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Dirhodiumtetracarboxylate Beads

Bottom-Up Synthesis of Acrylic and Styrylic Rh^{II} Carboxylate Polymer Beads: Solid-Supported Analogs of $Rh_2(OAc)_4$

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Abstract: We have developed a short and efficient bottom-up synthesis of acrylic and styrylic polymer beads containing dirhodium(II) tetracarboxylates. The solid supported dirhodium(II) tetracarboxylate catalysts were synthesized in as little as two steps overall from dirhodium tetratrifluoroacetate and commercially available carboxylic acids, making the bottom-up approach a viable alternative to the post-modification approach commonly used. The dirhodium(II) tetracarboxylate polymer beads have a convenient size (ca. 100 µm), are easy to handle, and can be considered solid-supported analogs of $Rh_2(OAc)_4$. Beads generated from dirhodium(II) tetracarboxylates with four polymerizable carboxylate ligands displayed the best catalytic performance and compared favorably to $Rh_2(OAc)_4$ in benchmarked cyclopropanation reactions. The results imply that the cumbersome synthesis of monomeric dirhodium(II) tetracarboxylates with mixed ligands systems can be avoided and that immobilized dirhodium(II)-catalysts with a higher degree of cross-linking is a viable option to catalysts linked in an anchor-like fashion. We demonstrate recovery and recycling, and a potential use of the beads as catalysts in a cyclopropanation reaction towards the insecticide chrysanthemic acid.

Introduction

The development of novel synthetic methodology based on transient Rh-carbenes can be traced back to work published by Teyssie and co-workers in the beginning of the 1970s.[1] Two of their key findings were the unusually high kinetic activity of $Rh_2(OAc)_4$ in reactions with ethyl diazoacetate (EDA) and the highly efficient insertion of the transient Rh-carbenes into O–H bonds. Ever since then, the development and use of dirhodium(II) tetracarboxylates as catalysts for the generation of rhodium-carbenes from diazo compounds have gained an enormous momentum in organic chemistry. Due to the unique properties of Rh-carbenes to undergo C-H insertion reactions, they play a vital role in the field of C-H functionalization.[2] Transient Rh-carbenes are also versatile intermediates in other state-of-the-art organic reactions as they can for example partake in cyclopropanations, cyclopropenation, [4+3] cycloadditions, insertion reactions (X-H, X = Si, O, N, S) and ylide formations.[3] Characteristic traits in many of these transformations are exceptionally high turnover-numbers and -frequencies in addition to high levels of chemo-, regio-, diastereo- and enantioselectivity. Rhodium is an expensive and precious metal, and consequently solid-supported dirhodium(II) catalysts to facilitate catalyst recovery and recycling have received increasing attention over the last two decades.[4] There are two general strategies available for making solid-supported catalysts: A post-modification approach and a bottom-up approach.[5] In the post-modifications approach, the catalysts of choice are grafted onto a premade resin after the macromolecular synthesis. The primary function of the premade resin is to work as an inert scaffold after anchoring of the catalyst. In the bottom-up approach, the catalysts are introduced as a part of the macromolecular synthesis. The immobilization of the catalysts is modular at the monomeric rather at the polymeric level and usually consists of some sort of copolymerization. The majority of reports on solid-supported dirhodium(II) tetracarboxylates fall into the post-modification category, and they have been immobilized in two ways: 1. By covalent grafting onto silica,[6,7] polymeric hollow fibers[8] and Merrifield resins.[9] 2. By encapsulation and axial coordination to various pyridine-containing resins.[10–13] The only examples of beads containing dirhodium(II) catalysts using a bottom-up approach have been reported by Hashimoto's group.[14,15] They introduced one polymerizable carboxylate ligand into well-known chiral catalyst and performed suspension polymerizations to make heterogeneous polymer beads, which performed very well in asymmetric benchmark reactions.

The post-modification approach using encapsulation and axial coordination to pyridine-containing resins is highly attractive due to its simplicity and generality, but unfortunately leaching is an inevitable drawback. Most other reports towards heterogeneous catalysts with covalently immobilized dirhodium(II) tetracarboxylates have some features in common. They are almost all chiral catalysts and they are linked to the inert scaffold in an "anchor-like" fashion where only one of the four carboxylate ligands is connected to the heterogeneous network. Both the post modification and the bottom-up strategy usually require

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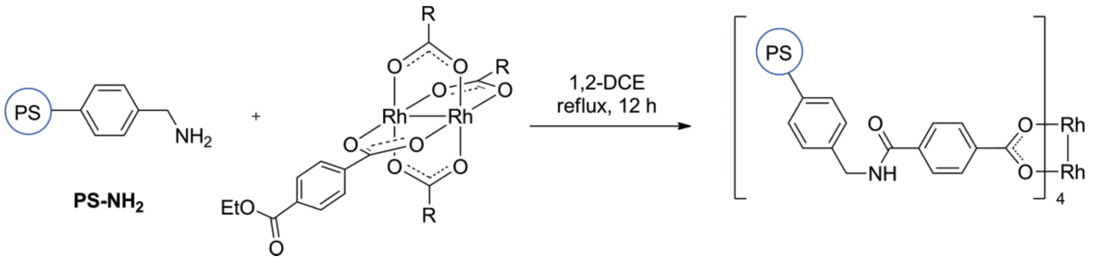


Scheme 1. Immobilization of a dirhodium(II) tetracarboxylate using a post modification approach.[17]

some sort of modification of the original chiral catalyst and/or the premade resin in order for the immobilization to take place.

