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Dirhodium(II) tetrakis(perfluoroalkylbenzoates) as partially recyclable catalysts for carbene transfer reactions with diazoacetates

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Abstract—Three highly fluorinated dirhodium(II) tetrakis(benzoates), $[Rh_2(O_2CR_F)_4$, $R_F=C_6H_4$-4-C_6F_{13} (**3**) and C_6H_3-3,5-di(C_nF_{2n+1}) (n=6: **4**; n=8: **5**)], have been prepared and characterized. Only **4** and **5** are suited for applications in fluorous synthesis due to their excellent solubility in fluorous solvents. They were found to catalyze the following carbenoid reactions of diazo compounds in the fluorous solvents 1,1,2-trichloro-1,2,2-trifluoroethane and perfluoro(methylcyclohexane): cyclopropanation of styrenes using methyl diazoacetate, intermolecular carbene C–H insertion into hexane with methyl diazoacetate, and intramolecular aromatic C–H insertion of an α-diazo-β-ketoester. Except for the second reaction type, the catalyst could be recovered to a high extent by a liquid–liquid extraction (fluorous solvent—dichloromethane) due to its preference for the fluorous solvent. For the cyclopropanation reactions, the recovered catalyst was used in four subsequent reaction/workup cycles without significant loss of activity. In contrast, the catalyst could not be recovered from the carbenoid C–H insertion reaction with hexane; apparently, some by-products of this sluggish reaction, such as carbene dimers and oligomers, caused the deactivation or destruction of the catalyst.

1. Introduction

Dinuclear rhodium(II) tetracarboxylates and amidates are highly versatile catalysts for several effective transformations which involve carbene transfer from diazo compounds to appropriate substrates.[1,2] Although it was shown in a few cases that 0.1 mol% and less of the catalyst are sufficient for high-yielding carbenoid reactions,[3] the typical catalyst loadings are 1–3 mol%. Taking into account the costs of rhodium and its compounds, it could be desirable, at least for reactions at a larger scale, to recover the catalyst from the reaction mixture and to use it again. This can be achieved by attaching the rhodium catalyst to a polymeric support.[4] Another approach is located in the emerging field of fluorous phase chemistry introduced by Horvath and Rábai in 1994.[5] This technique takes advantage of the preferred solubility of highly fluorinated molecules in perfluorinated ('fluorous') solvents and of the temperature-dependent miscibility of fluorous and common organic solvents. In one of the applications of this concept, 'fluorous biphase catalysis', it has been shown for several important chemical transformations involving homogeneous catalysis that catalysts with fluorous labels perform well and can be recovered and reused.[5c,d]

Under the aspects of effectiveness and ease of recovery, the ideal catalyst for fluorous phase technology should have a good absolute solubility in a fluorous solvent, should display in fluorous–organic biphasic mixtures a high partition coefficient in favor of the fluorous solvent, and it should not form adducts with organic components of the reaction mixture so that the solubility in an organic solvent would increase. Some empirical rules[5h,6] can be observed in the catalyst design in order to meet the first two postulates (e.g. a fluorine content of ca. 60%, appropriate length, number, and spatial arrangement of perfluoroalkyl chains). Aspects of catalyst deactivation and reactivity are related to the electronic situation at the catalytically active metal center, and it may be necessary to place a spacer between the metal and the strongly electron-withdrawing perfluoroalkyl substituents by introducing a spacer between them and the metal center.[5b–g,7]

In a preliminary communication,[8] we have reported the use of dinuclear rhodium(II) perfluorooctanoate (**1**, Scheme 1) and rhodium(II) 4-(perfluorhexyl)benzoate (**3**) for the cyclopropanation of various alkenes. Both catalysts could be recycled and reused several times without significant drop in the yields of cyclopropanes, but the less electrophilic catalyst **3** gave distinctly higher yields. In another study,[9] we pepared several highly fluorinated dirhodium(II) tetrakis(alkanecarboxylates) $[Rh_2(OOCR_F)_4$ $R_F=CH_2C_6F_{13}$ (**2**), $CH_2CH_2C_6F_{13}$, $CH_2CH_2C_8F_{17}$, $CH_2CH_2C_{10}F_{21}$, $CH_2OCH_2CH_2C_{10}F_{21}]$ and found that two CH_2 groups were necessary for complete electronic separation of the perfluoroalkyl chain from the rhodium centers.

Keywords: rhodium and compounds; fluorous synthesis; diazo compounds.

