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Clean and efficient synthesis of air stable polymer-supported alkoxycarbonylcyclopentadienyl rhodium(I) complexes

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Abstract

Polymer-supported alkoxycarbonylcyclopentadienyl rhodium(I) complexes have been obtained through immobilization of $[Rh\{C_5H_4CO_2(CH_2)_2O_2C\text{-}Im\}(NBD)]$ (2) (Im = imidazole) on an (aminomethyl)polystyrene resin. An alternative approach toward the grafting of $[Rh\{C_5H_4CO_2(CH_2)_2OH\}(NBD)]$ (1) on a Wang resin has been also developed. Spectroscopic characterization of all the new functionalized resins with particular accent on ICP-OES measurements is presented and discussed.
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1. Introduction

The use of polymer-supported organometallics in the field of catalysis is continuing to gain interest within the chemical community [1]. The immobilization of transition metals on polystyrene supports, which is still one of the most popular polymeric materials used in synthesis due to its low cost, ready availability, mechanical robustness, chemical inertness, and facile functionalization [2], offers a number of advantages over traditional solution-phase chemistry. In an ideal case, the supported complexes can be recovered from the reaction mixtures by simple filtration [3], do not contaminate the product solution, can be recycled, and can help to increase selectivity [4].

Several examples of polymer- or silica-bound metal complexes bearing a cyclopentadienyl unit are reported [5]. These immobilized complexes have been used in hydroformylation [5h,5i], hydrogenation [5j,5k] and olefin polymerization catalysis [5b,5e,5g,5l,5m]. With regard to polymer-supported cyclopentadiene ligands, the conventional method for their preparation consists in the direct reaction of sodium cyclopentadienide (NaCp) with a suitable derivatized material such as Merrifield's resin or other halogen-functionalized supports [5h,5i,6]. The major problem related with this method consists in purification of the resin at the end of the reaction which can be difficult and time consuming.

A more convenient route is represented by the direct immobilization of the cyclopentadienyl complexes on polystyrene resins bearing different functional groups. In this contest, we have recently developed a new route for anchoring hydroxy-functionalized alkoxycarbonylcyclopentadienyl rhodium(I) complexes such as $[Rh\{C_5H_4CO_2(CH_2)_2OH\}(NBD)]$ (1) [7] on the surface of poly (propylenimine) dendrimers DAB-*dendr*-$(NH_2)_n$ $\{n = 8, 16, 32, 64\}$ [8].

In this paper, we report on the extension of this procedure to the direct immobilization of the CO_2-imidazole derivative $[Rh\{C_5H_4CO_2(CH_2)_2O_2C\text{-}Im\}(NBD)]$ (2) [8] on the –NH_2 functionalized (aminomethyl)polystyrene resin and also on the development of an alternative

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synthetic method toward the grafting of [Rh{C$_5$H$_4$CO$_2$-(CH$_2$)$_2$OH}(NBD)] (**1**) [7] on an imidazolide carbamates functionalized Wang resin.

The new materials have been characterized by means of spectroscopic (IR micro-spectroscopy) and analytical [inductively coupled plasma-optical emission spectrometry (ICP-OES)] measurements. In particular, with regards to the ICP-OES technique, an analytical protocol for the determination of rhodium has been set out and will be described in detail.

2. Results and discussion

2.1. Immobilization of [Rh{C$_5$H$_4$CO$_2$(CH$_2$)$_2$O$_2$C-Im}(NBD)] (2) on (aminomethyl)polystyrene resin

Following the immobilization procedure reported earlier for poly(propylenimine) dendrimers [8], complex **2** was covalently attached to the commercial (aminomethyl)polystyrene resin as outlined in the following equation:
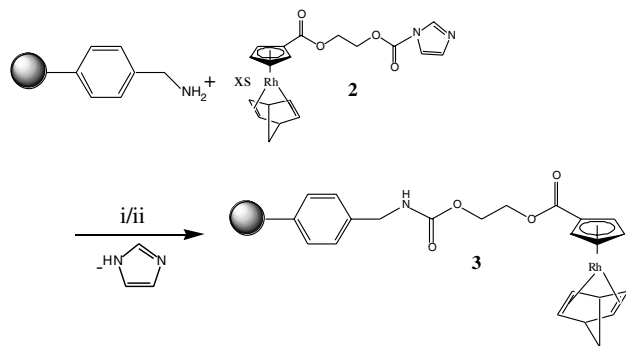
Reaction conditions: i) THF; r.t.; 3, 8, 10 d. ii) CH$_2$Cl$_2$; r.t.; 3, 8, 10 d.