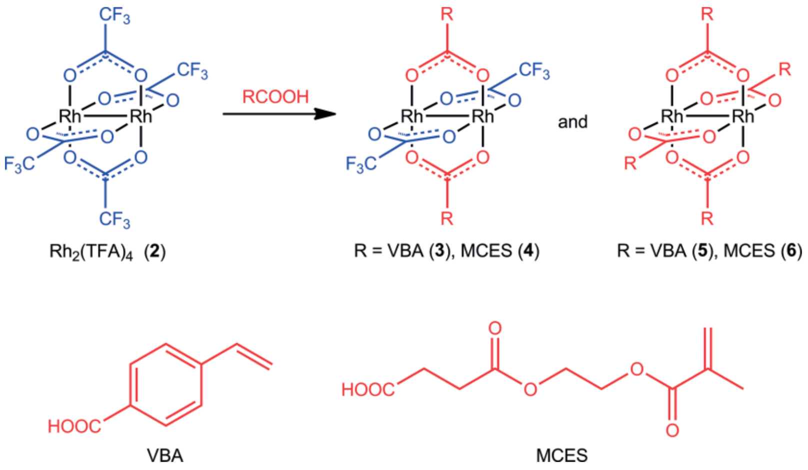
Even though many new chiral dirhodium(II) catalysts have been synthesized over the last 40 years, the generic achiral catalyst of choice is still $Rh_2(OAc)_4$. The development of solid-supported, achiral analogs of $Rh_2(OAc)_4$ has received very little attention compared to the chiral catalysts. There are several examples of dirhodium(II) tetracarboxylate catalysts where recovery and recycling is facilitated by liquid–liquid extraction.[16] However, the only examples of solid-supported achiral dirhodium(II) tetracarboxylates in the shape of beads, are a Merrifield resin[9] and benzylamine functionalized polystyrene(PS)-supported catalyst (Scheme 1).[17]

The approach falls into the post-modification category and has the advantage of being simple and straightforward. Major drawbacks of the post modification approach are the limited availability of polymer supports and the lack of flexibility concerning their properties such as porosity, swelling, and degree of cross-linking.

There are often significant differences in catalytic performance when comparing immobilized, heterogeneous catalysts prepared by a bottom-up approach relative to the post-modification approach.[18] The bottom-up approach is an unexplored method for the synthesis of beads containing achiral dirhodium(II) tetracarboxylate catalysts. We have previous experience with bottom-up immobilization of organocatalysts[19,20] and we envisioned that our methods for making heterogeneous organocatalysts could be applied to immobilization of dirhodium(II)-catalysts, to make dirhodium(II) tetracarboxylate beads with catalytic activity comparable to $Rh_2(OAc)_4$ (**1**). Rather than using only one of the four carboxylate ligands as a link to the solid support (standard anchor-like fashion), we wanted to explore the effect of using two and four attachment points to the solid support. This increased number of attachment points could possibly increase the stability, and affect turnover-numbers and the lifetime of the catalysts. We also wanted to explore the effect of an acrylic-based polymer network (relative to the standard styrenic network commonly used), since the presence of esters are compatible with the mild reaction conditions that apply to many Rh-carbene reactions.