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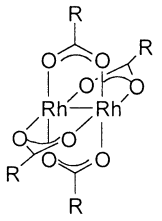


	R
1	C_7F_{15}
2	$CH_2C_6F_{13}$
3	C_6H_4-4-C_6F_{13}
4	C_6H_3-3,5-di(C_6F_{13})
5	C_6H_3-3,5-di(C_8F_{17})

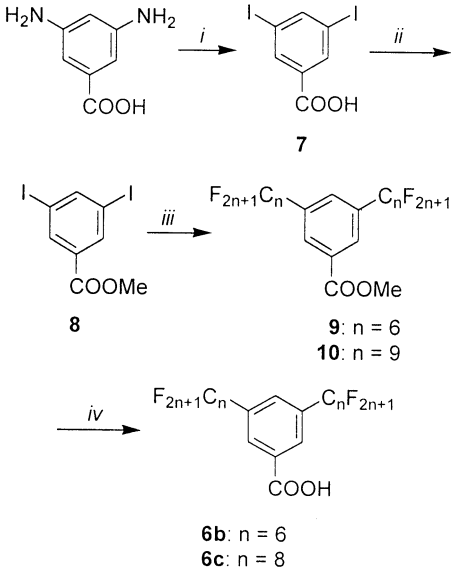
Scheme 1.

Unfortunately, however, all complexes with more than one methylene spacer were insoluble in perfluoro(methylcyclohexane) (PFMC), in spite of their high fluorine content (55.8–62.1%), and therefore not applicable for fluorous biphase catalysis. The PFMC-soluble catalysts **1** and **2** performed fairly well in the carbenoid C–H insertion into hexane with methyl diazoacetate (ca. 40% combined yield of insertion products), a notoriously difficult reaction, but only a minor fraction of the catalyst could be recovered by extraction into PFMC after one reaction cycle. We reasoned that the deterioration of **1** and **2** was related to their enhanced electrophilicity as compared to $Rh_2(OAc)_4$, the parent catalyst in rhodium carbenoid chemistry. We decided to take rhodium benzoate complex **3** as a lead for the development of fluorous rhodium catalysts which more closely meet the criteria described above. In this paper, we look at properties and performance of the two novel fluorous rhodium(II) benzoates **4** and **5**.

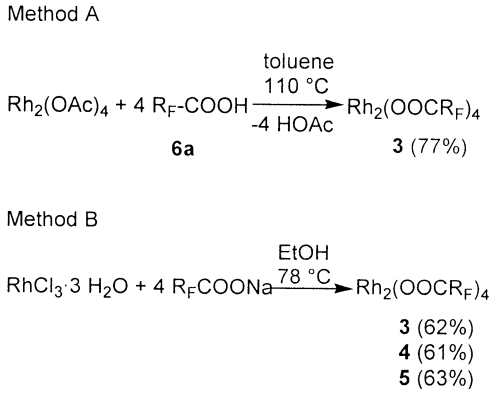
2. Results and discussion

2.1. Preparation and properties of complexes 3–5

The synthesis of rhodium complexes **3**–**5** requires the (perfluoroalkyl)benzoic acids **6a**–**c**. 4-(Perfluorohexyl)-benzoic acid (**6a**) was prepared according to a published procedure,[10] the 3,5-bis(perfluoroalkyl)benzoic acids **6b**,**c** were obtained from 3,5-diiodobenzoic acid (**7**) as shown



Scheme 2. (i) (1) $NaNO_2$, H_2SO_4; (2) KI; 82%; (ii) $(MeO)_2SO_2$, K_2CO_3, acetone; 82%; (iii) C_nF_{2n+1}, Cu powder, DMSO, 120–125°C; 54/56%; (iv) MeOH, KOH, H_2O; 82/79%.



Scheme 3. 6a=4-$F_{13}C_6$–C_6H_4COOH.

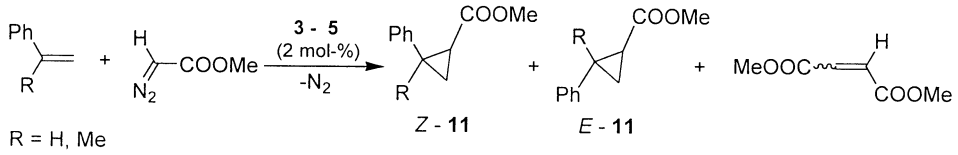
in Scheme 2. The latter compound was prepared on a novel route from 3,5-diaminobenzoic acid by a Sandmeyer reaction and converted into ester **8**. Copper-mediated coupling of **8** with the appropriate perfluoroalkyl iodide, using a known procedure,[11] gave the fluorous esters **9** and **10**, respectively, which were converted into the required acids **6b** and **6c**.

The fluorous rhodium(II) benzoates were prepared by two established procedures (Scheme 3). Complex **3** was obtained from $Rh_2(OAc)_4$ and acid **6a** by exchange of the carboxylate ligands (method A) in boiling toluene and with azeotropic removal of the liberated acetic acid. Using method B,[12] complexes **3**–**5** were obtained in moderate yields from the sodium salts of **6a**–**c** and rhodium(III) chloride hydrate in ethanol. In the cases of **4** and **5**, the concomitant formation of some elemental rhodium was observed which explains at least in part the incomplete formation of the complexes. Separation of **4** and **5** from most of the unreacted R_FCO_2Na was achieved by a simple biphasic extraction with PFMC/THF which delivered the complexes in the fluorous phase (97% purity according to ^1H NMR) and the more polar sodium carboxylates in the organic phase.

