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Invited Review

Novel Immobilized Hydrosilylation Catalysts Based on Rhodium 1,3-Bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidenes

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Summary. The reactivity of a well defined Rh (I) complex, *i.e.* Rh(CF_3COO)(*NHC*)(*COD*) (**1**, *NHC* = 1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene, *COD* = η^4-cycloocta-1,5-diene) in the hydrosilylation of 1-alkenes, alkynes, and α,β-unsaturated carbonyl compounds, respectively, is described. With this complex, excellent reactivity was observed and turn-over numbers (TONs) up to 1000 were reached. A supported version of **1** was realized by reaction of RhCl(*NHC*)(*COD*) with *PS-DVB*–CH_2–O–CO–CF_2–CF_2–CF_2–COOAg (*PS-DVB* = poly(styrene-*co*-divinylbenzene) to yield *PS-DVB*–CH_2–O–CO–CF_2–CF_2–CF_2–COORh(*NHC*)(*COD*). This supported version of **1** exhibited at least comparable, in some cases increased reactivity compared to **1** and allowed the rapid removal of the catalyst from the reaction mixture. Due to reduced catalyst bleeding, the synthesis of target compounds with a Rh-content of less than 130 ppm was accomplished.

Keywords. N-Heterocyclic carbenes; Heterogeneous catalysis; Homogeneous catalysis; Hydrosilylation; Rhodium.

Introduction

Hydrosilylation (or hydrosilation) reactions involve the addition of inorganic or organic silicon hydrides to multiple bonds such as alkyne, alkene, ketoxime, and carbonyl groups. Reactions first described by *Sommer et al.* proceeded *via* a radical mechanism and required the presence of peroxides [1].

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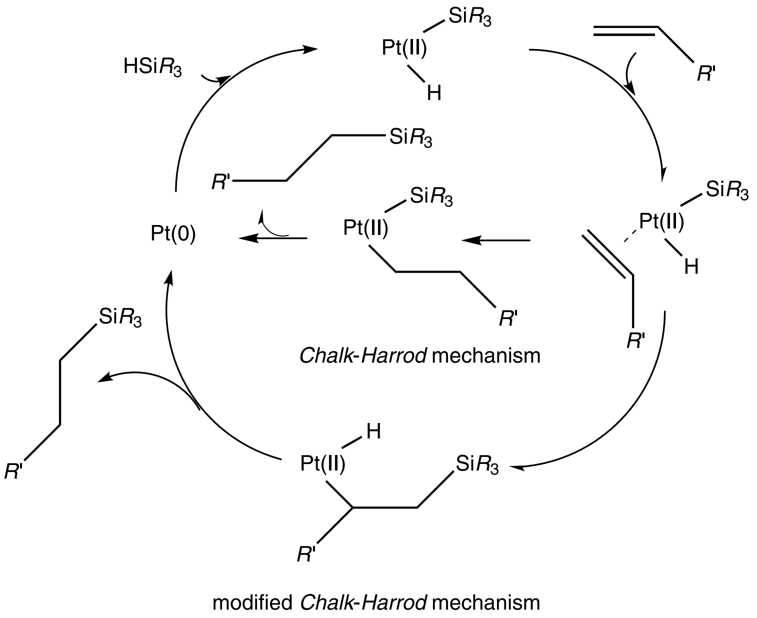


Scheme 1

Later, *Speier et al.* identified hexachloroplatinic acid as a quite efficient catalyst for these types of reactions [2]. Depending on the catalyst used, *e.g.* peroxides, tertiary amines, *Lewis* acids [3], supported metals, transition metal complexes, *Karstedt*'s catalyst [4], *etc*., the reaction mechanism may be based on free radicals [5] or on oxidative addition-reductive elimination steps (polar mechanism). The development of various hydrosilylation catalysts has already been summarized in some excellent reviews [6–9]. For hydrosilylations promoted by transition metal complexes, as is the case in the present report, the (modified) *Chalk-Harrod* mechanism [10, 11] (Scheme 1) is still the generally accepted one, however, other mechanisms have been suggested recently [9, 12, 13].