Results and Discussion

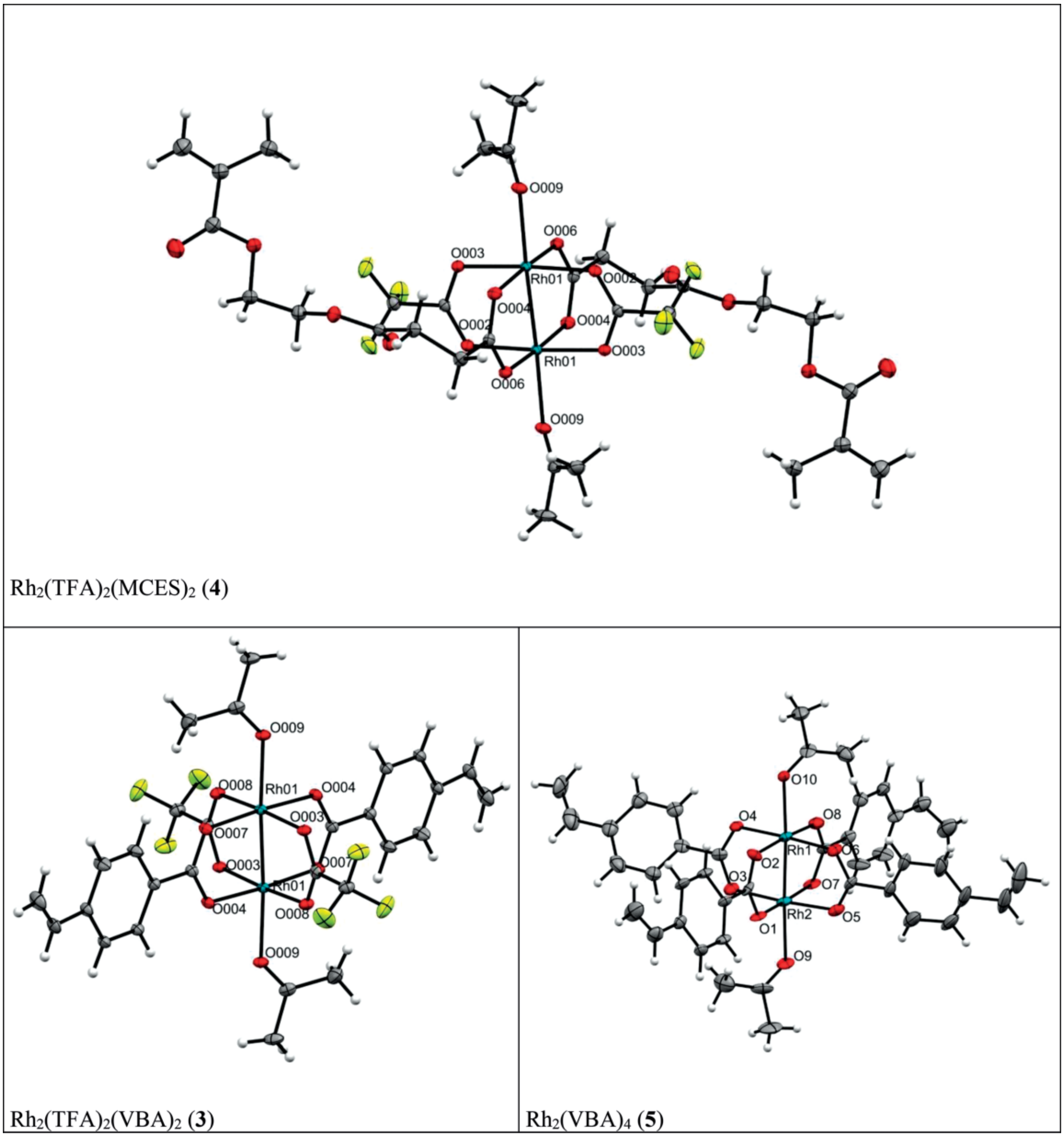
At the outset of the project we needed fast and easy access to dirhodium(II) tetracarboxylate monomers with the desired characteristics. We elected commercially available dirhodium(II) tetratrifluoroacetate [$Rh_2(TFA)_4$, **2**] as a starting material for two reasons. Stepwise replacements of the trifluoroacetate (TFA) ligands allow for a controlled ligand exchange with respect to the number of TFA-ligands and the *cis/trans* relationship of the ligands.[21] The ligand exchange reactions to replace TFA with the desired carboxylates take place under very mild conditions and are compatible with acrylates without decomposition. We synthesized four polymerizable dirhodium(II) carboxylate monomers in a controlled manner from **2** and commercially available 4-vinyl benzoic acid (VBA) or mono-2-(methacryloyloxy) ethyl succinate (MCES) as shown in Scheme 2.



Scheme 2. Synthesis of dirhodium(II) tetracarboxylate monomers **3**–**6** from $Rh_2(TFA)_4$.

Careful ligand exchange reactions with VBA or MCES replaced two of the four TFA-ligands in **2** and gave $Rh_2(TFA)_2(VBA)_2$ (**3**) and $Rh_2(TFA)_2(MCES)_2$ (**4**) in 57 % and 45 % yield, respectively. All four TFA-ligands in **2** were replaced with either VBA or MCES after applying slightly more forcing conditions. We obtained $Rh_2(VBA)_4$ (**5**) in 73 % yield and $Rh_2(MCES)_4$ (**6**) in 62 % yield. The molecular structures of **3**, **4**, and **5** were determined by single-crystal X-ray diffraction analyses (see Supporting Information for full details). The dirhodium species contained axially coordinated acetone molecules from the crystallization solvent (Figure 1).

Table 1 contains bond lengths for the first coordination shell of rhodium for **3**, **4**, and **5**, and for $Rh_2(TFA)_4$ for comparison. The geometrical features are as expected for such dinuclear dirhodium paddlewheel structures, and the Rh–Rh and Rh–O bond lengths are rather nonexceptional.[22]



$Rh_2(TFA)_2(MCES)_2$ (**4**)

$Rh_2(TFA)_2(VBA)_2$ (**3**)

$Rh_2(VBA)_4$ (**5**)

Figure 1. ORTEP plots of dirhodium(II) tetracarboxylates **3**–**5** with 50 % ellipsoids. Each molecule contains two axially coordinated acetone molecules from the crystallization solvent.

Table 1. Selected bond lengths [Å] in dirhodium tetracarboxylates **3**–**5**.