The IR and NMR spectra (^1H and ^{13}C) confirmed the absence of starting materials ($Rh_2(OAc)_4$, carboxylic acids) from products **3**–**5**. In addition, **3** and **4** were characterized by laser desorption time-of-flight mass spectrometry (positive ion mode). In both cases, the molecular ion peak was observed; complex **4** gave additional peaks corresponding to the successive loss of C_6F_{13} fragments. The IR spectra of the complexes (Table 1) exhibit three characteristic absorptions in the ranges 1564–1587, 1408–1412, and 1118–1242 cm^{-1}, corresponding to the antisymmetric and symmetric stretching

Table 1. Characteristic IR absorptions of rhodium carboxylate complexes

Complex	$Rh_2(OOCR)_4$ R=	IR (KBr, cm^{-1})		
		$\nu(CO)_{asym}$	$\nu(CO)_{sym}$	$\nu(CF)$
3	$OOCC_6H_4$-4-C_6F_{13}	1564	1409	1146/1203/1242
4	$OOCC_6H_3$-3,5-C_6F_{13}	1588	1412	1146/1203/1242
5	$OOCC_6H_3$-3,5-C_8F_{17}	1587	1408	1118/1209/1238
	OOCPh	1551	1399	–
	$OOCCH_3$	1577	1413	–



Scheme 4.

Table 2. Cyclopropanation of styrenes with methyl diazoacetate; see Scheme 4

Alkene	Catalyst	Yield of cyclopropane **11** (%, upper line) *E*/*Z* ratio (lower line)				
		Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Styrene	**3**[a,b]	71	70	70	71	
		1.43	1.44	1.44	1.46	
	4[c]	70.0	68.1	67.6	66.8	67.4
		0.99	0.97	0.99	0.89	1.04
	5[c]	76.4	75.9	76.1	75.6	75.1
		0.88	0.85	0.88	0.87	0.86
α-Methyl-styrene	**3**[a,b]	83	79	76	76	
		1.04	1.00	1.11	1.11	
	4[c]	71.8	69.9	67.0	65.7	65.0
		1.05	1.00	1.04	1.04	1.03

Yields and diastereomer ratios were determined by GC.
[a] Ref. 8.
[b] Solvent CH_2Cl_2.
[c] Solvent FC-113.

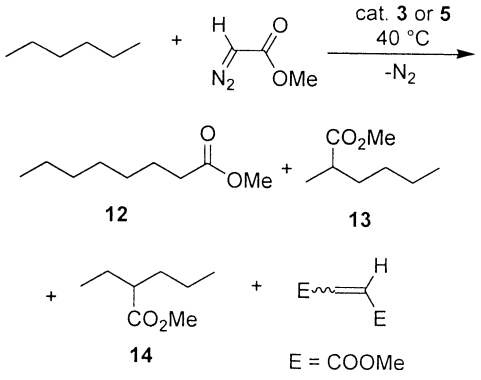
modes of the carboxylate ligands[12] and the C–F stretching vibrations. The ν_{asym}(OOCR) vibration is a good indicator for the electron-withdrawing effect of the fluorinated alkyl chain. It can be expected from these data that complexes **3**–**5** are clearly more electrophilic at the metal centers than the non-fluorinated complexes $Rh_2(OOCPh)_4$ and $Rh_2(OOCMe)_4$. While this property should raise the effectiveness of the diazo decomposition step and the coordination of donor molecules at the free axial coordination site at the rhodium center, it does not allow a simple prediction of the selectivity for potentially competing carbene transfer reactions.[13]

Complex **3** was obtained as microcrystalline dark-green needles, complexes **4** and **5** as dark-green waxy materials. The fluorine contents of the three compounds are 50.3, 61.1, and 64.0%, respectively. While the solubility of **3** in perfluoro(methylcyclohexane) (PFMC, C_6F_{11}–CF_3), perfluorohexane, and 1,1,2-trichloro-1,2,2-trifluoroethane (FC-113) is rather low, complexes **4** and **5** are highly soluble in these media. Furthermore, **4** and **5** are insoluble in standard organic solvents such as Et_2O, CH_2Cl_2, $CHCl_3$, THF, toluene, and ethyl acetate; no visible leaching from PFMC into heptane, CH_2Cl_2, toluene, and THF was noticed. Based on these properties, the two complexes are expected to be well suited for applications in fluorous phase chemistry.