The transition metals most commonly employed in hydrosilylation reactions are Pd [14], Pt, Rh, Ir, Ni, and Cu [9, 15–17]. In terms of transition metal complexes used for catalysis, two major groups need to be mentioned. The first comprises of transition metal ions complexed by neutral ligands where the metal ion is bonded to a heteroatom, *e.g.* bipyridyls [18], ethylene diamines [19], diphosphines [20, 21], (P,O)-ligands such as 2-methoxy-2′-diphenylphosphinobinaphthyl, as well as (P,N)-ligands [22], (P,S)-ligands [23], *etc.* Particularly the latter have successfully been used for asymmetric hydrosilylations [24–26]. The second group is based on transition metal N-heterocyclic carbene (*NHC*) complexes [27, 28]. So far, solely Rh-1,3-R_2-imidazol-2-ylidenes have been used for hydrosilylations [29–38]. In this contribution, we describe the reactivity of a novel Rh(I)-NHC complex, Rh(CF_3COO)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(*COD*) (**1**, mesityl = 2,4,6-trimethylphenyl, *COD* = η^4-cycloocta-1,5-diene) in the hydrosilylation of various alkynes, alkenes, and carbonyl compounds.

Results and Discussion

*Synthesis and Reactivity of Rh(CF_3COO)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene) (COD, **1**)*

The synthesis of compound **1** is described elsewhere [39–41]. Briefly, RhCl(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene) (*COD*) was formed by reaction of [RhCl(*COD*)]$_2$ with 2 equiv. of LiO-*tertBu* and 1,3-dimesityl-3,4,5,6-tetrahydropyrimidinium bromide or tetrafluoroborate. This precursor was subject to reaction with CF_3COOAg to yield the desired target compound **1**. It crystallizes in the monoclinic space group $P2_1/c$, $a = 1449.58(3)$, $b = 1216.53(4)$, $c = 3451.4(1)$ pm, $\alpha = 90$, $\beta = 97.698(2)$, $\gamma = 90°$, $Z = 8$ (Fig. 1). Selected X-ray data are summarized in Table 1, selected bond lengths and angles are given in Table 2.

The Rh-*NHC* distance (Rh(1)–C(9)) is 206.5(8) pm and comparable to the distance of Rh to the *NHC* in RhBr(*NHC*)(*COD*) (204.7(3) pm, NHC = 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene) [39, 40]. The same accounts for the distance Rh-*COD* (208.2(8), 209.3(8), 216.6(11), and 219.5(11) pm in **1** *vs.* 210.3(3), 211.5(3), 219.7(3), and 223.4(3) pm in RhBr(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(*COD*)). In a first step, the reactivity of **1** in the hydrosilylation of both internal and 1-alkynes was investigated. For this purpose, phenylacetylene, 1-hexyne, trimethylsilylacetylene, and diphenylacetylene, respectively, were reacted with a series of organosilanes, *i.e.* triethylsilane, dichloromethylsilane, triphenylsilane, and trimethoxysilane. Scheme 2 summarizes the possible products of these hydrosilylation reactions.

The results are summarized in Table 3, entries 1–10. Using 0.08 mol-% of **1**, yields in the range of 17–72% were observed. Whereas virtually quantitative yields may be achieved using 0.5 mol-% of catalyst, the reduced amounts of catalyst, *i.e.* 0.08 mol-%, were used in order to determine the maximum turn over numbers (TONs) that can be achieved. As can be deduced from Table 3, entries 1–10, these

