Catalysts on Functionalized Polymer Chips (PC) as Recyclable Entities

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Dedicated to Professor Steven V. Ley on the occasion of his 60th birthday

Abstract: We describe surface-modified sintered polyethylene sheets as a suitable carrier system for various catalysts. The material shows high rigidity and no swelling properties and allows for easy removal and reuse of the supported catalysts. The application was demonstrated for Pd-, Rh-, and Ru-catalysts in Suzuki couplings, hydroformylation, and olefin metathesis, respectively.

Key words: solid support, heterogeneous catalysis, palladium, rhodium, ruthenium, Suzuki reaction, hydroformylation, olefin metathesis

Development of new versatile, environmentally benign and robust carrier systems for immobilization of different transition-metal catalysts is of great importance due to their applications in organic synthesis. Nowadays synthetic chemistry is no longer conceivable without the use of catalysts. Easy removal and recycling of expensive and poisonous transition-metal catalysts is thus becoming more and more significant.

Different soluble polymers[2] and solid supports[3] are used as carriers to recover catalysts. Furthermore, various solvent systems such as perfluorinated[4] solvents, ionic liquids,[5] or supercritical CO_2[6] are employed for this purpose.[7]

Over the last few years, functionalized polystyrene beads have been increasingly used for immobilization of different catalysts.[8] However, only a few examples are known for polymeric carrier systems, which are easy to handle.

One system is the monolithic polymer disc of Stevenson, which has good swelling characteristics in different solvents.[9] Another characteristic of this soft carrier is its resistance to osmotic shock. These discs were prepared by polymerizing styrene with different cross-linkers [divinylbenzene, poly(ethylene glycol) (PEG)400 bisacrylate or PEG 1000 bisacrylate] in a suitable solvent and used in the Suzuki reaction.

The second type of support was reported by Bradley et al.[10] The main idea of this new methodology is to sinter the resin into a polymer matrix. These 'resin plugs' were used like normal resins in solid phase organic synthesis (SPOS) or in solid phase peptide synthesis (SPPS), and they can be used for catalyst immobilization.[11] In general, these methods were developed to prepare resins which are more practical to handle.

Here we report on a new, easy to handle, and very stable support (functionalized Polymeric Chip [PC]) for the immobilization of catalytic systems (e.g., Pd, Rh, and Ru). The advantage of PCs is their exclusive functionalization on the highly porous surface so that swelling of the polymer is not an issue anymore.

Furthermore, these PCs can be applied in continuous flow-type processes due to their porous structure.

These PCs, which are made of polyethylene and functionalized with Boc-protected primary amines, are now commercially available.[12] Different ligands can be attached to them to immobilize transition metals for catalytic reactions or SPOS and SPPS can be performed directly or after functionalization with different linker systems. Here, we report the immobilization of Pd-, Rh-, and Ru-complexes on this new carrier system and demonstrate its various applications in catalysis.

Immobilized Pd on PC in Suzuki Reactions

Pd-complexes are well-known for their ability to catalyze various types of reactions, e.g., Suzuki and Stille cou-

Figure 1 Catalyst-modified PC (left) during reaction and (right) simple separation of the immobilized catalyst from the reaction mixture.

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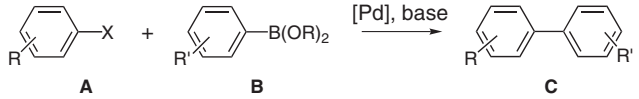
plings, Heck reactions, carbonylations, asymmetric allylations, aminations, *sp*–*sp*^{2} cross-couplings, just to name a few. Here, we present the application of immobilized Pd on PC in Suzuki coupling reactions.

Suzuki coupling is one of the most important carbon–carbon bond-formation reactions.[13] Generally, this reaction is utilized to prepare biaryl systems. Commonly, a Pd(0) species is used as catalyst; an aryl halide (**A**) and an aryl boronic acid or ester (**B**) as components to be coupled in the presence of a base (Scheme 1).

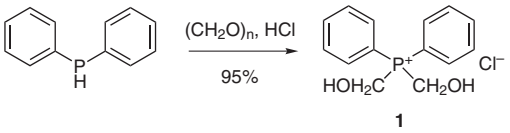


Scheme 1 Suzuki reaction.

Different ligand systems and solid phases are known for the immobilization of Pd, and different soluble[2] and non-soluble[3] polymers have been employed as supports. Here, we use a novel type of functionalized polyethylene (PE) polymer chips (Figure 1) as a highly porous non-soluble support for palladium. The immobilization of Pd on solid supports has been known for several years.[3,14] However, recycling is still problematic, because the used polymer matrices are not stable under mechanical conditions.[15] For example, agitating with a stirrer bar typically destroys a weakly cross-linked polymeric support.[16] Reactions are only possible under shaking conditions or by stirring very slowly, which has a negative effect on reaction kinetics. The use of PCs is very advantageous because of the nearly unrestrained mechanical stability. They are also easy to handle as they can be separated from the product by just removing them from the reaction mixture with tweezers (Figure 1). No filtration step is required! After a simple washing procedure, they can be reused in the next reaction or run.

From a variety of different Pd-ligand systems we selected the versatile bis(diphenylphosphanyl)methyl ligand system, which is attached to amine-functionalized surfaces in quantitative yields as has been demonstrated by several groups. This bidentate anchor group is versatile in the complexation of various transition metals, e.g., Pd, Rh, Ir, and Ni as demonstrated by Reetz et al. by immobilization on dendrimer shells.[17]

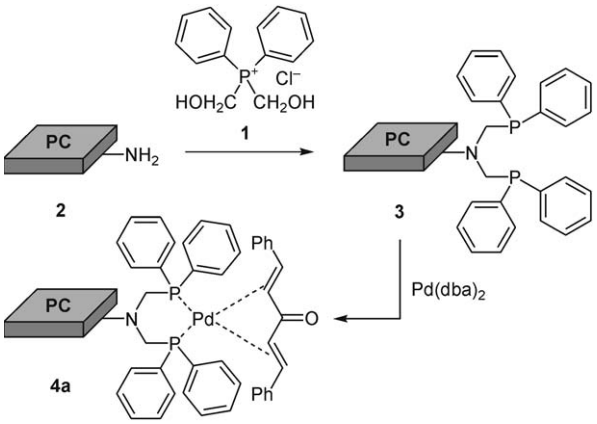
In general, bis(diphenylphosphanyl)methyl functionality is introduced by methylphosphanylation of amines (Mannich-type reaction) using diphenylphosphine and paraformaldehyde. This method was demonstrated by Alper et al. on amino-functionalized dendrimers.[18] In this work we introduced the bis(diphenylphosphanyl)methyl functionality via reaction of the primary amine with a preformed phosphonium salt (Scheme 2) in the presence of Et_3N. The easily accessible phosphonium salt has several advantages compared to free diphenylphosphine due to its easier handling, oxidation stability, and non-pyrophoricity.[19,20]



Scheme 2 Synthesis of the phosphonium salt.

The reaction of phosphonium salt **1** with amine-functionalized PC in the presence of Et_3N gave the anchor ligand for immobilization of palladium (Scheme 3).

Reaction of $Pd(dba)_2$ with **3** resulted after ligand exchange reaction in a PC-immobilized Pd(dba) species **4a**. The Pd content was determined by ICP–MS measurements.

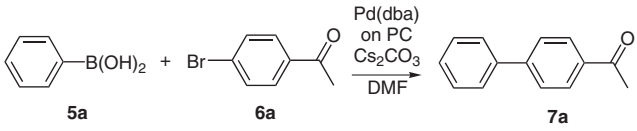


Scheme 3 Construction of anchor and complexation of $Pd(dba)_2$ with functionalized PC (**3**).