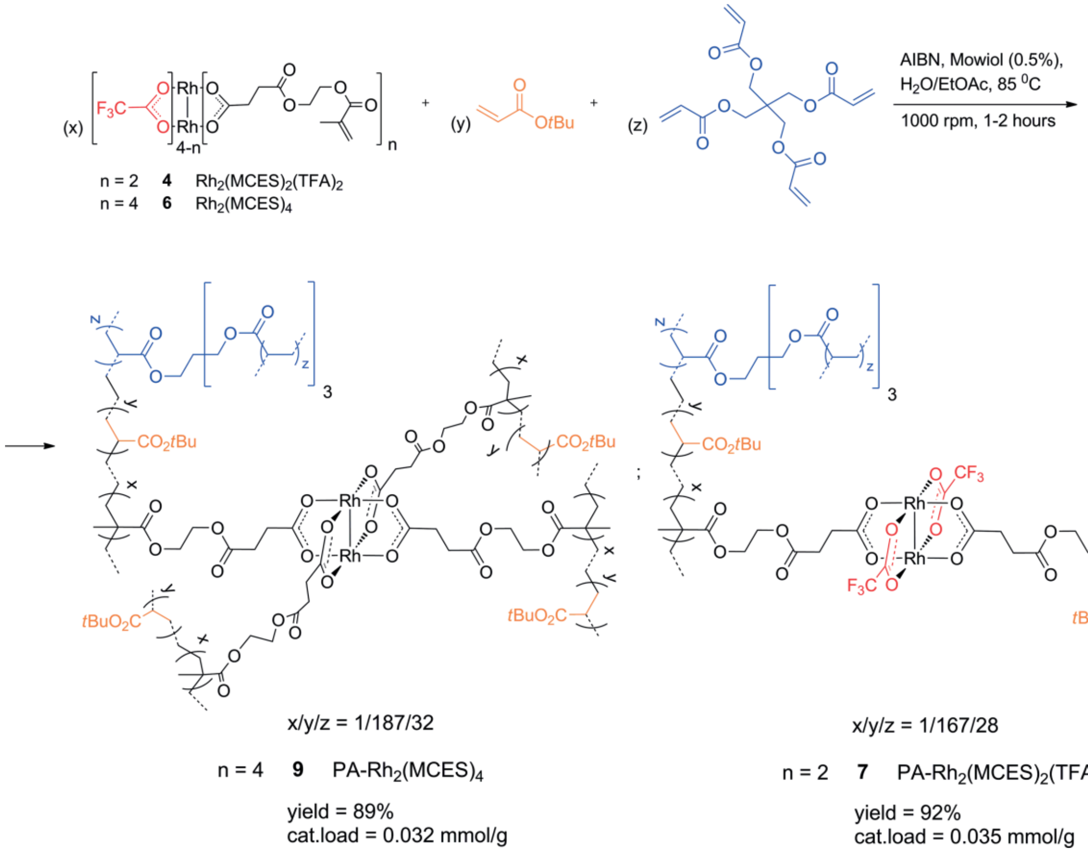
Compd.	Rh–Rh	Rh–O_{TFA}	Rh–O_{RCOO}	Rh–O_{OCMe2}
(**3**) $Rh_2(TFA)_2(VBA)_2$•$2Me_2CO$	2.3976(2)	2.041(1), 2.043(1)	2.028(2), 2.031(2)	2.260(1)
(**4**) $Rh_2(TFA)_2(MCES)_2$•$2Me_2CO$	2.3987(3)	2.035(1), 2.045(1)	2.035(1), 2.036(1)	2.2829(9)
(**5**) $Rh_2(VBA)_4$•$2Me_2CO$	2.381(1)	n.a.	2.005(7)–2.055(8) (2.027 ave.)	2.281(8), 2.293(8)
$Rh_2(TFA)_4$•$2Me_2CO$[a]	2.4060(27)	1.957(15)–2.061(13) (2.008 ave.)	n.a.	2.240(15)

[a] Data obtained from ref.[23]

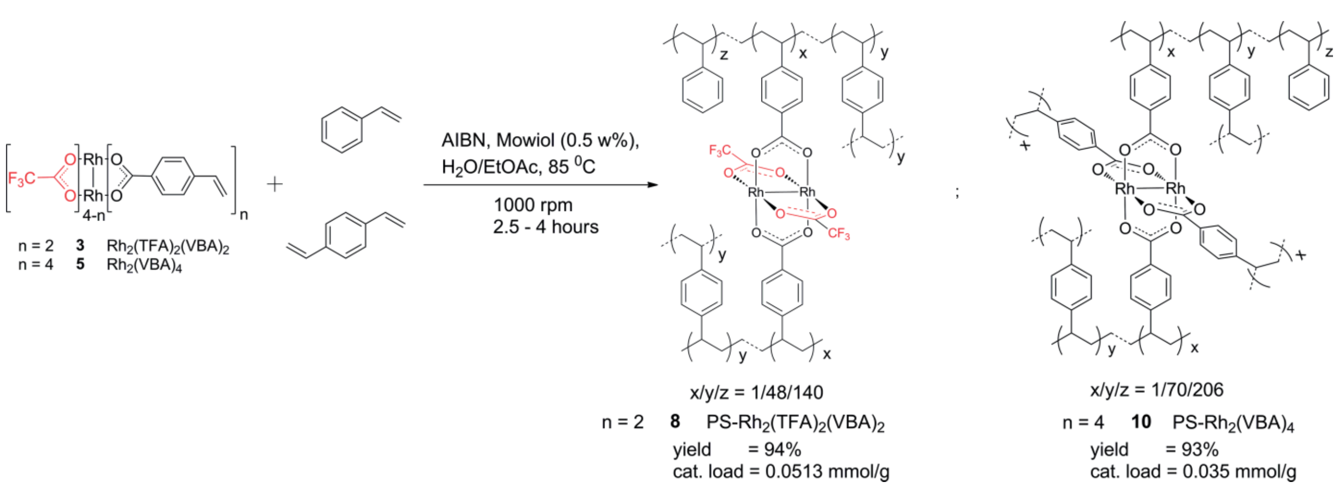
With the four monomers **3**–**6** in hand, we synthesized four dirhodium(II) carboxylate polymer systems, differing with respect to the nature of the polymer network [polyacrylate (PA) or polystyrene (PS)] and the number of attachment points (two or four) from the dirhodium(II) catalyst to the polymer network. The two PA-systems were made from either **4** (two polymerizable ligands) or **6** (four polymerizable ligands) and the monomers *tert*-butyl acrylate and pentaerythritol tetraacrylate using the suspension polymerization conditions displayed in Scheme 3.