(1)

A series of experiments carried out in THF and CH$_2$Cl$_2$ with different reaction times (3, 8, 10 days) were directed toward the optimization of the reaction conditions for the immobilization. In all cases gentle shaking of the resin in a solution of a 4:1 excess of **2** (see Section 3) caused the color of the resin to change from white to yellow. The color was retained even after extensive washing, thus indicating the successful immobilization onto the solid support. Noteworthy although a fourfold excess of **2** is needed, the unreacted rhodium complex can be recovered and re-used for further batches of (aminomethyl)polystyrene resin.

The formation of carbamate linkers in the functionalized resin **3** was monitored by means of IR micro-spectroscopy. In Fig. 1, spectra of the (aminomethyl)polystyrene resin (**A**) and **3** (**B**) are showed.

Spectrum **B** clearly shows the strong absorbance at 1716 cm^{-1} ascribable to both v(C=O, –CpCO$_2$–) and v(C=O, –O$_2$CNH–) of **3** which is comparable to that previously reported for functionalized poly(propylenimine) dendrimers DAB-*dendr*-[NH(O)COCH$_2$CH$_2$OC(O)C$_5$H$_4$-Rh(NBD)]$_n$ ($n = 4, 8, 16, 32, 64$) [8]. Furthermore, the signals appearing in the finger print region of spectrum **B**

($v = 1374$ (m); 1274 (m); 1125 (m); 1027 (m) cm^{-1}), assigned to the double bond stretching frequencies of the Rh(NBD) moieties [9] and the degenerate vC–C vibrations of the cyclopentadienyl ligand [9b,10] (cf. also with the IR spectrum of **1** in the experimental part), confirm the presence of the alkoxycarbonylcyclopentadienyl rhodium(I) terminal groups in **3**. Finally, by comparing the spectra of the starting (aminomethyl)polystyrene resin and **3** in the 3000–3500 cm^{-1} region, we observed the disappearance of the stretching vibrations of the –NH$_2$ terminal groups (at 3380 and 3304 cm^{-1}) replaced by a single weak band v(NH) at 3423 cm^{-1} due to the stretching of the carbamate–NH bond.

In order to determine the supported rhodium we attempted the hydrolysis of the carbamate linkers by stirring the resin **3** in a 1:1 mixture of CH$_2$Cl$_2$ and trifluoroacetic acid (TFA) [11]. This procedure, largely employed in solid-phase organic synthesis [12], failed owing to decomposition of the complex. A quantitative determination of the rhodium has been obtained by means of ICP-OES as follow: 20–30 mg of the polymer-supported rhodium complex are weighed in polytetrafluoroethylene vessels, thus a mixture of concentrated nitric acid (8.5 mL, 65% p.a.), sulfuric acid (0.5 mL, 98% p.a.) and hydrogen peroxide (1 mL, 30% w/w p.a.) is added to the sample. High pressure microwave digestion is performed with a predetermined power program in order to achieve complete dissolution of the sample within half an hour. The digest is then diluted to 50 mL with 18 MΩ reagent grade water. Rhodium is determined at 343.49 nm (I) and its quantification is performed using the standard addition method. External calibration is made with matrix matched rhodium standards and blank. Calibration curve is linear, with correlation coefficients greater than 0.995, till 50 µg mL^{-1} at least and the absolute detection limit (calculated as 3δ + average noise) is 20 ng mL^{-1}. Standards are freshly diluted from 10,000 µg mL^{-1} stock solution (Aldrich) to levels appropriate to the operating range. In the absence of standards, the recovery and precision of the procedure were investigated by spiking the (aminomethyl)polystyrene resin and submitting it to the complete process.