These catalytically active PCs were then used in different Suzuki coupling reactions.

In order to evaluate the catalysts recycling, the Suzuki reaction of phenylboronic acid (**5a**) and *p*-bromoacetophenone (**6a**) was repeated five times (Table 1).

Table 1 Recyclable Suzuki Reaction of Phenylboronic Acid (**5a**) and *p*-Bromoacetophenone (**6a**)



Cycle	Temp. (°C)	Conversion after 2 h (%)[a]	Conversion after 6 h (%)[a]
1	120	95.6	98.0
2[b]	100	55.1	96.7
3	120	93.6	97.3
4	120	76.4	97.8
5	120	63.5	96.0

[a] Conversion determined by ^{1}H NMR or GC–MS.
[b] Reaction temperature: 100 °C for 2 h and 120 °C for 4 h.

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The reaction of phenylboronic acid (**5a**) and *p*-bromoacetophenone (**6a**) was performed in DMF in the presence of Pd-loaded PC and Cs_2CO_3 as a base on a 0.5 mmol scale. In order to study the temperature effect in cycle two, the temperature was decreased to 100 °C and a significant effect on reaction kinetics was observed. In cycles three to five, the reaction temperature was increased again to 120 °C and no big difference in conversion was observed after six hours reaction time compared with the first cycle. In all cases high conversions (> 95%) were obtained after six hours. The conversion only decreased slightly after two hours in cycles four and five.

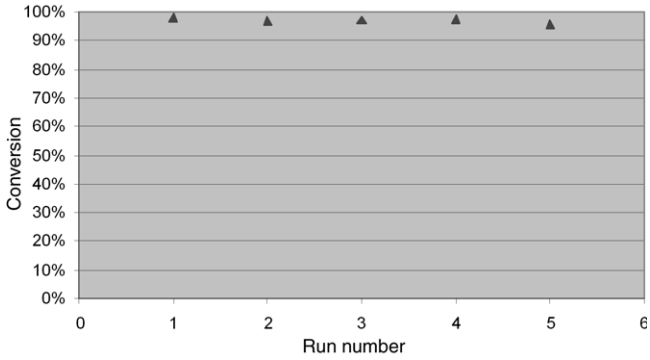


Figure 2 Recycling of the PC (**4a**) using **5a** and **6a** as substrates in Suzuki reaction.

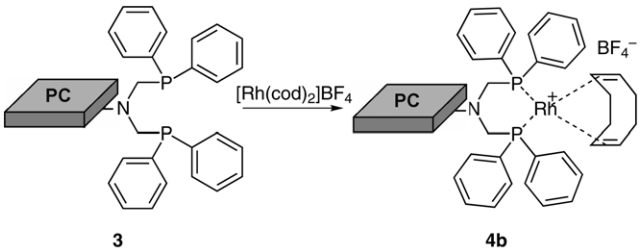
Due to the relatively small quantity of starting material, a 5-mmol scale-up of this reaction was performed. The amount of catalytically active Pd-PC was kept nearly on the same level (scale-up: 0.157 mol% as opposed to 1.55 mol% for the reaction in small scale). This reaction demonstrated the easy handling of immobilized Pd on PC. After completion of the Suzuki reaction **4a** was fished out with tweezers (Figure 1) and **7a** was isolated in nearly quantitative yields (99.5%) after an extraction to remove inorganic salts produced without using any tedious column chromatography.

To determine the immobilized Pd amount, an ICP–MS measurement was performed which resulted in 1191.6 ppm Pd. This means 11.20 mmol Pd per kg PC and 0.157 mol% immobilized Pd in the scale-up reaction, which is a very low amount for heterogeneous reaction conditions. After additional experiments the TON and TOF could be calculated for the catalytic active **4a** (TON = 360; TOF = 36 h^{-1}).

In order to show the general activity of prepared Pd-PC (**4a**) species, various boronic acids and also an electronically disfavored aryl halide were utilized in Suzuki reactions. In entry 2 of Table 2, the reaction of phenylboronic acid (**5a**) with *p*-bromoanisole (**6b**) is shown. This reaction gave the desired biaryl system **7b** in over 75% conversion. For variation on the boronic acid side, *p*-nitrile- (**5b**), *p*-acetophenone- (**5c**), and *p*-methoxyphenylboronic acid (**5d**) were chosen. Only the reaction with the *p*-nitrile substituent (**5b**) worked with moderate conversions (65%). The experiment of **5c** (entry 3) and **5d** (entry 4) resulted in good conversions (83% and 70%) and no starting material could be detected. All reactions were performed overnight (15 h) to get maximum conversions in an acceptable time range.

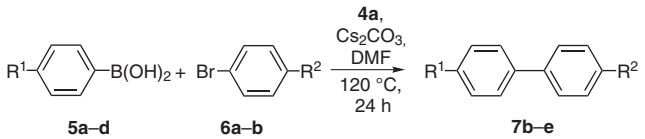
Immobilization of Rh on PC for Hydroformylation Reactions

PC **3** with the bisdiphenylphosphanyl ligand, which was used for the immobilization of Pd, also proved useful to support rhodium complexes. Here we immobilized a rhodium (I) species, which is a very common homogeneous catalyst for hydroformylation reactions (Scheme 4).



Scheme 4 Immobilization of $[Rh(cod)]BF_4$ on functionalized PC **3** to form **4b.**

Table 2 Suzuki Reaction with Various Substituted Aryl Halides and Aryl Boronic Acids



Entry	R^1	Boronic acid	R^2	Aryl halide	Yield (%)	Product
1	H	**5a**	OMe	**6b**	75	**7b**
2	CN	**5b**	COMe	**6a**	65	**7c**
3	COMe	**5c**	COMe	**6a**	83	**7d**
4	OMe	**5d**	COMe	**6a**	70	**7e**

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The immobilization of homogeneous rhodium catalysts is currently being investigated by several groups.[18,21] Besides polymer beads, which are commonly used as solid supports, silica was also utilized to immobilize rhodium.

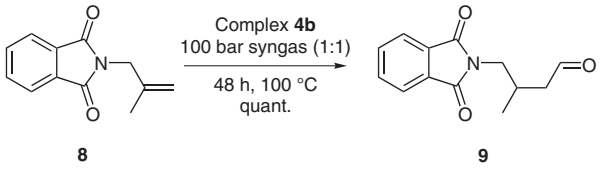
In both cases, significant leaching has been observed. Hydroformylation reactions are atom-economic,[22] but they are still cost- and purification-intensive.

Hydroformylation is the reaction between an olefin and syngas (CO, H_2) in the presence of a homogeneous transition-metal catalyst, which results in a linear (*n*-) or branched (*iso*-) aldehyde.

This reaction and their applications in synthetic organic chemistry is part of extensive research in several groups.[18,23,24,25]

Here, we used Rh-PC (**4b**) as an easily recyclable catalyst in hydroformylation reactions. The starting material for this representative reaction was methallylphthalimide (**8**). This compound has the advantage that it forms only the *n*-product and no side-products such as *iso*-product or isomerization products.[26a] This compound is also interesting, because primary amines are accessible after deprotection of the phthalimide functionality, which makes it even more attractive for different investigations as demonstrated by Eilbracht et al. over the last two years.[26]

The hydroformylation was performed in a stainless autoclave whereby methallylphthalimide (**8**) was dissolved in toluene (Scheme 5). PC-Rh **4b** was inserted into the reaction mixture, and the mixture was pressurized with a 100 bar 1:1 mixture of syngas (CO/H_2) before heating up to 100 °C for 48 hours. After reaction the PC-Rh **4b** catalyst was fished out with tweezers and after solvent removal the target aldehyde **9** was isolated without any further purification in quantitative yield and very high purity (see the ^1H NMR spectrum in Figure 3).