2.2. Cyclopropanation of styrenes with methyl diazoacetate

We have already reported[8] that complex **3** is well suited to catalyze the formation of cyclopropanes **11** from alkenes and methyl diazoacetate (Scheme 4, Table 2). These transformations did not require a fluorous solvent, since the catalyst dissolved in the alkene/dichloromethane phase or at the latest after addition of a few drops of the diazoester to the reaction medium. Only when styrene was used as the alkene, some of the catalyst remained undissolved during the whole reaction. At the end of the cyclopropanation reactions, the catalyst was recovered by extraction into PFMC and was reused without further purification. The yield of **11** decreased only marginally over four reaction cycles, although the recovery rate of catalyst after each cycle was not quantitative (the percentage of available catalyst after four cycles was 56, 27, 21, and 11% for the cyclopropanation of styrene, 1-hexene, 2-methyl-2-propene and α-methylstyrene, respectively).

In contrast to **3**, complexes **4** and **5** were found not to be soluble in CH_2Cl_2-alkene mixtures. Therefore, cyclopropanations of styrene and α-methylstyrene with these catalysts were performed in the fluorous/organic hybrid solvent[5d] FC-113. A tenfold excess of the alkene was applied to minimize the formation of the formal carbene dimers, dimethyl fumarate and maleate. At the end of the reaction, the solvent was replaced by the biphasic system PFMC/CH_2Cl_2 which allowed the extraction of the catalyst into the fluorous phase. Again, the recovered catalyst was submitted to another reaction cycle. Table 2 shows that the cyclopropane yields remained almost the same over five cycles. However, a gravimetric determination of the amount of recovered catalyst showed a significant decrease after each cycle, with a total loss of 51% of **4** and 38% of **5** after five cycles in the reaction with styrene. This loss cannot be attributed to leaching of the intact fluorous catalyst into the organic phase (see above); rather, it is associated with a partial deterioration or destruction of the complex. In fact, IR and ^1H NMR spectra of the recovered catalysts indicated the presence of small amounts of the corresponding free acids **6b**,**c**; furthermore, some elemental rhodium, separating as a very fine black powder, was also observed.

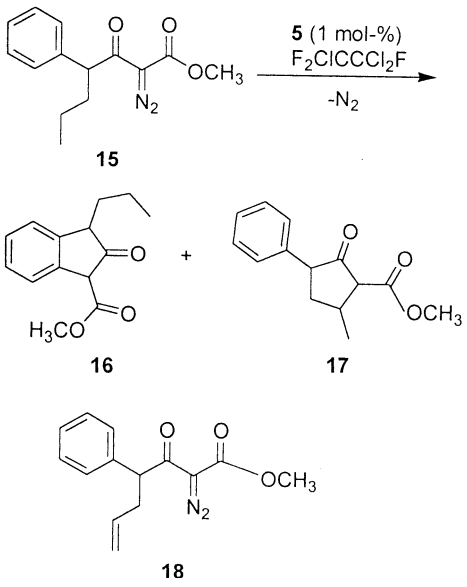


Scheme 5.

Instead of using FC-113 as the reaction medium, the cyclopropanation of styrene catalyzed by **5** was also performed in the vigorously stirred biphasic system PFMC/dichloromethane. This variation was operationally more simple, because at the end of the reaction the PFMC phase, containing the fluorous catalyst, could be separated and reused directly. While the yields of cyclopropanes **11** in the first two reaction cycles were nearly the same as for the reaction performed in FC-113, they dropped considerably in the next two cycles, with a concomitant increase in carbene dimers (combined yields of 4 and 24%, respectively). After the fourth cycle, no fluorous catalyst could be recovered.

2.3. Intermolecular carbenoid C–H insertion of methyl diazoacetate

Carbenoid insertion of simple diazoacetate esters into the non-activated C–H bonds of alkanes is sluggish with most of the transition-metal catalysts investigated so far. The best results are obtained with the highly electrophilic catalyst dirhodium(II) tetrakis(trifluoroacetate), while simple rhodium alkanoates such as $Rh_2(OAc)_4$ and Rh_2(octanoate)$_4$ are almost uneffective.[14,15] Hence we investigated the intermolecular carbenoid C–H insertion of methyl diazoacetate into hexane with catalysts **3** and **5** (Scheme 5). The reactions were carried out in a large excess of hexane to reduce the extent of dimerization and oligomerization of the carbenes. While catalyst **3** was applied as a suspension in hexane, the much more fluorophilic complex **5** was dissolved in the solvent system PFMC–hexane which becomes homogeneous at ca. 40°C. The results are given in Table 3. It can be seen that catalyst **3** is not very effective, while catalyst **5** provides a remarkably high combined yield of insertion products **12**–**14** (ca. 64%), which is significantly better than with catalyst **2** investigated by us before. In combination with the results obtained in this earlier



Scheme 6.

study,[9] we conclude that both the electrophilicity of **5** and its high solubility in the reaction medium account for its good performance in this reaction.