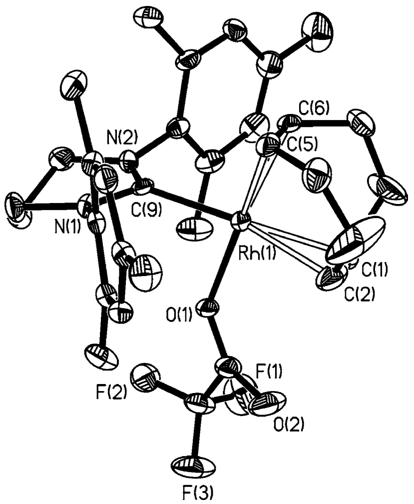


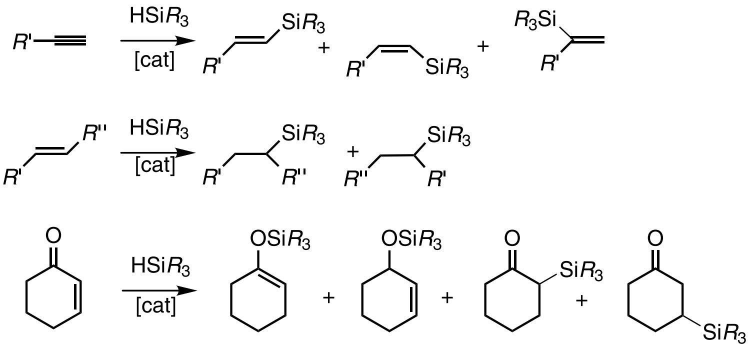
Fig. 1.

Table 1. Selected crystal data and structure refinement for **1**

	1
mol formula	$C_{32}H_{40}F_3N_2O_2Rh$
fw	644.57
crystal system	monoclinic
space group	C2/c (No. 15)
a/pm	1449.58(3)
b/pm	1216.53(4)
c/pm	3451.4(1)
α/°	90
β/°	97.698(2)
γ/°	90
V/nm^3	6.0315(3)
Z	8
temp/K	233(2)
density (calcd)/Mg/m^3	1.42
abs coeff/mm^{-1}	0.616
color, habit	colorless plate
no. of rflns with $I > 2\sigma(I)$	2703
goodness-of-fit on F^2	1.033
R indices $I > 2\sigma(I)$	$R_1 = 0.0645$ $\omega R^2 = 0.1252$

Table 2. Selected bond lengths [pm] and angles [°] for **1**

Rh(1)–C(9)	206.5(8)	C(9)–Rh(1)–C(6)	98.8(3)
Rh(1)–C(6)	208.2(8)	C(9)–Rh(1)–C(5)	98.4(3)
Rh(1)–C(5)	209.3(8)	C(9)–Rh(1)–O(1)	82.3(2)
Rh(1)–O(1)	212.4(5)	C(9)–Rh(1)–C(1)	161.7(6)
Rh(1)–C(1)	216.6(11)	C(9)–Rh(1)–C(2)	162.2(5)
Rh(1)–C(2)	219.5(11)		



Scheme 2

Table 3. Summary of results for the hydrosilylation of alkynes, alkenes, and carbonyl compounds using **1** and **2**