The rhodium content determined in samples obtained in different reaction conditions is reported in Table 1.

The most attractive feature of this immobilization strategy is the fact that the functionalized resin **3** is generated in good yields under mild conditions by simply mixing the homogeneous catalyst with the polymer. The complex loading on the beads is varying in a range of 2.9–4.8% (wt/wt) corresponding to 0.136–0.466 mmol rhodium/g of resin **3** showing that the process is solvent- and time-dependent. The best grafting yield (up to 95%) has been achieved after 8 days in THF. Prolonged reaction times resulted in a slight reduction of the yield (8 days: 95%; 10 days: 91%).

It is noteworthy that, when the reaction is carried out in CH$_2$Cl$_2$, the yields decrease significantly. At present we do not have a rational explanation of this behavior.
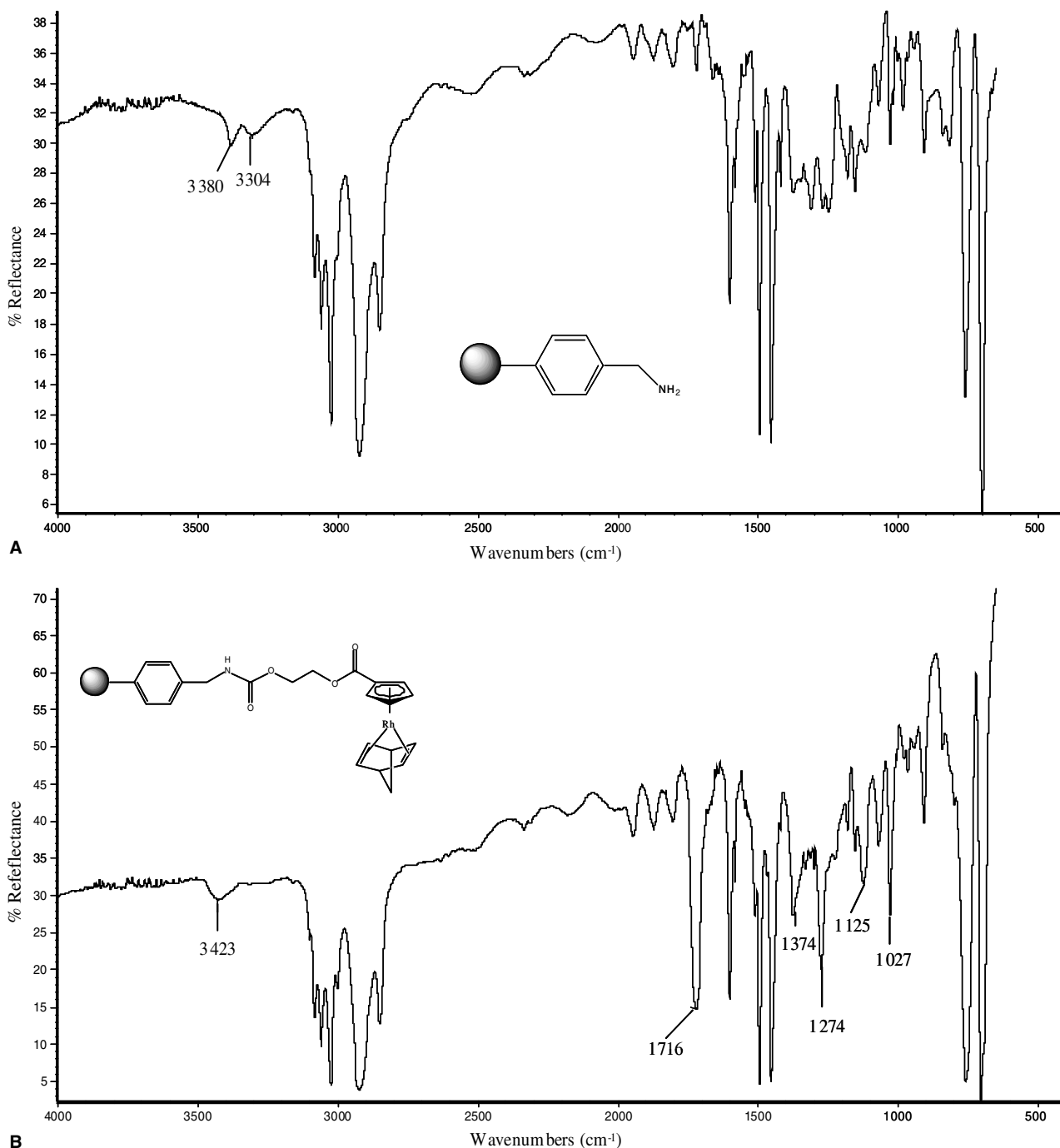
Fig. 1. Illustration of IR monitoring of (aminomethyl)polystyrene resin functionalization: (A) (aminomethyl)polystyrene resin; (B) functionalized resin **3**.