Similarly, the two PS-systems were made from either **3** (two polymerizable ligands) or **5** (four polymerizable ligands) with the monomers styrene and divinyl benzene. The dirhodium(II) tetracarboxylate beads were synthesized in a bottom-up fashion using the suspension polymerization conditions shown in Scheme 4.

The suspension polymerization resulted in two types of beads with mixed ligands systems: PA-$Rh_2(TFA)_2(MCES)_2$ (**7**) and PS-$Rh_2(TFA)_2(VBA)_2$ (**8**) in 92 and 94 % yield, respectively. The beads with mono ligand systems, PA-$Rh_2(MCES)_4$ (**9**) and



Scheme 3. Synthesis of PA-beads **7** and **9** using bottom-up immobilization of monomers **4** and **6**.

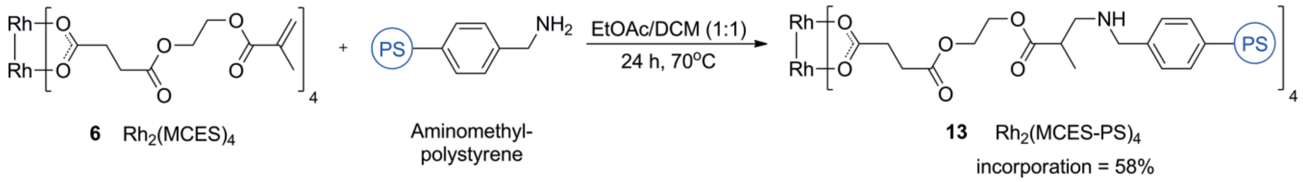


Scheme 4. Synthesis of PS-beads **8** and **10** using bottom-up immobilization of monomers **3** and **5**.

PS-$Rh_2(VBA)_4$ (**10**), were isolated in similarly high yields (89 % and 93 %, respectively). The glass-like polymer beads are easy to handle, and microscopy pictures of the beads (see SI) show a perfect spherical shape and average diameter of 100 µm. The beads were analyzed and characterized by microscopy, SEM-EDX, TEM-analysis and surface area measurements (see SI for details). The BET absorption and SEM analysis of beads **7**–**10** indicated absence of porosity or inner cavities in the dry state. Since the beads did not swell after soaking in organic solvents, there is probably no or a negligible degree of solvent-penetration in the polymer network. In order to increase the porosity of the polymer network and to give access of solvent molecules and reactants to the inner part of the beads, we performed a second iteration of polymerization reactions with monomers **5** and **6**. The reactions were executed according Scheme 3 and Scheme 4, but the degree of crosslinking was significantly reduced and a mixed PA-PS polymer network was generated from the monomers styrene and pentaerythritol tetraacrylate. Standard suspension polymerization gave polymer beads PA-PS- $Rh_2(MCES)_4$ (**11**) and PA-PS-$Rh_2(VBA)_4$ (**12**), in 51 and 50 % yield. The beads are spherical, hard and glass-like in the dry state, but they become soft when swollen in dichloromethane. The degree of swelling was measured to be 120 % for **11** and 100 % for **12**.

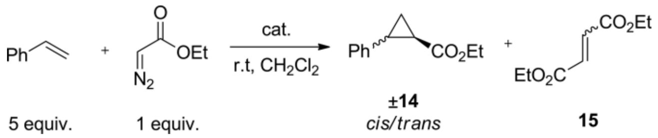
We also wanted to make dirhodium(II) tetracarboxylate beads by a post-modification approach for comparison of catalytic performance. We grafted dirhodium(II) tetracarboxylate monomer **6** onto commercially available (aminomethyl)polystyrene by means of a 1,4-addition reaction according to Scheme 5. By using the dirhodium(II) monomer **6** as a catalyst/monomer source, we obtained “post-modification beads” $Rh_2(MCES\text{-}PS)_4$ **13**, containing a similar (but not identical) dirhodium(II) tetracarboxylate catalyst to “bottom-up beads” **10**.