Scheme 5 Hydroformylation of methallylphthalimide (**8**).

Further observation during this reaction was that the mixture of solvent and product was colorless after the reaction. This is good evidence that no leaching occurred during this reaction. Generally, the reaction mixture with homogenous catalyst, product, and solvent has an intense color after hydroformylation. The same Rh-PC catalyst **4b** was used three times in the same hydroformylation reaction without any loss of reactivity (> 98% conversion according to ^1H NMR).

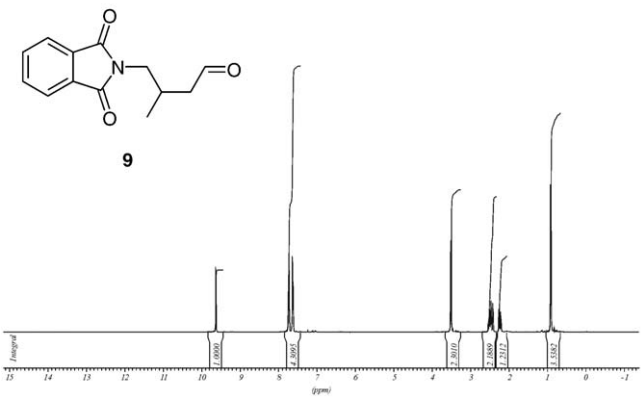


Figure 3 ^1H NMR spectrum of crude 4-(phthalimidyl)-3-methylbutyraldehyde (**9**).

Olefin Metathesis

Since the development of Ru catalysts by Grubbs et al., olefin metathesis has become a valuable tool in the synthetic repertoire of organic chemistry (Figure 4).[27] Diverse applications like ring-closing metathesis (RCM), ring-opening metathesis (ROM), cross metathesis (CM), and enyne metathesis have offered new synthetic pathways in the development of synthetic routes to important organic compounds.[28] The common catalysts **10a**,**b** are easy to handle and show a wide tolerance for functional groups. Their only drawback is that they cannot be recovered and that the leaching of Ru into the product is difficult to control.

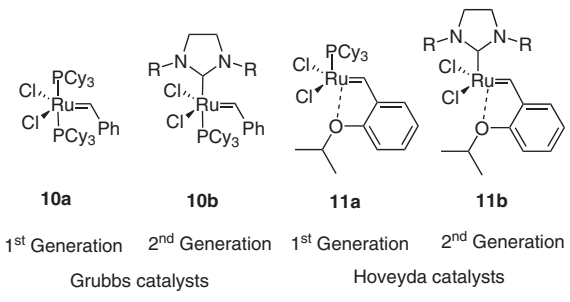


Figure 4 Olefin metathesis catalysts.

Hoveyda et al. prepared the catalysts **11a**,**b** (Figure 4).[29] These complexes were stable to air and moisture and could even be successfully recycled by chromatography on silica gel. The remarkable stability is caused by the ether chelate which provides an additional coordination site. During the catalytic cycle, the ligand is liberated, and after having consumed the substrate, the styrene ligand recaptures the Ru^{2+} so that the catalyst is reformed.[30]

Several groups soon realized that Hoveyda's complex would be easily amenable to immobilizations on solid supports. In the meantime, Hoveyda et al. reported a dendrimeric analogue as well as the immobilization on sol-gel.[31,32] Blechert et al. used polymeric supports like Wang

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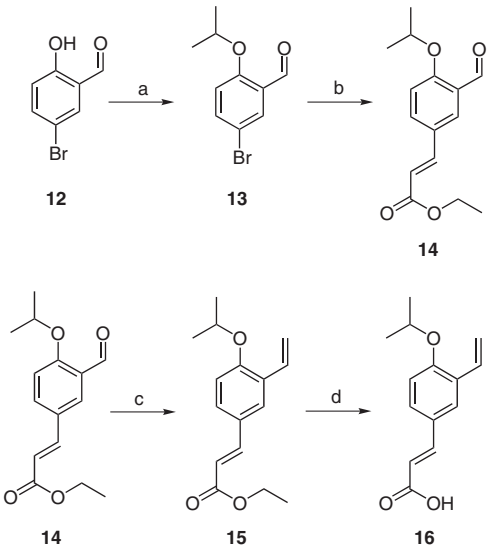
resin, Merrifield resin, or PEGA.[33] Examples of soluble polymer-bound catalysts were also reported.[34]

The general immobilization strategy involves the synthesis of a modified styrene, which allows a covalent attachment of the ligand to the support. Reaction with one of the Grubbs catalysts (**10a** or **10b**) then yields the immobilized catalyst.

We present here a new version of an immobilized Hoveyda-type catalytic system in which the catalyst is attached to the surface of amino-modified sintered polyethylene plates or polypropylene membranes via an amide bond. This required ligand modification with a carboxyl function. As the starting point, we chose the cheap and readily available 4-bromosalicylic aldehyde **12**. Both the necessary vinyl group as well as the isopropoxy ether function could be introduced in a straightforward manner, and a Heck reaction allowed for the modification with a carboxyl group to yield **16** as outlined in Scheme 6.

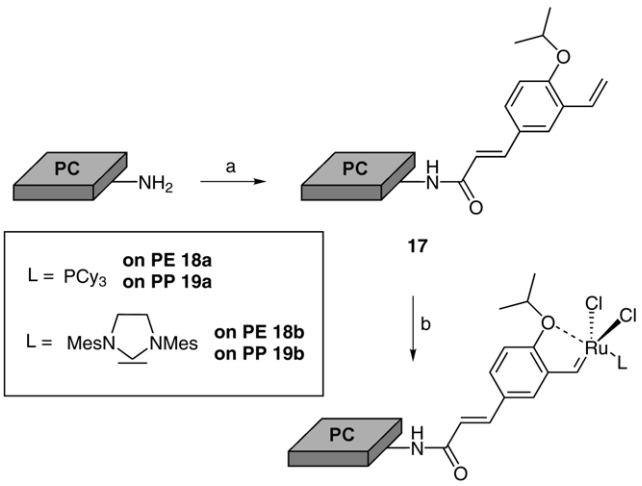


Scheme 6 Synthesis of **16**: (a) *i*-PrI, K_2CO_3, Cs_2CO_3, DMF, 24 h, r.t., 96%; (b) ethyl acrylate, $Pd(OAc)_2$, $P(o\text{-Tol})_3$, Et_3N, DMF, 5 h, 100 °C, 89%; (c) Ph_3PCH_3Br, *n*-BuLi, THF, 24 h, 0 °C → r.t., 72%; (d) KOH, H_2O–dioxane, 24 h, r.t., 92%.

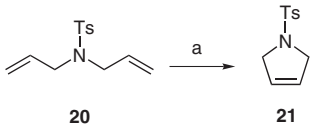
All steps proceeded with fair to high yields. We envisaged that the incorporated double bond would not interfere with the metathesis reaction.

Both solid-phase materials,[12] the polyethylene as well as the polypropylene supports, were available in a length and width of 12 cm by 8 cm. This size proved to be problematic for the immobilization of **16** and its conversion into the catalyst. Fortunately, due to curling of the polypropylene membrane in DMF and CH_2Cl_2, it was possible to perform the immobilization of the whole sheet in a round bottom flask. The sintered polyethylene, however, proved to be a very rigid material. Therefore, it was cut into several small pieces, which were modified simultaneously. The coupling of ligand **16** to the amino-modified supports was performed using DCC and HOBt for 24 hours (Scheme 7). The completion of the coupling was monitored by the TNBS test.[35] Possibly unreacted amino functions were masked by an acylation step with Ac_2O. Finally, catalysts **18a**,**b** and **19a**,**b** were prepared by a Ru exchange employing 1.3 equivalents of catalysts **10a** and **10b**, respectively. The reaction with **10a** led to a higher Ru content than with **10b** as determined by ICP–MS, on the polypropylene sheet as well as on the polyethylene plate.