Table 1
ICP-OES rhodium determination on the functionalized resin **3** obtained with different reaction conditions

| Solvent	Reaction time	[Rh] (%)	Sr[RSDr] (%)	Yield (%)
THF	3 days	2.893	0.121[4.20]	58
THF	8 days	4.811	0.138[2.88]	95
THF	10 days	4.611	0.073[1.58]	91
CH$_2$Cl$_2$	3 days	1.421	0.026[1.85]	28
CH$_2$Cl$_2$	8 days	3.771	0.101[2.67]	75
CH$_2$Cl$_2$	10 days	3.219	0.074[2.31]	64

Values reported are medium value ($n = 10$) with proper standard deviation.

2.2. Immobilization of $[Rh\{C_5H_4CO_2(CH_2)_2OH\}(NBD)]$ (**1**) on imidazolide carbamates functionalized resin

An alternative approach toward the immobilization of **1** has been provided by the reaction with a Wang imidazolide carbamate resin, readily obtained from the commercially available –OH functionalized Wang resin [11].

The yellow resin **4** was obtained by refluxing for 8 h in THF the mixture of the complex **1** with the imidazolide carbamate resin polymer (Eq. (2)). As described above,

the formation of the carbonate linker in **4** was monitored by IR spectroscopy.

$$(2)$$
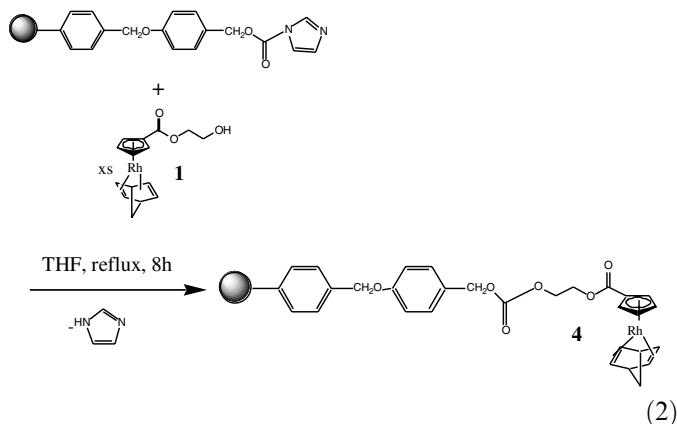
The strong absorbance at 1761 cm^{-1} typical of the imidazolide carbamates stretching v(C=O, –O$_2$CIm–) [11] present in the spectrum of the starting resin is replaced in the spectrum of **4** by two absorption bands due to the carbonate linker v(C=O, –OC(O)O–) and the ester group of the organometallic moieties v(C=O, –CpCO$_2$–), respectively, at 1757 and 1710 cm^{-1}. These spectral properties are similar to those observed for the carbonate and ester moieties of the complex [Rh$_2${μ-(C$_5$H$_4$CO$_2$(CH$_2$)$_2$OC(O)O(CH$_2$)$_2$O$_2$CC$_5$H$_4$)}-(NBD)$_2$] fully characterized in a previous work [8].

ICP-OES spectroscopy measurements showed rhodium on the beads of ca. 3.2% (wt/wt) (43% yield based on loading of the starting Wang resin) corresponding to a complex loading of 0.311 mmol rhodium/g of resin **4**.