Table 3 also shows that the selectivity of the insertion reaction is not influenced markedly by the catalysts. The preference for insertion into the C-2 methylene group of linear alkanes has also been observed with all other rhodium catalysts studied so far; insertion at the terminal CH_3 position becomes more significant only with very bulky rhodium catalysts.[1,16]

It is unfortunate that complex **5**, which has now emerged as a promising catalyst for carbenoid C–H insertion reactions into alkanes, cannot be recovered efficiently in this environment: Formation of an olive-green solid was observed already during the reaction, and after phase separation at −18°C, only a small fraction of the intact catalyst could be recovered.

2.4. Intramolecular carbenoid C–H insertion

As a test case for an intramolecular C–H insertion, we looked at the reaction of α-diazo-β-keto esters **15** and **18** catalyzed by **5** (Scheme 6). Ikegami et al.[16] have shown that the selectivity of the intramolecular carbenoid reactions in these systems[17] are more dependent on steric factors operating in the catalyst than on its electrophilicity; rhodium catalysts with bulky ligands strongly favored the aromatic

Table 3. C–H insertion of methyl diazoacetate into *n*-hexane; see Scheme 5

Catalyst	Solvent	Yield (%) of insertion at			Dimers[a] (%)	Relative yield of insertion		
		C-1 **12**	C-2 **13**	C-3 **14**		C-1	C-2	C-3
3	Hexane	0.3	7.0	2.6	17.1	1	24.8	9.4
5	PFMC–hexane	1.7	40.7	21.4	7.8	1	24.5	12.9

The product distribution was determined by GC.
[a] Dimethyl fumarate and dimethyl maleate.

Table 4. Carbenoid intramolecular C–H insertion of **15** catalyzed by **5**; see Scheme 6

Cycle	**16** (%)	**17** (%)	Catalyst (brought in/ recovered) (%)
1	67	3	100/96
2	59	3	96/91

C–H insertion product **16** over the aliphatic insertion product **17**, the best catalyst being $Rh_2(OOCCPh_3)_4$. We found that the treatment of diazo ester **15** with catalyst **5** in FC-113 also resulted in a high selectivity for **16** (Table 4). The catalyst could be recovered by partioning of the product mixture between PFMC and dichloromethane to the extent of 96% in each of two reaction cycles. For comparison, treatment of **15** with fluorous catalyst **2** was both lower-yielding and less selective (**16**/**17**=68:32, total yield 38%) and could not be recovered by fluorous extraction. Thus, complex **5** should also be considered as a candidate for other intramolecular carbenoid reactions. We noticed, however, that complex **5** was not able to decompose the unsaturated diazo ester **18** effectively even after 2 weeks at 45°C in FC-113.

3. Conclusion

This study has shown that the dirhodium tetrakis[3,5-bis(perfluoroalkyl)benzoates] **4** and **5**, due to their excellent solubility in fluorous solvents and their high fluorophilicity, are promising candidates for reactions in fluorous phases and for fluorous extraction procedures. However, when they are applied to catalytic carbene transfer reactions with diazoacetates, the possibilities to recover and to reuse **4** and **5** are limited because they are partly destroyed or transformed into less fluorophilic species. There are indications that formal carbene dimers and oligomers are involved in one of the deactivation pathways of these catalysts. Therefore, the stability of these catalysts may be higher when diazoesters are used that do not easily form carbene dimers under rhodium catalysis, e.g. phenyl- and vinyldiazoacetates.

4. Experimental

4.1. General

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 a 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 [D_8]-THF (δ=1.73 and 3.58); ^{19}F: CF_2Cl–$CFCl_2$ (δ=−68 and −73 ppm)]. IR spectra were recorded on Perkin–Elmer 883 and Bruker Vector 22 spectrometers. Laser desorption mass spectra were obtained with a Bruker Reflex III instrument. GC analyses were performed on a Varian 3800 instrument. Elemental analyses were obtained on a 'elementar vario EL' instrument—PFMC=perfluoro(methylcyclohexane); FC-113=1,1,2-trichloro-1,2,2-trifluoroethane.

4.1.1. 3,5-Diiodobenzoic acid (7). To an ice-cooled, stirred suspension of 3,5-diaminobenzoic acid (3.00 g, 19.7 mmol) in 25% sulfuric acid (70 ml) was added dropwise a 2.5 M aqueous solution of sodium nitrite (17.1 ml, 42.0 mmol). The color of the originally red suspension changed to orange. After 2 h, urea (3.0 g, 50 mmol) was added, and then the solution was added slowly to an ice-cooled solution of potassium iodide (16.4 g, 98.6 mmol) in water (15 ml). After 5 h at 20°C, the suspension was cooled to 4°C and the brown solid was filtered off, washed with water, and dried. It was decolorized by treatment with charcoal in boiling THF (50 ml). Recrystallization from a large volume of toluene gave a beige powder; yield: 6.04 g (82%); mp 231°C (lit.:[18] 233°C). R_f=0.76 (THF). ^{1}H NMR ([D_6]-DMSO): δ=8.17 (s, 2H, 2,6-H), 8.31 (s, 1H, 4-H). ^{13}C NMR ([D_6]-DMSO): δ=96.44 (C-3,5), 129.24 (C-1), 137.34 (C-2,6), 148.53 (C-4), 164.99 (C=O). IR (KBr): ν=3649 (w), 3069 (m), 2830 (m), 2638 (m), 2516 (w), 1686 (s), 1275 (s) cm^{-1}. Anal. calcd for $C_7H_4O_2I_2$ (373.9): C 22.49, H 1.08; found: C 22.42, H 1.13.