At first, we examined the recycling ability of **18a**, **18b**, **19a**, and **19b** in a ring-closing metathesis employing **20** as a substrate in five consecutive runs (Scheme 8). Usually, 2.5–5 mol% of catalyst were applied to olefin metathesis reactions. In preliminary experiments we had already observed that 1 mol% was sufficient for this reaction. Hence, we decided to use this amount for the further experiments. Furthermore, all reactions were performed in reagent-grade solvent and without an inert atmosphere.



Scheme 7 Synthesis of the catalysts **18a**,**b** and **19a**,**b**: (a) **16**, DCC, HOBt, Hünigs base, DMF, 24 h, r.t. and then Ac_2O, Et_3N, DMAP, CH_2Cl_2, 5 h, r.t., (b) **10a** or **10b**, CuCl, CH_2Cl_2, 4 h, reflux.



Scheme 8 a) 1 mol% catalyst, CH_2Cl_2, reflux, 1.5 h.

For the second-generation catalysts, high conversions were observed in the first three runs (Figures 5 and 6). In runs four and five, a drop in activity took place. This level of performance was not reached by the first-generation catalyst.

Next, we tested the supported catalysts **18a**, **18b**, **19a**, and **19b** on different α,ω-olefins as substrates. Here we also used 1 mol% of catalyst. The reactions were performed in a parallel manner to guarantee identical reaction conditions. As shown in Table 3, high conversions were obtained with almost all olefins. Although the ring-closure of the tosyl amides **20** (entry 1) and **22** (entry 2) ran smoothly, the olefin **24** (entry 3) hardly reacted. Surpris-

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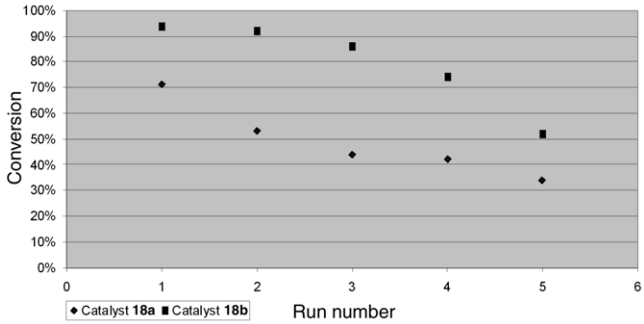


Figure 5 Recycling of the catalysts on polyethylene using **20** as substrate.

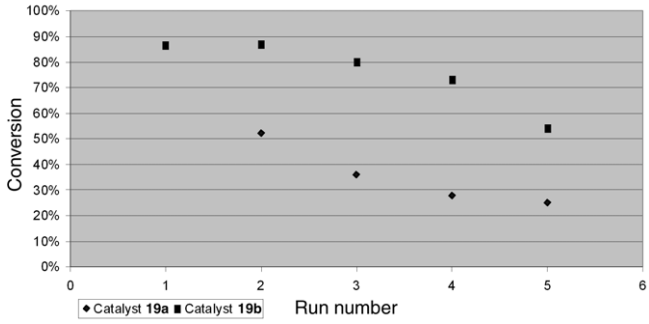
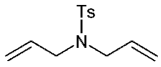
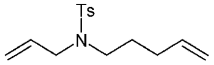
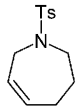
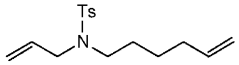
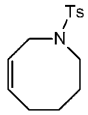
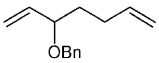
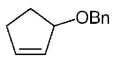
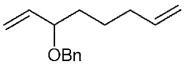
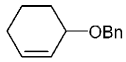
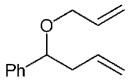
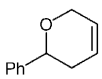
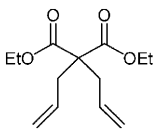
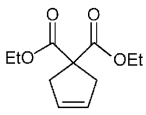


Figure 6 Recycling of the catalysts on polypropylene using **20** as substrate.

ingly, catalysts **18a** and **19a** were more active than **18b** or **19b**. Reaction of **24** with higher catalyst loadings led to an increase of the conversion with **18a** and **19a**, whereas the activity of **18b** and **19b** remained still low. Besides the desired **25**, we observed a low amount of side-products which might correspond, according to ^{1}H NMR and to mass spectra, to the dimer and trimer of **24**, possibly formed by cross metathesis. With olefin **30** (entry 6), we also observed low to moderate conversions which could be improved by employing 2.5 mol% of catalyst.

In summary, we have prepared new solid-supported olefin metathesis catalysts by attaching them to the surface of amino-modified polyethylene and polypropylene sheets

Table 3 Ring-Closing Methathesis of Several α,ω-Olefins

Entry	Starting material[a]	RCM product	Catalyst	Conversion[b]
1	**20** 	**21** 	**18a**	71%
			18b	> 98%
			19a	> 98%
			19b	96%
2	**22** 	**23** 	**18a**	90%
			18b	> 98%
			19a	95%
			19b	97%
3	**24** 	**25** 	**18a**	19% (36%,[c] 36%[d])
			18b	9% (20%,[c] 20%[d])
			19a	29% (40%,[c] 59%[d])
			19b	6% (15%,[c] 17%[d])
4	**26** 	**27** 	**18a**	83%
			18b	95%
			19a	89%
			19b	96%
5	**28** 	**29** 	**18a**	82%
			18b	96%
			19a	> 98%
			19b	95%
6	**30** 	**31** 	**18a**	5% (89%)[c]
			18b	27% (87%)[c]
			19a	45% (94%)[c]
			19b	43% (90%)[c]
7	**32** 	**33** 	**18a**	31%
			18b	84%
			19a	71%
			19b	63%

[a] Reaction conditions: CH_2Cl_2, reflux, 1.5 h, 1 mol% catalyst.
[b] Determined by NMR.
[c] Catalyst (2.5 mol%).
[d] Catalyst (5 mol%).

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via an amide bond. The modified ligand was synthesized in a straightforward manner. These catalysts revealed high activity even with a catalyst loading of 1 mol%. They showed high stability when used in reagent-grade solvents and in air. Furthermore, the supported catalyst could easily be removed after reaction and had the potential for reapplication when **18a**, **18b**, **19a**, or **19b** were applied although slight decreased yields were observed in consecutive runs. The ligand applied here has the further advantage that it can be attached to any kind of amino-modified solid support.

Polymer chips and membranes were obtained from PolyAn GmbH[12] (polyethylene sinter material: Amino 3-D Matrix, order no.: 10100031 polypropylene membrane: Amino 3-D Matrix, order no.: 10100013).

All reagents were obtained from Aldrich, Fluka, or Lancaster and were of highest purity available. THF was dried over Na/benzophenone and freshly distilled before use. CH_2Cl_2 was dried over CaH_2. Melting points were measured with the electrothermal digital melting device IA 9200 and are uncorrected. Column chromatography was performed using commercially available MN Silica gel 60 (0.063–0.2 mm/70–230 mesh) ASTM for CC from Baker. ^{1}H NMR spectra were measured at 250, 300, 400, and 500 MHz and ^{13}C NMR spectra at 100.6 MHz and 125.7 MHz on Bruker AC 250, DRX400, and DRX500 spectrometers, respectively. Chemical shifts (δ) are given in ppm relative to TMS (δ = 0 ppm) for ^{1}H NMR and relative to $CHCl_3$ (δ = 77.0 ppm) for ^{13}C NMR. *J* values are given in Hz. MS data were recorded on TSQ-700 (EI, CI, ESI) mass spectrometer. IR spectra were recorded on a Perkin–Elmer SpectrumOne spectrometer. Elemental analyses were performed on a Vario EL.