The catalytic performance of $Rh_2(OAc)_4$ (**1**) and catalysts **2**–**13** were investigated using the standard cyclopropanation of styrene with EDA as a benchmark reaction. The results are summarized in Table 2. In general, the diasteromeric ratios of the desired products *cis*- and *trans*-1-carbethoxy-2-phenyl-cyclopropane (**14**) were almost independent of the catalyst structure. The most surprising result when comparing the performance of the monomeric catalysts **1**, **2**, **5** and **6** (entry 1–6), was the high yield of **14** in entry 6. Not only did monomer **6** perform similarly to $Rh_2(OAc)_4$ at a hundred times lower catalyst loading, but the undesired byproducts (ethyl maleate and fumarate, **15**)



Scheme 5. Synthesis of $Rh_2(MCES\text{-}PS)_4$ **13** by grafting of **6** onto (aminomethyl)-PS.

Table 2. Results from the reactions of styrene (5 equiv.) with EDA (1 equiv.) catalyzed by **1**–**13**.



Entry	Catalyst	Cat load [mol-%]	Yield **14** [%][a]	*cis/trans*	Yield **15** [%][b]
1	$Rh_2(OAc)_4$, **1**	1	82	39:61	< 3
2	$Rh_2(OAc)_4$, **1**	0.1	72	36:64	7
3	$Rh_2(OAc)_4$, **1**	0.01	60[c]	42:58	< 3
4	$Rh_2(TFA)_4$, **2**	1	40	45:55	6
5	$Rh_2(VBA)_4$, **5**	0.01	30[c]	46:54	< 3
6	$Rh_2(MCES)_4$, **6**	0.01	81[c]	42:58	–
7	PA-$Rh_2(TFA)_2(MCES)_2$, **7**	1	46[d]	48:52	7
8	PS-$Rh_2(TFA)_2(VBA)_2$, **8**	1	39[e]	50:50	< 3
9	PS-$Rh_2(TFA)_2(VBA)_2$, **8**	1	24[f]	42:58	< 3
10	PA-$Rh_2(MCES)_4$, **9**	1	63	41:59	< 3
11	PS-$Rh_2(VBA)_4$, **10**	1	81	51:49	< 3
12	PA-PS- $Rh_2(MCES)_4$, **11**	1	81	42:58	< 3
13	PA-PS- $Rh_2(MCES)_4$, **11**	1	74[g]	45:55	< 3
14	PA-PS- $Rh_2(MCES)_4$, **11**	0.01	9[c]	44:58	–
15	PA-PS-$Rh_2(VBA)_4$, **12**	1	91	47:53	< 3
16	PA-PS-$Rh_2(VBA)_4$, **12**	0.01	15[c]	42:58	–
17	$Rh_2(MCES\text{-}PS)_4$, **13**	0.01	–	–	11

[a] Combined yield for the two diastereomers *cis* and *trans* **14**. [b] Combined yield for diethyl fumarate and maleate measured by ^{1}H-NMR spectroscopy. [c] Dropwise addition of EDA over 1.5 h and 24 h stirring time. [d] 84 % conversion of EDA in 2 h. [e] Full conversion of EDA in 24 h. [f] 82 % conversion of EDA in 2 h. [g] Addition of EDA in one portion.

from the dimerization reactions were suppressed to the detection limit in the analysis of the crude ^1H-NMR spectrum. Beads **7** and **8** with mixed ligand systems performed poorly (entry 7–9). Even though **8** decomposed EDA to 82 % conversion after two hours, the yield of **14** was only 24 %. Beads **9** and **10**, where all the TFA-ligands have been displaced with VBA or MCES, performed significantly better (entry 10–11). An interesting observation is the reversal in performance when comparing the monomeric catalysts **5** and **6** to the polymeric beads **10** and **9**. At the monomeric stage, the acrylate-based catalyst **6** gave higher yield of **14** than styrene-based catalyst **5**, but as polymeric beads the PS-catalyst **10** outperformed PA-catalyst **9**. Beads **10** have catalytic activity similar to $Rh_2(OAc)_4$, and this is rather surprising since BET and SEM analysis of **10** indicated no or negligible solvent penetration. Catalysis most likely occur on the surface of the beads with no or very low access to the internal Rh-sites within the polymer network. All beads **7**–**12** were soaked in CH_2Cl_2 prior to the cyclopropanation reaction in order for the beads to swell and allow access to the interior of the network. However, only beads **11** and **12** had a measureable degree of swelling, and this increased degree of swelling had a significant impact on the yields of **14** (entries 12, 15). The PA-PS beads **11** were similar to $Rh_2(OAc)_4$ in performance (entry 12) while PA-PS beads **12** outperformed $Rh_2(OAc)_4$ and gave the desired product in 91 % yield (entry 15). At very low catalyst loadings (0.01 mol-%), however, the immobilized catalysts performed poorly and gave much lower yields compared to their monomeric precursors (entries 14, 16). The PS-beads **13** (entry 17) were tested only at very low catalyst loading (0.01 mol-%). The post-modification catalyst decomposed EDA to 22 % conversion, but no cyclopropane **14** was detected in the crude reaction mixture.