4.1.2. Methyl 3,5-diiodobenzoate (8). A suspension consisting of acid **7** (1.00 g, 2.67 mmol), K_2CO_3 (437 mg), and dimethyl sulfate (0.27 ml) in dry acetone (25 ml) was refluxed for 8 h. After addition of water (6 ml) and stirring for 12 h, the solvent was removed. The resulting beige residue was extracted with dichloromethane (3×20 ml). The combined organic phases were washed with brine (20 ml), dried (Na_2SO_4), and evaporated. The residue was filtered through a short bed of silica [petroleum ether/ether (7/3)]. The solution was concentrated, and the product separated as colorless needles; yield: 846 mg (82%), mp 94°C. R_f=0.93 (petroleum ether/ether, 7:3 v/v). ^{1}H NMR ($CDCl_3$): δ=3.85 (s, 3H, OCH_3), 8.15 (s, 1H, 4-H), 8.24 (s, 2H, 2,6-H). ^{13}C NMR ($CDCl_3$): δ=52.58 (OCH_3), 94.28 (C-3,5), 133.13 (C-1), 137.63 (C-2,6), 149.09 (C-4), 164.09 (C=O). IR (KBr): ν=1741(s), 1240 (s), 1198 (s), 1142 (s) cm^{-1}. MS (CI): m/z=389 $[M+1]^+$, 262 $[M-I]^+$. Anal. calcd for $C_8H_6O_2I_2$ (387.95): C 24.77, H 1.56; found: C 24.65, H 1.59.

4.1.3. Methyl 3,5-bis(perfluorohexyl)benzoate (9). A mixture of a few iodine crystals and copper dust (3.00 g) in acetone (20 ml) was stirred for 30 min. After removal of the solvent, the copper was washed with aq. HCl (6N) in acetone (20 ml, 2:3 v/v) and acetone (2×10 ml) and dried in vacuo. The activated copper powder (819 mg, 12.9 mmol) was mixed with ester **8** (500 mg, 1.29 mmol), perfluorohexyl iodide (0.6 ml, 2.71 mmol), and dry DMSO (9 ml). The suspension was stirred for 6 h at 125°C. After cooling down, water and ether (10 ml each) was added and stirred for 10 min. Then the mixture was filtered through a Büchner funnel. The residue was washed with ether (2×20 ml). The combined ether phases were dried (Na_2SO_4) and evaporated. The resulting pale-brown solid was purified by chromatography [silica gel, petroleum ether/ether (7:3)]. Yield: 547 mg (55%); mp 59°C. ^{1}H NMR ($CDCl_3$/FC-113): δ= 4.02 (s, 3H, OCH_3), 7.99 (s, 2H, 2,6-H), 8.50 (s, 1H, 4-H). ^{13}C NMR ($CDCl_3$/FC-113): δ=52.8 (OCH_3), 131.05 (C-2,6), 131.54 (C-3,5), 132.24 (C-4), 129.3, 136.8, 139.5 (m, C(R_F)), 139.5 (C-1), 164.15 (C=O). ^{19}F NMR ($CDCl_3$/FC-113): δ=−81.4 (t, 6F, CF_3), −112.5, −121.8, −122.1, −123.2, −126.6 (all m, CF_2). IR (KBr): ν=2965 (m), 1741 (s, C=O); 1240, 1198, 1142, 1122 (all s, C–F) cm^{-1}.

4.1.4. Methyl 3,5-bis(perfluorooctyl)benzoate (10). The compound was prepared, as described above for **9**, from copper dust (819 mg, 12.9 mmol), ester **8** (500 mg, 1.29 mmol), and perfluorooctyl iodide (1.48 g, 2.71 mmol) in dry DMSO (9 ml). Yield: 702 mg (56%); mp 62–63°C. ^{1}H NMR ($CDCl_3$/FC-113): δ=4.01 (s, 3H, OCH_3), 7.98 (s, 2H, 2,6-H), 8.49 (s, 1H, 4-H). ^{13}C NMR ($CDCl_3$/FC-113): δ=53.7 (OCH_3), 129.42 (C-2,6), 130.9 (C-3,5), 131.6 (C-4), 113.5–131.5 (m, C(R_F)), 132.3 (C-1), 164.4 (C=O). ^{19}F NMR ($CDCl_3$): δ=−82.2 (t, ^3J=10.8 Hz, 6F, CF_3), −112.4 (t, ^3J=14.3 Hz, 4F), −122.4 (m, 4F), −123.2 (m, 16F), −124.1 (m, 2F), −127.4 (m, 2F).