Suzuki Coupling Experiment

Synthesis of Bis(hydroxymethyl)diphenylphosphonium Chloride (1)[20]

To diphenylphosphine (5.00 g, 26.85 mmol) were slowly added under Ar formaldehyde solution (35%, 5.0 mL, 66.25 mmol) and concd HCl (2.5 mL), which was slightly exothermic. Upon cooling the warm solution, bis(hydroxymethyl)diphenylphosphonium chloride (**1**) precipitated. The product was recrystallized from MeOH. Product **1** (7.21 g, 25.50 mmol, 95%) was isolated as a colorless crystalline powder.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 4.89 (s, 2 H, OH), 5.15 (s, 4 H, CH_2OH), 7.67–7.95 (m, 10 H, arom).

^{13}C NMR (100.6 MHz, DMSO-d_6): δ = 54.8, 55.4, 117.0, 117.7, 131.1, 131.3, 134.8, 134.9, 136.2, 136.2.

^{31}P NMR (121 MHz, DMSO-d_6): δ = 17.7 (s, 1 P).

Phosphinylation of PC[17]

Before coupling with **2**, the Boc-protecting groups of the amino-functionalized PC were cleaved off. Therefore, the material was suspended in a 5–6-M HCl soln in *i*-PrOH for 30 min and successively washed with *i*-PrOH, MeOH and a solution of Hünig's base in DMF.

For the coupling, the amino-functionalized PC **2** (616 mg) was suspended in water (5 mL) and anhyd MeOH (10 mL), both degassed under Ar. Then bis(hydroxymethyl)diphenylphosphonium chloride (**1**) (452 mg, 1.60 mmol) and Et_3N (209 μL, 151 mg, 1.50 mmol) were added and the mixture was refluxed for 72 h. After cooling, the PC **3** was isolated by filtration under Ar. It was then dried under high vacuum.

PC-Lig (3)

IR (neat): 3645, 3602, 3270, 2923, 1563, 1456, 1366, 1358, 1334, 1258, 1178, 1121, 1089, 1021 cm^{-1}.

Solid-Phase Bound Catalyst for Suzuki Reactions

Bisdiphenylphosphine-modified PC **3** was suspended in anhyd CH_2Cl_2 (10 mL, degassed under Ar). To this suspension, a soln of $Pd(dba)_2$ (35 mg, 60.87 μmol) in anhyd CH_2Cl_2 (5 mL, degassed under Ar) was added dropwise. After shaking for 24 h at r.t., PC **4a** was obtained by filtration under Ar. After drying under high vacuum, a Pd-loading of 11.20 μmol/g was determined by ICP–MS measurements.

4a

IR (neat): 3647, 3602, 3454, 3375, 3299, 3270, 2923, 1784, 1765, 1683, 1573, 1456, 1367, 1348, 1336, 1254, 1176, 1123, 1077, 1034 cm^{-1}.

Recycling Experiment Using 4a; General Procedure

To a soln of aryl halide (0.49 mmol) and aryl boronic acid (0.53 mmol) in DMF (12 mL, degassed under Ar) was added Cs_2CO_3 (0.398 g, 1.22 mmol). The mixture was heated to 120 °C, then **4a** (688 mg, 7.70 μmol, 1.55 mol%) was added. After 2 h, a sample of 1 mL of the reaction mixture was taken with a syringe. After evaporation of the solvent, the residue was dissolved in $CDCl_3$. The conversion was determined by ^{1}H NMR while the reaction was still running. After 6 h, the conversion was determined again in the same fashion. In total, five consecutive runs were performed like this. At the end, **4a** was removed from the product mixture using tweezers.

Scale-Up of the Recycling Experiment

To a soln of *p*-bromoacetophenone (**6a**; 1.00 g, 5.02 mmol) and phenyl boronic acid (**5a**; 5.30 mmol) in DMF (120 mL, degassed under Ar) was added Cs_2CO_3 (4.08 g, 12.52 mmol). The mixture was heated to 120 °C, then **4a** (703 mg, 7.87 μmol, 0.157 mol%) was added. After 24 h, **4a** was taken out of the reaction mixture with tweezers. Then, the solvent was removed under vacuum, and the residue was dissolved in water (50 mL). After extraction with EtOAc (3 × 50 mL) and drying over Na_2SO_4, analytically pure **7a** (980 mg, 5.00 mmol, >98%) was isolated.

4-Phenylacetophenone (7a)[36]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.62 (s, 3 H, COMe), 7.38–7.49 (m, 3 H, arom), 7.60–7.63 (m, 2 H, arom), 7.66–7.69 (m, 2 H, arom), 8.00–8.03 (m, 2 H, arom).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 26.3, 127.2, 127.3, 128.3, 128.9, 129.0, 135.8, 139.8, 145.7, 197.7.

MS (EI, 70 eV): *m*/*z* (%) = 196 (45) [M$^+$], 181 (100), 153 (36), 152 (54), 151 (20), 76 (65).

Suzuki Reaction; General Procedure

To a soln of aryl halide (0.38 mmol) and aryl boronic acid (0.41 mmol) in DMF (10 mL, degassed under Ar) was added Cs_2CO_3 (0.31 g, 0.95 mmol). The mixture was heated to 120 °C, then **4a** (140 mg, 0.41 mol%) was added. After 24 h, the reaction was cooled and the catalyst removed using tweezers. After the solvent was removed under vacuum, the conversion was determined by ^{1}H NMR.

4-Methoxybiphenyl (7b)[37]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.83 (s, 3 H, OMe), 6.95–6.97 (m, 2 H, arom), 7.25–7.40 (m, 2 H, arom), 7.50–7.54 (m, 5 H, arom).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 55.4, 114.2, 126.6, 126.7, 128.2, 128.7, 135.2.

MS (EI, 70 eV): *m*/*z* (%) = 184 (100) [M$^+$], 169 (39), 141 (35), 115 (21), 75 (10).

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4′-Acetylbiphenyl-4-carbonitrile (7c)[38]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.68 (s, 3 H, COMe), 7.70–7.78 (m, 6 H, arom), 8.10 (d, *J* = 8.4 Hz, 2 H, arom).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 27.0, 118.8, 127.6, 128.1, 129.4, 132.9, 133.2, 137.2, 143.8, 144.5, 197.7.

MS (EI, 70 eV): *m*/*z* (%) = 221 (40) [M$^+$], 206 (100), 177 (34), 151 (32).

1-(4′-Acetylbiphenyl-4-yl)ethanone (7d)[39]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.60 (s, 6 H, COMe), 7.90–8.10 (m, 8 H, arom).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.0, 128.4, 129.5, 136.5, 142.1, 197.1.

MS (EI, 70 eV): *m*/*z* (%) = 238 (50) [M$^+$], 223 (100), 152 (20).

1-(4′-Methoxybiphenyl-4-yl)ethanone (7e)[40]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.63 (s, 3 H, COMe), 3.87 (s, 3 H, OMe), 7.00 (d, *J* = 8.5 Hz, 2 H, arom), 7.58 (d, *J* = 8.5 Hz, 2 H, arom), 7.65 (d, *J* = 8.3 Hz, 2 H, arom), 8.01 (d, *J* = 8.3 Hz, 2 H, arom).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 31.4, 55.4, 114.4, 121.7, 126.6, 128.3, 128.9, 136.4, 142.0, 161.2, 197.1.

MS (EI, 70 eV): *m*/*z* (%) = 226 (70) [M$^+$], 211 (100), 183 (15), 168 (20), 152 (15), 139 (25).