We elected the best catalysts, **11** and **12**, for a study of recovery and recycling. We used the same benchmark cyclopropanation reaction and measured the yields of **14** over 7 cycles (Table 3). Both catalysts showed a similar activity trend. The yields were generally high and reproducible for the first four cycles followed by a steady drop towards moderate yields after seven cycles. Beads **12** appear to be more robust as the drop in yield of **14** was slightly lower for reactions catalyzed by **12** compared to **11**.

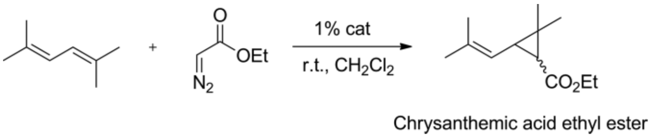
Table 3. Data from the reactions of styrene (5 equiv.) with EDA (1 equiv.) catalyzed by 1 mol-% **11** or **12**.

Catalyst	Cycle[a]	1	2	3	4	5	6	7
12	Yield[b] [%]	91	96	92	88	85	62	78
	trans/cis[b] [%]	55:45	55:45	55:45	55:45	55:45	55:45	55:45
11	Yield[b] [%]	81	81	82	82	57	43	44
	trans/cis[b] [%]	58:42	58:42	58:42	58:42	58:42	58:42	58:42

[a] The catalyst was recovered by filtration, washed and recycled. [b] Yield of **14** and *cis/trans* ratios were measured by analysis of crude ^1H NMR spectra.

We picked catalysts **1**, **11** and **12** and investigated their catalytic performance in cyclopropanation reactions towards a synthesis of chrysanthemic acid. Chrysanthemic acid is a commercially available insecticide and it can be made by hydrolysis of ethyl chrysanthemate, which in turn can be made in a cyclopropanation reaction between EDA and 2,5-dimethylhexa-2,4-diene. We executed the reaction of ethyl chrysanthemate similarly to the benchmark cyclopropanation of styrene with EDA. The results are displayed in Table 4.

Table 4. Results from the reactions of 2,5-dimethylhexa-2,4-diene with EDA catalyzed by **1**, **11**, **12**.



Entry	Cat.	Cat. (mol-%)	Yield [%][a]
1	**1**	1	80
2	**12**	1	76
3	**11**	1	58

[a] Yield of ethyl chrysanthemate measured by analysis of crude ^1H NMR spectra.

All three catalysts gave a diastereomeric mixture of chrysanthemic acid ethyl esters. Catalyst **1** gave the desired products in 80 % yield, marginally better than the 76 % yield obtained from **12**. Beads **11** gave 58 % yield, significantly lower than **1** and **12**. These results imply that **12** can be used to synthesize ethyl chrysanthemate in similar yields to $Rh_2(OAc)_4$, but with two significant advantages. Catalyst **12** can be separated from the reaction mixture and recovered by simple filtration, and reused 4–5 times without any significant drop in yields.

Conclusions

The work presented here demonstrates four important aspects with regard to synthesis of solid-supported dirhodium(II) tetracarboxylate catalysts: (1) It is feasible to make immobilized, heterogeneous dirhodium(II) tetracarboxylate catalysts efficiently, using a bottom-up approach, in only two steps from commercially available starting materials. Hence, the bottom-up approach can be a competitive alternative to the post-modification approach, which is commonly used for immobilization of high-value catalysts. (2) The heterogeneous dirhodium(II) tetracarboxylate bead catalysts can be as efficient catalysts as the homogeneous, generic $Rh_2(OAc)_4$. (3) Beads made from dirhodium(II) tetracarboxylate monomers with four polymerizable ligands are efficient catalysts despite a higher degree of cross-linking. This has an important implication: The link from the dirhodium(II) tetracarboxylate catalyst to the solid support does not have to be an "anchor-like" fashion for the beads to function properly. Hence, the cumbersome synthesis of mixed ligand dirhodium(II) tetracarboxylates with only one polymerizable ligand can be avoided. (4) Beads made of PA work just as well as PS beads with an inert scaffold. Since many acrylate monomers are commercially available, PA-dirhodium(II) tetracarboxylate beads with excellent catalytic performance and a large range of different chemical and physical properties should be readily available in only a few steps. By extending and further optimizing the bottom-up strategy, we believe it should be possible to prepare tailor-made immobilized dirhodium(II) catalysts that not only compete favorably with $Rh_2(OAc)_4$ as catalyst in Rh-carbene reactions, but are also easily available at a comparable price.

Experimental Section

Procedure for Monomer Synthesis Exemplified by the Synthesis of Monomer 3: A dry bottom flask was charged with $Rh_2(TFA)_4$ (30 mg, 0.046 mmol), 4-vinylbenzoic acid (61 mg, 0.41 mmol, 9.0 equiv.), $NaHCO_3$ (24 mg, 0.29 mmol, 6.4 equiv.) and dichloromethane (5 mL). The mixture was stirred at the ambient temperature for 20 h. The organic phase was washed with a saturated $NaHCO_3$ solution, dried ($MgSO_4$), filtered and concentrated under vacuum to give a green residue. Column chromatography (SiO_2, 1:1 EtOAc:hex) gave 19 mg (57 % yield) of **3** as a green solid. The structure was determined by single-crystal X-ray diffraction after recrystallization from acetone/hexane.