#	Main product	cat. (mol-%) yield/%	β-trans	β-cis	α^{a}	TON$_{max}$
1	1-phenyl-2-(triethylsilyl)ethene	**1** (0.08) 54	79	7	14	680
2	1-phenyl-2-(dichloromethylsilyl)ethene	**1** (0.08) 65	46	38	16	810
3	1-phenyl-2-(trimethoxysilyl)ethene	**1** (0.08) 34	73	11	16	430
4	1-(triphenylsilyl)hex-1-ene	**1** (0.07) 24	0	99	1	340
5	1-(dichloromethylsilyl)hex-1-ene	**1** (0.08) 72	100	0	0	900
6	1-(trimethylsilyl)-2-(dichloromethylsilyl)ethene	**1** (0.08) 41	99	0	1	510
7	1-(trimethoxysilyl)hex-1-ene	**1** (0.08) 61	70	0	30	760
8	1-(trimethylsilyl)-2-(trimethoxysilyl)ethene	**1** (0.08) 17	77	0	23	210
9	1-(triethylsilyl)stilbene	**1** (0.08) 62	–	–	–	780
10	1-(triethylsilyl)hex-1-ene	**1** (0.08) 71	61	11	27	890
11	1-(triethylsilyl)octane	**1** (0.1) 10	–	–	–	100
12	1-phenyl-2-(triethylsilyl)ethane	**1** (0.08) 37	–	–	–	460
13	1-(triethylsilyl)hexane	**1** (0.1) 18	–	–	–	180
14	1-(triethylsilyloxy)cyclohexene	**1** (0.08) 80	–	–	–	1000
15	1-(triphenylsilyloxy)cyclohexene	**1** (0.08) 25	–	–	–	310
16	triethylsilyloxymethylbenzene	**1** (0.1) 53	–	–	–	530
17	1-(triethylsilyloxy)-1-(4-chlorophenyl)ethane	**1** (0.09) 27	–	–	–	300
18	triethylsilyloxymethyl-4-fluorobenzene	**1** (0.09) 75	–	–	–	830
19	1-phenyl-2-(dichloromethylsilyl)ethene	**2** (0.07) 85	89	11	0	1210
20	1-(dichloromethylsilyl)hex-1-ene	**2** (0.07) 89	100	0	0	1270
21	1-(trimethylsilyl)-2-(dichloromethylsilyl)ethene	**2** (007) 34	100	0	0	490
22	1-(triethylsilyl)hex-1-ene	**2** (0.06) 34	45	20	35	570

(*continued*)

Table 3 (*continued*)

23	1-phenyl-2-(trimethoxysilyl)ethene	**2** (0.07) 46	70	3	27	660
24	1-(trimethoxysilyl)hex-1-ene	**2** (0.05) 66	58	0	42	1320
25	1-(triphenylsilyl)hex-1-ene	**2** (0.05) 45	0	94	6	900
26	1-phenyl-2-(triethylsilyl)ethene	**2** (0.07) 34	51	9	40	540
27	1-(triethylsilyl)stilbene	**2** (0.07) 52	–	–	–	740
28	1-phenyl-2-(triethylsilyl)ethane	**2** (0.05) 44	–	–	–	880
29	1-(triethylsilyl)hexane	**2** (0.07) 11	–	–	–	160
30	1-(triethylsilyloxy)cyclohexene	**2** (0.07) 51	–	–	–	730
31	1-(triphenylsilyloxy)cyclohexene	**2** (0.05) 11	–	–	–	220
32	triethylsilyloxymethylbenzene	**2** (0.09) 44	–	–	–	490
33	triethylsilyloxymethyl-4-fluorobenzene	**2** (0.07) 22	–	–	–	310
34	1-(triethylsilyloxy)-1-(4-chlorophenyl)ethane	**2** (0.1) 22	–	–	–	220

Reactions were run in dimethoxyethane (*DME*), reaction time: 12 h, $T = 80°C$; [a] different positional numbers for the substituents according to Scheme 2 apply