Hydroformylation Experiments

Solid-Phase Bound Catalyst for Hydroformylation Reactions

Bisdiphenylphosphine modified PC **3** was suspended in anhyd CH_2Cl_2 (10 mL, degassed under Ar). Then, a soln of $[Rh(cod)_2]BF_4$ (30.04 mg, 70.01 μmol) in anhyd CH_2Cl_2 (5 mL, degassed under Ar) was added dropwise. After shaking for 24 h at r.t., PC **4b** was filtered using a filtration setup under Ar. The PC **4b** was dried under high vacuum to give a PC with a Rh-loading of **4b** of 10.42 μmol/g (determined by ICP–MS measurements).

IR (neat): 3447, 3402, 3394, 3374, 3289, 3268, 2921, 1571, 1466, 1452, 1365, 1345, 1340, 1336, 1330, 1244, 1177, 1121, 1071 cm^{-1}.

Preparation of Phthalimidyl-3-methylbutyraldehyde (9)[26a]

A solution of methallylphthalimide (**8**; 250 mg, 1.24 mmol) in anhyd toluene (10 mL) and **4b** (150 mg, 0.41 mol%) was placed in an autoclave. The autoclave was pressurized with 100 bar CO–H_2 (1:1) and heated to 100 °C for 2 d. After cooling, **4b** was removed using tweezers. The solvent was removed in a rotary evaporator to give pure **9** (286 mg, 1.24 mmol, > 98%) as a colorless wax.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.01 (d, *J* = 6.8 Hz, 3 H, Me), 2.21–2.66 (m, 3 H, NCH_2CHR_2), 3.58–3.65 (m, 2 H, C*H*$_2$CHO), 7.68–7.88 (m, 4 H, arom), 9.72 (s, 1 H, CHO).

^{13}C NMR (125.7 MHz, $CDCl_3$): δ = 17.8, 30.0, 43.3, 48.5, 123.3, 131.9, 134.0, 168.6, 201.2.

Olefin Metathesis Experiments

5-Bromo-2-isopropoxybenzaldehyde (13)

To a solution of 5-bromo-2-hydroxybenzaldehyde (**12**; 10.22 g, 50.84 mmol) in DMF (150 mL) were added K_2CO_3 (13.88 g, 100.4 mmol) and Cs_2CO_3 (3.27 g, 10.0 mmol). To the resulting yellow suspension was added dropwise 2-iodopropane (15.0 mL, 25.5 g, 150 mmol). After stirring for 24 h at r.t., the reaction mixture was poured into H_2O (500 mL) and extracted with Et_2O (4 × 100 mL). The combined organic fractions were washed with H_2O (5 × 200 mL) and dried over $MgSO_4$. The product **13** (11.87 g, 48.83 mmol, 96%) was isolated as a yellow solid; mp 31–33 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40 [d, *J* = 6.0 Hz, 6 H, CH(C*H*$_3$)$_2$], 4.65 [septet, *J* = 6.0 Hz, 1 H, C*H*(CH$_3$)$_2$], 6.89 (d, *J* = 8.9 Hz, 1 H, H-3), 7.59 (dd, *J* = 2.6, 8.9 Hz, 1 H, H-4), 7.91 (d, *J* = 2.6 Hz, 1 H, H-6), 10.39 (s, 1 H, CHO).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.0, 71.8, 113.3, 116.1, 127.2, 131.1, 138.2, 159.5, 188.7.

MS (EI, 70 eV): *m*/*z* (%) = 244 (12), 242 (12) [M$^+$], 202 (85), 201 (64), 200 (100), 199 (64), 184 (14), 182 (11), 145 (13), 143 (13), 63 (20), 43 (17).

Anal. Calcd for $C_{10}H_{11}BrO_2$: C, 49.41; H, 4.56. Found: C, 49.23; H, 4.63.

(*E*)-3-(3-Formyl-4-isopropoxyphenyl)ethyl Acrylate (14)

To a suspension of $Pd(OAc)_2$ (0.35 g, 2.36 mmol, 5 mol%) and P(*o*-Tol)$_3$ (2.96 g, 9.73 mmol) in anhyd DMF (150 mL) were added anhyd Et_3N (13.6 mL, 9.87 g, 97.5 mmol), aldehyde **13** (11.83 g, 48.66 mmol) and ethyl acrylate (6.40 mL, 5.89 g, 58.9 mmol). The reaction mixture was heated for 5 h at 100 °C (oil bath). After cooling to r.t., the mixture was poured into H_2O (1.2 L) and extracted with Et_2O (10 × 100 mL). The combined organic fractions were washed with sat. NH_4Cl soln (300 mL) and dried over $MgSO_4$. After purification by flash column chromatography (cyclohexane–EtOAc, 50:1 → 5:1) the product (11.3 g, 43.1 mmol, 89%) was obtained as a yellow solid; mp 56–59 °C; R_f 0.32 (cyclohexane–EtOAc, 5:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.1 Hz, 3 H, OCH$_2$C*H*$_3$), 1.43 [d, *J* = 6.0 Hz, 6 H, CH(C*H*$_3$)$_2$], 4.26 (q, *J* = 7.1 Hz, 2 H, OC*H*$_2$CH$_3$), 4.74 [septet, *J* = 6.1 Hz, 1 H, C*H*(CH$_3$)$_2$], 6.38 (d, *J* = 16.0 Hz, 1 H, ArCH=C*H*COOEt), 7.01 (d, *J* = 8.8 Hz, 1 H, arom), 7.63 (d, *J* = 16.1 Hz, 1 H, ArC*H*=CHCOOEt), 7.68 (dd, *J* = 2.3, 8.8 Hz, 1 H, arom), 8.00 (d, *J* = 2.5 Hz, 1 H, arom), 10.47 (s, 1 H, CHO).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.4, 22.0, 60.5, 71.6, 114.2, 117.6, 125.7, 127.0, 128.2, 135.1, 143.0, 161.8, 167.0, 189.5.

MS (EI, 70 eV): *m*/*z* (%) = 262 (21) [M$^+$], 220 (100), 192 (51), 191 (14), 175 (85), 148 (47), 146 (28).

Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.68; H, 6.92. Found: C, 68.60; H, 7.11.

(*E*)-3-(4-Isopropoxy-3-vinylphenyl)ethyl Acrylate (15)

Methyltriphenylphosphonium bromide (18.6 g, 52.1 mmol) was suspended in anhyd THF (250 mL) and cooled to 0 °C. Under ice-cooling, BuLi (1.6 M in hexane; 32.3 mL, 51.7 mmol) was added dropwise over 50 min and the mixture was stirred for further 30 min at 0 °C. In the meantime, a soln of aldehyde **16** (11.3 g, 43.1 mmol) in anhyd THF (50 mL) was prepared and also cooled to 0 °C. After adding the ylide to the aldehyde soln via transfer needle, the reaction mixture was stirred overnight at r.t. Then, the solvent was removed in vacuo and the residue was taken up in Et_2O (200 mL). The precipitate was separated, and the filtrate was washed with sat. brine (150 mL). After drying over $MgSO_4$ the product was purified by column chromatography (cyclohexane–EtOAc, 20:1). A pale yellow-colored solid (8.09 g, 31.1 mmol, 72%) was obtained; mp 46–48 °C; R_f 0.59 (cyclohexane–EtOAc, 5:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.33 (t, *J* = 7.2 Hz, 3 H, CH$_2$C*H*$_3$; signal partially superimposed by the doublet of the isopropoxy group), 1.37 [d, *J* = 6.2 Hz, 6 H, CH(C*H*$_3$)$_2$], 4.26 (q, *J* = 7.1 Hz, 2 H, C*H*$_2$CH$_3$), 4.60 [sept, *J* = 6.1 Hz, 1 H, C*H*(CH$_3$)$_2$], 5.28 (dd, *J* = 1.3, 11.1 Hz, 1 H, CH=C*H*H), 5.76 (dd, *J* = 17.7 Hz, 1.3 Hz, 1 H, CH=CH*H*), 6.33 (d, *J* = 16.0 Hz, 1 H, ArCH=C*H*COOEt), 6.87 (d, *J* = 8.6 Hz, 1 H, arom), 7.02 (dd, *J* = 11.2, 17.8 Hz, 1 H, C*H*=CH$_2$), 7.38 (dd, *J* = 2.2, 8.6 Hz, 1 H, arom), 7.64 (d, *J* = 16.0 Hz, 1 H, ArC*H*=CHCOOEt; this doublet surrounds the following doublet), 7.64 (d, *J* = 2.2 Hz, 1 H, arom).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.4, 22.2, 60.4, 71.0, 113.7, 115.0, 116.0, 126.7, 126.9, 128.2, 128.9, 131.6, 144.5, 157.1, 167.4.

