmol), and $RhCl_3 \cdot 3H_2O$ (6.5 mg, 0.025 mmol). After a reaction time of 5 h, a dark grey solid had separated which was filtered off, treated with boiling THF (20 ml), and filtered hot to remove a small amount of a grey powder (rhodium). The filtered solution was concentrated and cooled at 4 °C to furnish **7** as a pale green microcrystalline solid. m.p. 162 °C; yield: 10 mg (30%). ^{1}H-NMR (THF-d_8–1,1,2-trichlorotrifluoroethane): $\delta = 1.54$ (t, 8 H, $^3J = 6.6$ Hz, $R_{f10}CH_2$), 2.39–2.49 (m, 8 H, $R_{f10}CH_2CH_2$), 3.82 (s, 8 H, H_α). ^{19}F-NMR (400.1 MHz, [d_8] THF–1,1,2-trichlorotrifluoroethane): $\delta = -82.29$ (t, 12 F, $^3J = 8.9$ Hz, CF_3), -114.45 (m, 8 F, CF_2), -122.69 (m, 40 F, CF_2), -123.7 (m, 8 F, CF_2), -124.68 (m, 8 F, CF_2), -127.29 (m, 8 F, CF_2). IR (KBr): $\nu = 2904$ (w), 1599 (s), 1414, 1373, 1343 (all m), 1211 (s), 1151 (s), 663, 644 (all m) (w) cm^{-1}. $C_{56}H_{24}F_{84}O_{12}Rh_2$ ($M = 2690.5$ g mol^{-1}).

4.2. Rh-catalyzed reaction of methyl diazoacetate with n-hexane

The catalyst (1 mol%) was dissolved (**2** and **3**) or suspended (**4**–**7**) in perfluoro(methylcyclohexane) (0.5 ml). After addition of hexane (4 ml), the temperature was raised to 40 °C. A solution of methyl diazoacetate (100 mg, 1.0 mmol) in hexane (0.5 ml) was added with the aid of a syringe pump within 6 h. After an additional reaction time (2 h, 40 °C) dibenzylether was added as an internal standard, and the yield and product distribution was determined by gas chromatography (column: fused silica, CP-WAX 52 CB as stationary phase, 25 m × 0.32 mm; variable temperature 50 → 250 °C). The mixtures of the insertion products were not separated on a preparative scale; rather, the components were identified by GC–MS and by characteristic ^{13}C-NMR signals.

4.2.1. Methyl octanoate (8)

Prepared independently by esterification of octanoic acid. ^{13}C-NMR ($CDCl_3$): $\delta = 13.96$, 22.53, 24.91, 28.86, 29.06, 31.59, 34.04, 51.31 (OMe), 173.01 (C=O). MS(EI): $m/z = 158$ $[M]^+$, 87 $[H_2C{=}CHCO_2Me + H]^+$, 74.

4.2.2. Methyl 3-methylheptanoate (9)

^{13}C-NMR ($CDCl_3$, partial): $\delta = 30.44$ (CH), 172.81 (C=O). MS(EI): $m/z = 158$ $[M]^+$, 143 $[M - Me]^+$, 101 $[M - Bu]^+$, 74.

4.2.3. Methyl 3-ethylhexanoate (10)

^{13}C-NMR ($CDCl_3$, partial): $\delta = 36.42$ (CH), 172.55

(C=O). MS(EI): $m/z = 158$ $[M]^+$, 129 $[M - Et]^+$, 127 $[M - OCH_3]^+$, 115 $[M - Pr]^+$, 74.

In an effort to recover catalyst **2**, PFMC (1.5 ml) was added to the reaction mixture after the reaction was over. At −18 °C, complete separation of the hexane and PFMC phases took place. From the green-colored PFMC phase, 32% of the original amount of **2** were recovered.

4.3. Intramolecular C–H insertion of *12*

A solution of diazo ester **12** [17] (65 mg, 0.25 mmol) in benzotrifluoride (0.5 ml) was added during 1 h via a syringe pump to a solution of catalyst **2** (7.0 mg, 1.5 mol%) or **3** (6.7 mg, 1.5 mol%) in benzotrifluoride (1.5 ml) and heated at 45 °C for 6 h, then at 80 °C for 8 h. With catalyst **2**, the reaction solution turned greenish-brown, with catalyst **3** it kept the original green color. The solvent was replaced by $CDCl_3$ and after addition of dibenzyl ether as a standard, the composition of the mixture was determined by ^{1}H-NMR spectroscopy. The chemical shifts of products **13** and **14** agreed with literature values [17], yields are given in Scheme 3.

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