2.3. Attempted grafting on a Merrifield resin: reactivity between [Rh{C$_5$H$_4$CO$_2$(CH$_2$)$_2$OH}(NBD)] (1) and NaH

With the aim of obtaining polymer-supported alkoxycarbonylcyclopentadienyl rhodium(I) complexes bearing the ether groups as linkers instead of the carbamate or carbonate ones, we attempted to anchor the OH functionalized rhodium complex [Rh{C$_5$H$_4$CO$_2$(CH$_2$)$_2$OH}(NBD)] (**1**) [7] on a (chloromethyl)polystyrene resin (Merrifield resin). In order to do that it was first necessary to deprotonate the alcoholic function with a non-nucleophilic base such as NaH [13]. In the event, even under the mild conditions

employed, the reaction takes a different course and after the immediate deprotonation, the straightforward formation in high yields of the yellow diester-bridged dinuclear complex [Rh$_2${μ-(C$_5$H$_4$CO$_2$CH$_2$)$_2$}(NBD)$_2$] (**5**) is observed (Scheme 1). This reaction is accompanied by evolution of H$_2$ (identified with a gas analysis) and the formation of the insoluble disodium salt of ethylene glycol NaOCH$_2$-CH$_2$ONa (**6**) (identified by alkylation with MeI to give dimethoxyethane). Complex **5** has been already isolated and completely characterized in a previous work as a by-product in the synthesis of the mononuclear complex **1** [7]. As found in that case, the transesterification process is promoted by the presence of a base and it represents a convenient method for the quantitative synthesis of the dimer **5**.

Monitoring the reduction of **1** by ^{1}H NMR (4×10^{-3} M, THF-d_8, room temperature) we could observe the very first step of the reaction, i.e., the immediate deprotonation of the alcoholic function to give the anionic complex [Rh{C$_5$H$_4$CO$_2$(CH$_2$)$_2$O}(NBD)]$^-$ (**7**). This intermediate is characterized by two equally intense AA′XX′ multiplets at δ 4.18 and 3.69 [cf. with ^{1}H NMR of **1** in the same range: 4.36 (AA′XX′, 2H; CO$_2$CH$_2$), 3.88 (AA′XX′M, 2H; CH$_2$OH), 3.34 (m, 6H, CH; NBD), 2.30 (t, ^3J(H,H) = 6.0 Hz, 1H; OH)]. The mononuclear anionic complex thus formed **7** then quantitatively converts (in ca. 6 h) into the dinuclear complex **5** and insoluble dianion **6**.

Studies on the catalytic activity of both the recently reported functionalized dendrimers [8] and the supported polymeric systems described in this paper in the hydroformylation and hydrogenation of 1-hexene and styrene are currently under investigation and will be presented in a follow-up paper.

3. Experimental

3.1. Materials and procedures

All reactions with organometallic reagents or substrates were carried out under argon or nitrogen using standard Schlenk techniques. Solvents were dried and distilled under nitrogen prior to use. CH$_2$Cl$_2$ was further purified by filtration on anhydrous alumina. The prepared derivatives were characterized by spectroscopic methods. Gas analyses were
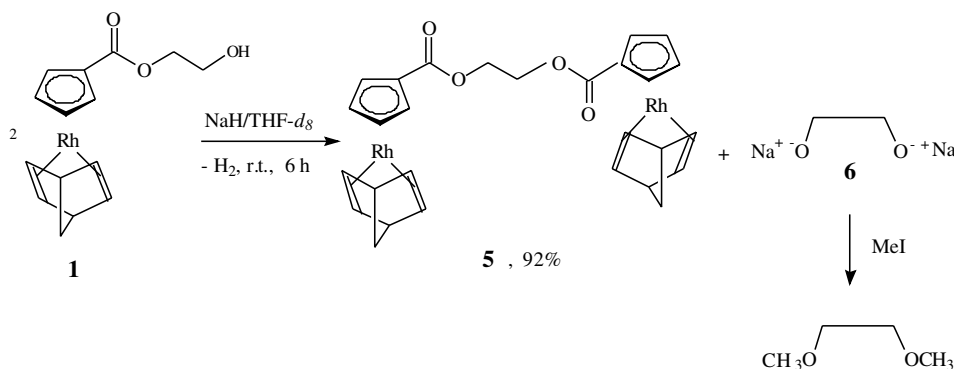
Scheme 1.