Procedure for Bead Synthesis Exemplified by the Synthesis of Beads 4: A 25 mL round-bottom flask was charged with $Rh_2(TFA)_2(MCES)_2$ **4** (25 mg, 0.028 mmol) *tert*-butyl acrylate (0.6 g, 4.68 mmol), pentaerythritol tetraacrylate (0.27 g, 0.77 mmol) and ethyl acetate (0.8 mL) containing a few drops of acetone (in order to increase the solubility of **4**). To this solution was added 0.5 % aqueous polyvinyl alcohol (Mowiol 40–88, 3.5 mL) together with 2 mg potassium iodide (inhibits polymerization in the aqueous phase). 2,2′-Azobisisobutyronitrile (AIBN, 8 mg, 0.049 mmol) was dissolved in 0.25 mL ethyl acetate and carefully added to the resulting mixture under vigorous stirring. The suspension was polymerized at 85 °C for 2.5 h at a constant rate of 1000 rpm. The suspension was cooled to room temperature and poured into beaker together with water/methanol (15/15 mL). The beads were allowed to settle by gravity and the supernatant was decanted off. The polymer beads were filtered, washed with water, dichloromethane and dried at the room temperature to give 0.8 g (92 %) of glassy, light-blue polymer beads **7**. The aqueous filtrate and the water from the washing process were extracted with dichloromethane. The organic layers were combined with the dichloromethane phase form the bead-washing process. The combined organic phase was dried ($MgSO_4$), filtered and concentrated under vacuum. ^1H-NMR analysis of the colorless residue showed no presence of signals from $Rh_2(TFA)_2(MCES)_2$, implying quantitative incorporation of the monomer **4**. The calculated loading of **4** in the beads is 0.035 mmol/g based on the isolated mass of the beads and quantitative incorporation of the monomer. The beads were characterized by FTIR, SEM, TEM and EDX, and had no measurable degree of swelling in CH_2Cl_2.

General Procedure for the Cyclopropanation of Styrene with EDA Catalyzed by Beads 7–13: A 50 mL round-bottomed flask equipped with a stirring bar was charged with beads of choice (**7–13**, 1 mol-% with respect to EDA) in CH_2Cl_2 (3 mL) and left stirring for 30 min for pre-swelling. A solution of ethyl diazoacetate (0.10 g, 0.88 mmol, 1 equiv.) in CH_2Cl_2 (12 mL) was added dropwise under vigorous stirring for 35 min. After stirring for additional 1 h, the polymeric catalyst was recovered by filtration and mesitylene (122 µL, 0.88 mmol, 1.0 equiv.) was added to the reaction filtrate. A small fraction of reaction mixture was then concentrated under reduced pressure. The yield of **14** and the *trans*/*cis* ratio were determined from analysis of the crude ^1H-NMR spectra.

General Procedure for the Synthesis of Ethyl Chrysanthemate: The dirhodium(II) tetracarboxylate catalyst (0.00876 mmol, 1 mol-%) and 2,5-dimethylhexa-2,4-diene (0.482 g, 4.38 mmol, 5 equiv.) were suspended in CH_2Cl_2 (6 mL) under vigorous stirring. After 30 min, a solution of EDA (0.100 g, 0.876 mmol, 1 equiv.) in CH_2Cl_2 (12 mL) was added dropwise and reaction mixture was stirred at room temperature for 24 h. The solid catalyst was recovered by filtration and mesitylene (105.3 mg, 0.876 mmol, 1 equiv.) was added as internal standard. The yield of ethyl chrysanthemate was calculated from analysis of the crude ^1H NMR spectrum.

CCDC 1847889 (for **5**), 1847891 (for **4**), and 1847890 (for **3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Supporting information (see footnote on the first page of this article): Full experimental procedures, pictures and spectroscopic data are given in the supporting information file free of charge.

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Keywords: Heterogeneous catalysis · Rhodium · Cyclopropanation · Immobilization · Carbene ligands · Bottom-up synthesis

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Dirhodiumtetracarboxylate Beads

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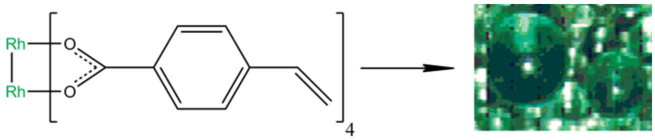
Bottom-Up Synthesis of Acrylic and Styrylic Rh^{II} Carboxylate Polymer Beads: Solid-Supported Analogs of $Rh_2(OAc)_4$



Polymer beads containing dirhodium(II) tetracarboxylates can be made in only two steps from commercially available starting materials. The beads can be considered immobilized analogs of $Rh_2(OAc)_4$ and compare favorably in benchmark cyclopropanation reactions of styrene with ethyl diazoacetate.

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