4.1.5. 3,5-Bis(perfluorohexyl)benzoic acid (6b). Ester **9** (250 mg, 0.32 mmol) was suspended in methanol (2 ml) and water (4 ml) and potassium hydroxide (130 mg, 2.32 mmol) was added. After heating at 100°C for 15 h, the solvents were removed and the solid residue was neutralized with 6 N hydrochloric acid. After extraction with ether (3×20 ml), drying of the combined ethereal phases (Na_2SO_4) and evaporation of the solvent, the residue was recrystallized from toluene to give a white powder. Yield: 201 mg (82%); mp 103°C. ^{1}H NMR ($CDCl_3$): δ=7.97 (s, 1H, 4-H), 8.47 (s, 2H, 2,6-H). ^{19}F NMR ($CDCl_3$): δ=−81.3 (m, 6H, CF_3), −111.6, −121.9, −122.2, −123.3, 126.7 (all m, CF_2). IR (KBr): ν=3442 (m), 3099 (m), 1710 (s), 1614 (m), 1281 (s), 1238 (s), 1198 (s), 1144 (s) cm^{-1}.

4.1.6. 3,5-Bis(perfluorooctyl)benzoic acid (6c). The acid was prepared, as described above for **6b**, from ester **10** (250 mg, 0.257 mmol) and potassium hydroxide (130 mg, 2.32 mmol) in methanol (2 ml) and water (4 ml). Yield: 205 mg (83%); mp 117°C. ^{1}H NMR ($CDCl_3$): 7.97 (s, 1H, 4-H), 8.47 (s, 2H, 2,6-H). IR (KBr): ν=3443 (m), 1712 (s), 1204 (s), 1149 (s) 1118 (m) cm^{-1}.

4.1.7. Tetrakis[μ-4-(perfluorohexyl)benzoato-*O*:*O′*] dirhodium (3). A solution of 4-(perfluorohexyl)benzoic acid[10] (**6a**) (80 mg, 181 μmol) in toluene (25 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 $Rh_2(OAc)_4$ (20 mg, 45.3 μmol) 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 (4×15 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 pale green solid separated, which was filtered off and dried. The pale green powder was boiled in ethanol (10 ml) and filtered hot. The resulting solid was boiled in THF (40 ml). filtration about 3/4 of the THF were removed. The product precipitated at 4°C as a green finely crystalline solid; yield: 68 mg (77%); mp 121°C (dec.). By slow evaporation of a solution in THF/FC-113, the complex was obtained as dark green needles. R_f=0.66 (petroleum ether/ether, 7:3). ^{1}H NMR (400.1 MHz, [D_8]-THF/FC-113): δ=7.44 and 7.95 (d, 16H, ^3J=8.2 Hz, AA′BB′ system). ^{13}C NMR (100.6 MHz, [D_8]-THF/FC-113): δ=184.55 (OCO). ^{19}F NMR ([D_8]-THF/FC-113): δ=−81.4 (t, 12F, ^3J(F,F)=8.0 Hz, CF_3), −111.0 (m, 8F), −121.4 (m, 8F), −122.1 (m, 8F), −122.9 (m, 8F), −126.4 (m, 8F). IR (KBr): ν=1604 (m), 1564 (s), 1409 (s), 1363 (m), 1286 (s), 1242 (s), 1203 (s), 1146 (s), 1122 (s), 1108 (m), 1094 (s) cm^{-1}. MS (LD-TOF): *m*/*z*: found 2409 (Rh_2L_5; calcd 2400.8) and 1962 (Rh_2L_4; calcd for $C_{52}H_{16}F_{52}O_8Rh_2$: 1961.8).