made on a VG 200 SX mass spectrometer gas analysis system LTD instrument. The IR spectra (on beads) were recorded with a Nexus 470 instrument configured with a Nicolet Continuum microscope and a MCT liquid nitrogen cooled detector. The spectra were collected in the near normal-reflection-absorption mode. The sample digestion process was carried out in a Milestone MLS 1200 MEGA microwave digestion system, controlled by a 240 Terminal (software revision 5.4), equipped with an MDR rotor and TFM Teflon vessels. ICP-OES analyses were performed on a Varian Liberty 200 sequential spectrometer equipped with a 1800 grooves mm^{-1} holographic grating, a 0.75 m focal length Czerny-Turner optical system, a V-groove nebulizer, a Sturman-Master inert nebulization chamber and a radial quartz torch. The RF generator is based on a 40.68 MHz crystal-controlled oscillator, the wavelength range is between 190 and 860 nm, power is 1.5 kW, plasma Ar flow rate is 15 L min^{-1} and auxiliary flow rate is 1.5 L min^{-1}. Rhodium ICP/DCP standard solution 10 000 µg/mL Rh in 7 wt.% HCl was purchased from Aldrich.

The reagents [Rh{$C_5H_4CO_2(CH_2)_2OH$}(NBD)] (**1**), [Rh{$C_5H_4CO_2(CH_2)_2O_2C$-Im}(NBD)] (**2**) and imidazolide carbamate functionalized resin were prepared according to the procedures previously reported [7,8,11]; 1,1′ carbonyldiimidazole (CDI) (Aldrich), (aminomethyl)polystyrene resin (capacity: ca. 0.6 mmol/g resin, 200–400 mesh, 1% DVB) and Wang resin (capacity: ca. 1 mmol/g resin, 200–400 mesh, 1% DVB) (Fluka) were used as purchased. The reagent NaH, 60% dispersion in mineral oil (Aldrich), was washed several times with petroleum ether and the resulting free-flow white powder was stored under Argon. NMR measurements were made in flame sealed tubes. THF-d_8 and toluene-d_8 were dried and stored under argon on potassium mirror, $CDCl_3$ was dried and stored under argon on molecular sieves.

3.2. Immobilization of [Rh{$C_5H_4CO_2(CH_2)_2O_2$-Im}-(NBD)] (2) on (aminomethyl)polystyrene resin

3.2.1. THF solvent

To a suspension of (aminomethyl)polystyrene resin (250 mg, 0.6 mmol NH_2/g, 0.160 mmol –NH_2) in THF (4 mL) pre-swelled overnight in a 50 mL reaction vessel equipped with a stir bar, a solution of [Rh{$C_5H_4CO_2$-(CH_2)$_2O_2C$-Im}(NBD)] (**2**) (265 mg, 0.6 mmol) in THF (4 mL) was added dropwise. The mixture was stirred gently at room temperature for 3, 8 or 10 days during three different experiments. The resin was collected on a Whatman medium $\varnothing = 90$ mm filter, washed with the follow solvents sequence THF (20 mL), Et_2O (20 mL), THF (20 mL), Et_2O (20 mL) and air-dried. The resin was then transferred in a vial and the remaining solvent removed under vacuum to yield yellow beads of the polymer-supported alkoxycarbonylcyclopentadienyl rhodium(I) (**3**). ICP-OES analysis of the beads showed a time-dependent yield of grafting. After 3 days: ca. 2.9% (wt/wt), rhodium on the beads, equivalent to 0.233 mmol/g loading of complex which corresponds to 48% reaction of the –NH_2 groups. After 8

days: ca. 4.8% (wt/wt), 0.466 mmol/g; 95% yield. After 10 days: ca. 4.6% (wt/wt); 0.447 mmol/g, 91% yield.