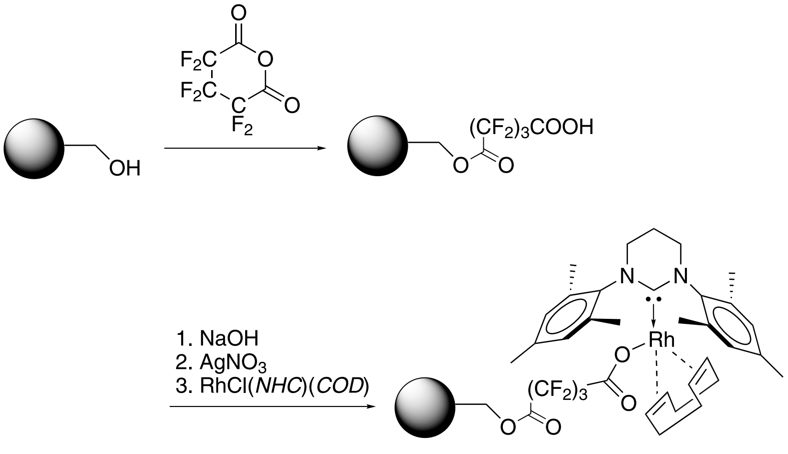
were in the range of 210–900. With one exception, *i.e.* 1-(triphenylsilyl)hex-1-ene, Table 3, entry 4, the *trans* products were predominantly formed. A somewhat reduced reactivity was observed for terminal alkenes (1-hexene, 1-octene, styrene), here TONs were in the range of 100–460 (Table 3, entries 11–13). Finally, and important enough, the hydrosilylation of aldehydes, aryl ketones, and α,β-unsaturated carbonyl compounds (*i.e.* cyclohex-2-en-1-one, benzaldehyde, 4-fluorobenzaldehyde, 4-chloroacetophenone) was investigated. As can be deduced from Table 3, entries 14–18, good reactivity was observed giving raise to TONs in the range of 300–1000. Cyclohex-2-en-1-one underwent selective 1,4-addition to yield 1-(triethylsilyloxy)cyclohexene and (triphenylsilyloxy)cyclohexene, respectively. Both the aromatic aldehydes and aryl ketones (Table 3, entries 16–18) were converted into the corresponding silylethers with good efficiency ($300 \leq \mathrm{TON} \leq 830$).

*Synthesis of the Immobilized Version of **1***

The immobilization of catalysts is nowadays an intensively investigated area of research. For various reasons, there is an increasing demand for supported versions of modern, highly selective, and active catalysts. First, contamination of products with metal ions and/or ligands needs to be low, particularly in cases relevant to pharmaceutical chemistry. Second, modern catalysts significantly add to the total costs of a product, therefore regeneration or reuse is highly desirable. And third, supported catalysts offer access to high-throughput techniques and continuous flow reactors, respectively. Key issues associated with supported catalysts are (i) preservation of the high activities, (enantio-)selectivities, and reaction rates observed with homogeneous catalysts, (ii) ease of catalyst separation, (iii) (multiple) catalyst recycling, and (iv) metal- and contaminant-free products. So far, immobilization has been accomplished by simply attaching phosphine- or diaminoethane-based ligands to a suitable support such as poly(styrene-*co*-divinylbenzene) or silica [9, 19, 42]. In addition, pyridine-containing polyamides as well as chiral N,N′- and N,P-ligand-derivatized zeolithes have been used [43–45]. Poly(styrene)-*b*-poly (butadiene) copolymers have been used to immobilize H_2PtCl_6 and $RhCl_3$, respectively [46]. Finally, issues mentioned above including recycling may be accomplished by a fluorous approach [47].

For the immobilization of **1**, an approach originally developed for the immobilization of ruthenium-based metathesis catalysts was chosen [48–51]. Thus, hydroxymethylated poly(styrene-*co*-divinylbenzene) (hydroxymethyl *PS-DVB*) was reacted with hexafluoroglutaric anhydride to yield the corresponding polymer-immobilized perfluorocarboxylic acid (Scheme 3). Conversion into the silver salt was accomplished *via* reaction with NaOH and $AgNO_3$. Finally, this polymer-bound silver salt was reacted with RhCl(1,3-bis(2,4,6-trimethylphenyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene(*COD*) to yield **2**, the polymer-supported analogue of **1**. Following this synthetic protocol, a catalyst loading of 0.6% *w*/*w* was accomplished.