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MS (EI, 70 eV): *m*/*z* (%) = 260 (57) [M$^+$], 218 (100), 190 (25), 173 (72), 146 (69), 145 (22), 127 (15), 115(31), 57 (24), 43 (34).

Anal. Calcd for $C_{16}H_{20}O_3$: C, 73.82; H, 7.74. Found: C, 73.83; H, 7.88.

(*E*)-3-(4-Isopropoxy-3-vinylphenyl)acrylic Acid (16)

The cinnamate derivative **15** (8.09 g, 31.1 mmol) was dissolved in 1,4-dioxane (220 mL) and an aq 1 M KOH–solution (220 mL) was added slowly at r.t. After stirring for 24 h at r.t., the mixture was acidified with 2 M HCl (120 mL) until the precipitation of the product was complete. The precipitate was filtered and washed with cold H_2O (10 mL). After treatment with MeCN, the pure **16** (6.64 g, 28.6 mmol, 92%) was obtained as a colorless solid; mp 124–128 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.38 [d, *J* = 6.0 Hz, 6 H, CH(C*H*$_3$)$_2$], 4.62 [septet, *J* = 6.1 Hz, 1 H, C*H*(CH$_3$)$_2$], 5.30 (dd, *J* = 1.2, 11.3 Hz, 1 H, CH=C*H*H), 5.78 (dd, *J* = 1.2, 17.7 Hz, 1 H, CH=CH*H*), 6.34 (d, *J* = 16.0 Hz, 1 H, ArCH=C*H*COOH), 6.88 (d, *J* = 8.6 Hz, 1 H, arom), 7.02 (dd, *J* = 11.1, 17.9 Hz, 1 H C*H*=CH$_2$), 7.42 (dd, *J* = 2.1, 8.6 Hz, 1 H, arom), 7.67 (d, *J* = 2.1 Hz, 1 H, arom), 7.75 (d, *J* = 16.0 Hz, 1 H, ArC*H*=CHCOOH).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.2, 71.0, 113.7, 114.9, 115.2, 126.5, 127.1, 128.3, 129.3, 131.5, 147.0, 157.5, 172.8.

MS (EI, 70 eV): *m*/*z* (%) = 251 (13) [M$^+$], 236 (10), 222 (20), 186 (13), 155 (77), 96 (63), 91 (100), 84 (29), 41 (31).

Anal. Calcd for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.10; H 6.92.

(*E*)-3-(4-Isopropoxy-3-vinylphenyl)acrylic Acid 16 Coupled to Solid Support

Before the coupling with **16**, the Boc-protecting group of the amino-functionalized polymer was cleaved off. Therefore, the material was suspended in a 5–6 M HCl solution in *i*-PrOH for 30 min, and successively washed with *i*-PrOH, MeOH and a soln of Hünig's base in DMF.

For the coupling, HOBt (0.27 g, 2.00 mmol) and **16** (0.46 g, 1.99 mmol) were dissolved in DMF (40 mL). To this solution DCC (0.41 g, 1.99 mmol) and Hünig's base (0.68 mL, 0.52 g, 4.03 mmol) were added. After 10 min, the coupling mixture was added to the solid phase (9.80 g, 127–137 μmol) suspended in fresh DMF and the flask was shaken at r.t. When the TNBS test for amino groups was negative, the solid phase was removed from the reaction and washed consecutively with DMF, H_2O, DMF, and CH_2Cl_2. Next, the solid phase was suspended in CH_2Cl_2. A solution of Et_3N (0.62 mL, 0.45 g, 4.45 mmol) and DMAP (48 mg, 390 μmol) in CH_2Cl_2 (4 mL) was added, followed by a solution of Ac_2O (0.37 mL, 0.40 g, 3.92 mmol) in CH_2Cl_2 (2 mL), and the reaction mixture was shaken at r.t. for 4 h. Finally, the solid phase was washed with CH_2Cl_2, DMF, H_2O, DMF, CH_2Cl_2, and Et_2O and dried in a desiccator.

PE-Lig

IR (neat): 3978, 3903, 3647, 3606, 3370, 2919, 2662, 2529, 2417, 2327, 2019, 1897, 1820, 1663, 1470, 1368, 1353, 1306, 1260, 1176, 1117, 1083, 1019, 799, 731, 719, 540 cm^{-1}.

PP-Lig

IR (neat): 3300, 3071, 2923, 2839, 2723, 2582, 2123, 1658, 1622, 1600, 1548, 1491, 1456, 1377, 1359, 1304, 1253, 1168, 1116, 998, 974, 956, 900, 857, 841, 811, 752, 704, 653, 607, 531, 459 cm^{-1}.

Solid-Phase-Bound Catalyst for Metathesis Reactions (18a,b; 19a,b)

The solid phase **2** was suspended in anhyd CH_2Cl_2 under Ar. Grubbs catalyst **10a** or **10b** (1.3 equiv) and CuCl (1.3 equiv) were added and the reaction was heated to reflux for 4 h. After cooling to r.t., the solid phase was removed from the reaction mixture, washed with CH_2Cl_2, and dried in a desiccator.

The loading of Ru was determined by ICP–MS.

18a

Ru loading: 7.8 μmol/g.

IR (neat): 3979, 3915, 3647, 3606, 3373, 2940, 2662, 2529, 2417, 2327, 2151, 2019, 1897, 1820, 1661, 1468, 1368, 1353, 1306, 1253, 1176, 1103, 1080, 925, 852, 731, 719, 518, 480 cm^{-1}.

18b

Ru loading: 4.5 μmol/g.

IR (neat): 3979, 3915, 3647, 3606, 3372, 2874, 2662, 2528, 2417, 2327, 2150, 2019, 1897, 1820, 1660, 1623, 1465, 1368, 1353, 1305, 1256, 1176, 1106, 982, 956, 854, 721, 580, 469 cm^{-1}.

19a

Ru loading: 210 μmol/g.

IR (neat): 3334, 3061, 2922, 2839, 2723, 2582, 1943, 1735, 1660, 1539, 1489, 1455, 1377, 1359, 1304, 1250, 1168, 1103, 998, 974, 926, 899, 851, 842, 812, 746, 727, 703, 649, 623, 565, 518, 479 cm^{-1}.

19b

Ru loading: 134 μmol/g.

IR (neat): 3314, 3061, 2920, 2839, 2723, 2582, 1948, 1730, 1658, 1623, 1600, 1544, 1489, 1456, 1377, 1359, 1303, 1255, 1168, 1113, 998, 974, 956, 927, 900, 855, 841, 811, 750, 704, 647, 580, 460 cm^{-1}.