4.1.8. Tetrakis[μ-3,5-bis(perfluorohexyl)benzoato-*O*:*O′*] dirhodium (4). A solution of acid **6b** (600 mg, 0.791 mmol) and sodium hydroxide (31.5 mg, 0.791 mmol) in ethanol (20 ml) was added to a stirred solution of $RhCl_3$×$3H_2O$ (52.3 mg, 0.198 mmol) in refluxing ethanol (15 ml). The color of the solution changed from red to yellow and yellow brown. After 7 h a green waxy solid precipitated. Then half of the solvent was removed (40°C/120 mbar) and after cooling to 4°C it was fully decanted. The dark-green residue which contained some rhodium powder was dried (50°C/1 mbar), then dissolved in PFMC (2 ml). After filtration, and liquid-liquid extraction with THF (2×1.5 ml), the fluorous solvent gave a solid which was subjected to flash chromatography [silica gel, petroleum ether/ether (7:3)] to remove left-overs of **6b**-sodium salt. Complex **4** was obtained as a dark-green waxy solid; yield: 189 mg (61%). R_f=0.97 (petroleum ether/ether, 7:3). ^{1}H NMR ($CDCl_3$/FC-113): δ=7.85 (s, 4H, 4-H), 8.41 (s, 8H, 2,6-H). ^{19}F NMR ($CDCl_3$/FC-113): δ=−82.5 (m, 24F, CF_3), −112.3 (m, 16F, CF_2), −122.7 (m, 32F), −124.3 (m, 16F), −127.7 (m, 16F). IR (KBr): ν=1627 (m), 1588 (m), 1412 (s), 1364 (s), 1322 (s), 1240 (vs), 1203 (vs), 1146 (vs), 1124 (s), 1103 (s), 1061 (m) cm^{-1}. MS (LD-TOF): *m*/*z*: 3236.9 (Rh_2L_4; calcd for $C_{76}H_{12}F_{104}O_8Rh_2$: 3234.2); further fragments at $M-n$×318 [n=1,2,3,…; M(C_6F_{13})=319.0].

4.1.9. Tetrakis[μ-3,5-bis(perfluorooctyl)benzoato-*O*:*O′*] dirhodium (5). The complex was prepared and purified, as described above for **4**, from a solution of acid **6c** (100 mg, 0.104 mmol) and sodium hydroxide (4.1 mg, 0.104 mmol) in ethanol (20 ml) and a solution of $RhCl_3$×3 H_2O (9.00 mg, 34.6 μmol) in refluxing ethanol (15 ml). Yield: 44 mg (63%) of a dark-green waxy solid. R_f=0.97 (petroleum ether/ether, 7:3). ^{1}H NMR ($CDCl_3$/FC-113): δ=7.83 (s, 1H, 4-H), 8.37 (s, 2H, 2,6-H). ^{13}C NMR ($CDCl_3$/FC-113): δ=182.64 (OCO). ^{19}F NMR ($CDCl_3$/FC-113): δ=−82.5 (t, 24F, ^3J=10.3 Hz, CF_3), −112.3 (m, 16F, CF_2), −122.5 (m, 16F, CF_2), −122.7 (m, 16F, CF_2), −123.3 (m, 32F, CF_2), −124.1 (m, 16F, CF_2), −127.7 (m, 16F, CF_2). IR (KBr): ν=3097 (w), 1626 (m), 1587 (s), 1463 (m), 1408 (s), 1369 (s), 1314 (s); 1238 (vs, broad), 1209 (vs, broad), 1150 (vs), 1118 (s) cm^{-1}. $C_{92}H_{12}F_{136}O_8Rh_2$: M=4034.4 g/mol.

4.1.10. Cyclopropanation of styrene with methyl diazoacetate. A solution of methyl diazoacetate (100 mg, 1.00 mmol) in FC-113 (0.5 ml) was added with the aid of a syringe pump within 8 h to a stirred solution of the catalyst (**4** or **5**, 1 mol%) and a tenfold excess of styrene (1.13 ml, 10.0 mmol) in FC-113 (1.5 ml). After an additional reaction time of 4 h at 20°C, the solvent was removed and the residue was stirred with PFMC (0.7 ml) and dichloromethane (2.5 ml) for 20 min. After the phase separation, the fluorous phase was evaporated and the recovered catalyst so obtained was used in an additional reaction cycle. Cyclopropane **11** (R=H) was found in the dichloromethane phase, and after addition of dibenzyl ether as an internal standard the yield and *E*/*Z* ratio was determined by GC (Table 2).

The cyclopropanation of α-methylstyrene was done analogously. The cyclopropanes gave ^{1}H NMR spectra which were in agreement with published data.

4.1.11. Rh-catalyzed reaction of methyl diazoacetate with *n*-hexane. The catalyst (1 mol%) was dissolved (**5**) or suspended (**3**) in PFMC (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) dibenzyl ether 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 insertion products **12**–**14** were not separated on a preparative scale; rather, the components were identified by GC-MS and by characteristic ^{13}C NMR signals, see lit.[9]

4.1.12. Intramolecular carbenoid C–H insertion of 15. A solution of diazo ester **15**[17] (65 mg, 0.25 mmol) in FC-113 (0.5 ml) was added during 1 h via a syringe pump to a solution of catalyst **5** (8.0 mg, 1.0 mol%) in FC-113. After additional 12 h, the solvent was removed and a mixture of dichloromethane/PFMC (1.4 ml, 1:1) was added and stirred for 30 min. The catalyst collected in the PFMC phase was used for a further cycle. The dichloromethane 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; yields are given in Table 4. The chemical shifts of products **16** and **17** agreed with the published data.[16]

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