To retrieve information about the reactivity of **2** in comparison with **1**, it was again used in the hydrosilylation of alkynes, 1-alkenes, aldehydes, and carbonyl compounds. The results are summarized in Table 3, entries 19–34. Interestingly, **2** displayed an even enhanced reactivity in the hydrosilylation of both alkynes and 1-alkenes. Thus, TONs in the range of 160–1320 were obtained using 0.05–0.07 mol-% of catalyst (Table 3, entries 19–29). This may be explained by the heterogeneous nature of the catalysts, effectively reducing bimetallic decomposition reactions. The influence on regioselectivity turned out to be non-predictable. Thus, the product distribution of some reactions obtained by



Scheme 3

the action of **2** remained virtually unchanged (Table 3, entries 20, 21, 23, 25), other distributions were subject to change in either direction. Finally, a comparable yet somewhat lower reactivity was observed in the hydrosilylation of aldehydes, α,β-unsaturated ketones and aryl ketones, respectively. Here TONs were in the range of 220–730 (Table 3, entries 30–34). Again 100% 1,4-selectivity was observed in the hydrosilylation of cyclohex-2-en-1-one. Leaching of the metal from **2** into reaction mixture was comparably low, resulting in an average Rh-content of 130 ppm.

Conclusion

The N-heterocyclic carbene-derived Rh (I) complex, Rh(CF_3COO)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(η^5-1,5-cyclooctadiene) is an efficient catalyst for the hydrosilylation of both terminal and internal alkynes, 1-olefins, aromatic aldehydes and ketones, and α,β-unsaturated carbonyl compounds, rivaling existing Rh-, Pd-, and Pt-based systems. TONs up to 1000 may be obtained. Its *PS-DVB*-supported version shows at least similar, in some cases even enhanced reactivity for the same substrates and allows the synthesis of the target compounds with a comparably low Rh content.

Experimental

All experiments involving transition metals were performed under a nitrogen atmosphere in a MBraun glove box or by standard *Schlenk* techniques. Reagent grade dimethoxyethane (*DME*), tetrahydrofurane (*THF*), diethyl ether, toluene, and pentane were distilled from sodium benzophenone ketyl under argon. Dichloromethane and chloroform were distilled from calcium hydride under argon. All other reagents were commercially available and used as received. Column chromatography was performed on silica gel 60 (220–440 mesh, Fluka, Buchs, Switzerland). NMR spectra were recorded at 25°C on a Bruker Spektrospin 300 at 300.13 MHz for proton and at 75.47 MHz for carbon in the indicated solvent and referenced using the solvent peaks ($CDCl_3$: $\delta = 7.24$, 77.0 ppm; CD_2Cl_2: $\delta = 5.32$, 54.0 ppm). Coupling constants are listed in Hertz. FT-IR spectra were recorded on a Bruker Vector 22 using ATR technology. Bands are listed in cm^{-1} and characterized as broad (br), strong (s), medium (m), and weak (w). GC-MS measurements were carried out on a Shimadzu GCMS QP 5050, using a SPB-5 fused silica column (30 m×0.25 mm×25 μm film thickness) and helium as carrier gas. A split ratio of 70 was used throughout. The column flow was 2 cm^3/min, the total flow was 146.2 cm^3/min. The temperature program was as follows: 70°C (1 min and 3 min for low boiling compounds, respectively), 300°C (25°C/min), 300°C (9 min), 70°C. Injector temp. 150°C, interface temp. 300°C. A JOBIN YVON JY 38 plus was used for ICP-OES measurements, a MLS 1200 mega for microwave experiments. Further instrumentation is described elsewhere [51]. RhCl(*NHC*)(*COD*) [39, 40] and Rh(CF_3COO)(*NHC*)(*COD*) (*NHC* = 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene) [41] were prepared according to published procedures.

Standard Procedure for Hydrosilylation Reactions

The catalyst (for the amount refer to Table 3) was dissolved in *DME* (2 cm^3). Tetradecane (100 mm^3) was added as an internal standard followed by the silane (0.50 mmol) and the unsaturated compound (alkyne-, alkene-, or carbonyl compound, 0.50 mmol). The mixture was stirred at 80°C until no further conversion was monitored by GC-MS. Yields and turn over numbers (TONs) were determined by GC-MS using the conversion of the educts. For the alkyne compounds the ratio of the product isomers was determined by integration of the GC-MS peaks. These were correlated with the results taken from NMR measurements.