Recycling Experiment Using 20; General Procedure

For each catalyst, five flasks filled with 1 mL of a 0.05-M stock soln of **20** in CH_2Cl_2 were prepared. The catalyst was added to the first flask and shaken for 90 min at 60 °C oil bath. Then, 20 μL of the reaction mixture were taken to determine the conversion by HPLC. The piece of catalyst was removed from the reaction using tweezers, washed with CH_2Cl_2 (2 mL) and the next run was started. In total, five consecutive runs were performed like this.

Ring-Closing Metathesis; General Procedure

To a stock soln of the α,ω-olefin (160 μL, 50 μmol, 0.3 M in CH_2Cl_2) were added CH_2Cl_2 (850 μL) and the catalyst (1.0 mol%, 0.5 mol). The reaction mixture was heated to reflux (60 °C oil bath) and shaken for 90 min. Then, the catalyst was removed with tweezers and the reaction mixture was quenched with 0.001 M ethyl vinyl ether (0.1 mL) in CH_2Cl_2. The solvent was removed in vacuo and the conversion was determined by ^{1}H NMR.

1-(Toluene-4-sulfonyl)-2,5-dihydro-1*H*-pyrrole[41] (21)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.42 (s, 3 H, ArCH$_3$), 4.12 (s, 4 H, C*H*$_2$CH=CHC*H*$_2$), 5.65 (s, 2 H, CH$_2$C*H*=C*H*CH$_2$), 7.32 (m$_{AA'BB'}$, J_{app} = 8.1 Hz, 2 H, arom), 7.72 (m$_{AA'BB'}$, J_{app} = 8.1 Hz, 2 H, arom).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.6, 54.9, 125.5, 127.5, 129.8, 134.4, 143.5.

MS (EI, 70 eV): *m*/*z* (%) = 223 (50) [M$^+$], 155 (52), 91 (92), 86 (13), 84 (20), 68 (100), 65 (24), 41 (24).

1-(Toluene-4-sulfonyl)-2,3,4,7-tetrahydro-1*H*-azepine[42] (23)

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.80 (m$_c$, 2 H), 2.18 (m$_c$, 2 H), 2.41 (s, 3 H, CH$_3$Ar), 3.39 (t, *J* = 6.1 Hz, 2 H, NC*H*$_2$CH$_2$), 3.83 (d, *J* = 4.5 Hz, 2 H, NC*H*$_2$CH=CH), 5.64 (dt, *J* = 5.1, 10.6 Hz, 1 H, H-2, H-3), 5.77 (dt, *J* = 5.3, 10.9 Hz, 1 H, H-2, H-3), 7.28 (m$_{AA'BB'}$, J_{app} = 8.2 Hz, 2 H, arom), 7.68 (m$_{AA'BB'}$, J_{app} = 8.1 Hz, 2 H, arom).

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^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 21.5, 26.9, 31.0, 46.4, 49.7, 126.7, 127.3, 129.6, 133.0, 136.5, 143.1.

MS (EI, 70 eV): *m*/*z* (%) = 251 (100) [M$^+$], 236 (7), 184 (85), 155 (40), 96 (87), 91 (37), 69 (35), 67 (30), 41 (24).

1-(Toluene-4-sulfonyl)-1,2,3,4,5,8-hexahydroazocine[42] (25)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50–1.61 (m, 2 H, CH_2), 1.63–1.72 (m, 2 H, CH_2), 2.35–2.41 (m, 2 H, 5-CH_2), 2.42 (s, 3 H, CH_3), 3.29 (t, *J* = 5.4 Hz, 2 H, 8-CH_2), 3.81 (d, *J* = 5.8 Hz, 2 H, 2-CH_2), 5.40 (dt, *J* = 5.6, 11.2 Hz, 1 H, NCH_2CH=CH), 5.78 (dt, *J* = 8.5, 11.1 Hz, 1 H, NCH_2CH=C*H*), 7.29 ($m_{AA'BB'}$, J_{app} = 7.9 Hz, 2 H, arom), 7.67 ($m_{AA'BB'}$, J_{app} = 7.9 Hz, 2 H, arom).

MS (EI, 70 eV): *m*/*z* (%) = 265 (17) [M$^+$], 250 (8), 224 (38), 184 (100), 155 (99), 138 (29), 110 (38), 91 (66), 82 (11), 79 (17), 68 (10).

(Cyclopent-2-enyloxymethyl)benzene[43] (27)
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.82–1.89 (m, 1 H, H_A-4′, H_B-4′), 2.12–2.19 (m, 1 H, H_A-4′, H_B-4′), 2.23–2.30 (m, 1 H, H_A-5′, H_B-5′), 2.47–2.55 (m, 1 H, H_A-5′, H_B-5′), 4.51 (d, J_{AB} = 11.7 Hz, 1 H, HC*H*Ar), 4.55 (d, J_{AB} = 11.7 Hz, 1 H, *H*CHAr), 4.67 (m_c, 1 H, CHOR), 5.88–5.91 (m, 1 H, H-3′), 6.01–6.04 (m, 1 H, H-2′), 7.24–7.37 (m, 5 H, arom).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 29.8, 31.1, 70.6, 84.5, 127.4, 127.8, 128.3, 130.8, 135.7, 138.9.

MS (CI, NH_3, 130 eV): *m*/*z* (%) = 192 (12) [M + NH_4]$^+$, 175 (4) [M + H]$^+$, 157 (10), 126 (21), 108 (17), 91 (36), 84 (100), 67 (7).

(Cyclohex-2-enyloxymethyl)benzene[44] (29)
^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.51–1.59 (m, 1 H), 1.71–1.89 (m, 3 H), 1.91–1.99 (m, 1 H), 2.02–2.10 (m, 1 H), 3.93–3.98 (br m, 1 H, H-1), 4.55 ($d_{AA'}$, *J* = 12.0 Hz, 1 H, C*H*HO), 4.61 ($d_{AA'}$, *J* = 12.0 Hz, 1 H, CH*H*O), 5.79–5.89 (m, 2 H, H-2, H-3), 7.24–7.37 (m, 5 H, arom).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 19.3, 25.3, 28.4, 70.0, 72.2, 127.4, 127.6, 127.8, 128.3, 130.9, 139.1.

MS (EI, 70 eV): *m*/*z* (%) = 188 (5) [M$^+$], 130 (9), 97 (48), 91 (100), 84 (8), 81 (13), 79 (13), 77 (7), 69 (22), 65 (11), 55 (10), 41 (15).

2-Phenyl-3,6-dihydro-2*H*-pyran[45] (31)
^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.20–2.44 (m, 2 H), 4.33–4.39 (m, 2 H), 4.56 (dd, *J* = 3.8, 10.0 Hz, 1 H, OCHAr), 5.77–5.85 (m, 1 H), 5.88–5.96 (m, 1 H), 7.25–7.41 (m, 5 H, arom).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 32.9, 66.6, 75.7, 124.5, 125.9, 126.4, 127.5, 128.4, 142.6.

MS (EI, 70 eV): *m*/*z* (%) = 160 (16) [M$^+$], 105 (100), 77 (18), 54 (75).

Cyclopent-3-ene-1,1-dicarboxylic Acid Diethyl Ester[46] (33)
^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, *J* = 7.1 Hz, 6 H, 2 × CH_2CH_3), 3.01 (s, 4 H, CH_2CH=$CHCH_2$), 4.20 (q, *J* = 7.1 Hz, 4 H, 2 × CH_2CH_3), 5.61 (s, 2 H, CH_2CH=$CHCH_2$).

^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 14.0, 40.9, 58.9, 61.2, 127.8, 172.3.

MS (EI, 70 eV): *m*/*z* (%) = 212 (63) [M$^+$], 166 (60), 138 (100), 111 (38), 93 (32), 79 (40), 66 (54).

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