For NMR-measurements, the solvent of the reaction mixture was removed *in vacuo* and the residue was taken up in $CDCl_3$. Integration of the olefinic region provided the ratio of the product isomers of the reaction of an alkyne compound with a silane. Concerning the reaction of the $\alpha\beta$-unsaturated carbonyl compound with a silane, the 1,4-addition was confirmed by NMR, the lack of olefinic proton-signals and the appearance of a singlett around 5 ppm.

*Generation of Polymer-Supported **1** [Rh(polymer–CH_2–O–CO–CF_2–CF_2–CF_2–COO)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(COD)]*

The modified poly(styrene-*co*-divinylbenzene) support Ag(polymer–CH_2–O–CO–CF_2–CF_2–CF_2–COO) was synthesized according to a previous disclosure [51]. Ag(polymer–CH_2–O–CO–CF_2–CF_2–CF_2–COO) (500 mg) was suspended in *THF* (10 cm^3) and a solution of RhCl(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(*COD*) (40 mg, 0.071 mmol) in *THF* (3 cm^3) was added dropwise. After stirring for 90 min at room temperature the reaction mixture was filtered, the residue was washed with *THF* and dried *in vacuo* to yield a yellow powder (495 mg, 99%). FTIR (ATR mode): $\bar{\nu} = 3057$ (w), 3024 (w), 2919 (m), 2852 (w), 1672 (w), 1596 (m), 1488 (m), 1446 (m), 1362 (m), 1304 (m), 1155 (m), 1058 (m), 1026 (m), 908 (m), 828 (m), 753 (m), 695 cm^{-1} (s). For the determination of the rhodium content, Rh(polymer–CH_2–O–CO–CF_2–CF_2–CF_2–COO)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)(*COD*) (30.9 mg) was placed inside a high pressure Teflon tube. Nitric acid (1 cm^3) and aqueous hydrochloric acid (3 cm^3) were added and the mixture was exposed to microwave conditions (50, 600, and 450 W pulsed, $t = 32$ min). After cooling to room temperature the mixture was filtered and water was added up to a volume of roughly 10 cm^3 (the solution was weighed). The rhodium content as determined by ICP-OES was 61.4 μmol/g polymer, corresponding to 6.32 mg/g polymer (0.6% w/w catalyst loading).

Determination of Leaching in Heterogeneous Reactions

The reaction mixture was filtered, dried in vacuo, dissolved in dichloromethane (2 cm^3), and transferred into a high pressure Teflon tube. The solvent was then removed at ambient conditions. Nitric acid (1 cm^3) and aqueous hydrochloric acid (3 cm^3) were added and the mixture was exposed to microwave conditions (50, 600, and 450 W pulsed, $t = 32$ min). After cooling to room temperature, the mixture was filtered and water was added up to a volume of roughly 10 cm^3 (the solution was weighed). The rhodium content was determined by ICP-OES.

Rh Measurements

Rh was measured by ICP-OES ($\lambda = 233.477$ nm, ion line). The background was measured at $\lambda = 233.4904$ and 233.4602 nm. Standardization was carried out with a Rh standard containing 10 ppm of Rh. Leaching of rhodium into the reaction mixture: 130 ppm.

*X-Ray Measurement and Structure Determination of **1***

Data collection was performed on a Nonius Kappa CCD equipped with graphite-monochromatized Mo-K_α-radiation ($\lambda = 0.71073$ Å) and a nominal crystal to area detector distance of 36 mm. The structures were solved with direct methods SHELXS86 and refined against F^2 using SHELX97 [52]. Hydrogen Atoms were calculated, with isotropic displacement parameters 1.2 and 1.5 times higher than for the carbon atoms; refined with bond restraints d(C–H) = 0.94 Å at C1, C2, C5, and C6. Since only small crystals with low diffraction were obtained, 100 reflections were omitted because of systematic twinning. CCDC-244481 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.; fax: (+44)-1223-336033; or deposit@ccdc.cam.ac.uk).

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