3.2.2. CH_2Cl_2 solvent

To a suspension of (aminomethyl)polystyrene resin (250 mg, 0.6 mmol $NH_2 \cdot g^{-1}$, 0.160 mmol –NH_2) in CH_2Cl_2 (4 mL) pre-swelled overnight in a 50 mL reaction vessel equipped with a stir bar, a solution of [Rh{$C_5H_4CO_2(CH_2)_2O_2C$-Im}(NBD)] (**2**) (265 mg, 0.6 mmol) in CH_2Cl_2 (4 mL) was added dropwise. The mixture was stirred gently at room temperature for 3, 8 or 10 days during three different experiments. The resin was collected on a Whatman medium $\varnothing = 90$ mm filter, washed with the follow sequence CH_2Cl_2 (20 mL), Et_2O (20 mL), CH_2Cl_2 (20 mL), Et_2O (20 mL) and air-dried. The resin was then transferred in a vial and the remaining solvent removed under vacuum to yield yellow beads of the polymer-supported alkoxycarbonylcyclopentadienyl rhodium(I) (**3**). ICP-OES analysis of the beads showed a time-dependent yield of grafting. After 3 days: ca. 1.4% (wt/wt), rhodium on the beads, equivalent to 0.136 mmol/g loading of complex which corresponds to 28% reaction of the –NH_2 groups. After 8 days: ca. 3.8% (wt/wt), 0.369 mmol/g, 75% yield. After 10 days: ca. 3.2% (wt/wt), 0.311 mmol/g, 64% yield. IR (refl./abs.) of **1**: v = 3492 (s, br); 3200–2850 (m, br); 1672 (s, br, C=O, CpCO$_2$–); 1472 (s); 1450 (w); 1397 (m); 1378 (s); 1357 (w); 1287 (s); 1226 (w); 1151 (s, br); 1080 (s); 1056 (w); 1040 (m); 1028 (w); 1016 (w); 989 (w); 931 (m); 918 (w); 893 (w); 883 (w) 846 (m); 808 (s); 765 (s), cm^{-1}. IR (refl./abs.) (aminomethyl)polystyrene resin: v = 3380 (w, br, NH_2); 3304 (w, br, NH_2); 3081–2843 (s, br); 1940 (w, br); 1869 (w, br); 1803 (w, br); 1720 (w); 1660 (w); 1602 (m); 1583 (w); 1510 (w); 1492 (s); 1452 (s); 1419 (w); 1374 (w, br); 1311 (w, br); 1256 (w, br); 1179 (w); 1154 (w); 1116 (w); 1071 (w); 1029 (w); 984 (w); 907 (w); 839 (w); 816 (w);758 (s); 702 (s), cm^{-1}. IR (refl./abs.) of **3**: v = 3423 (w, br, NH); 3090–2846 (s, br); 1940 (w, br); 1871 (w, br); 1799 (w, br); 1716 (s, br, (C=O, CpCO$_2$–) and (C=O, –OC(O)N–)); 1602 (s); 1583 (w); 1513 (w); 1492 (s); 1452 (s); 1374 (m); 1301 (w); 1274 (m); 1247 (w, br); 1224 (w, br); 1183 (m); 1125 (m, br); 1067 (w); 1027 (m); 907 (w); 762 (s, br); 702 (s), cm^{-1}.

3.3. Immobilization of [Rh{$C_5H_4CO_2(CH_2)_2OH$}(NBD)] (1) on imidazolide carbamates functionalized resin

To a suspension of imidazolide carbamates functionalized resin (300 mg, 0.7–1 mmol –CO_2Im/g) in THF (4 mL) pre-swelled overnight in a 50 mL reaction vessel equipped with a stir bar, a solution of [Rh{$C_5H_4CO_2$-(CH_2)$_2OH$}(NBD)] (**1**) (423 mg, 1.22 mmol) in THF (4 mL) was added dropwise. The mixture was refluxed under gently stirring for 8 h. The resin was collected on a Whatman medium $\varnothing = 90$ mm filter, washed with the following sequence THF (20 mL), Et_2O (20 mL), THF (20 mL), Et_2O (20 mL) and air-dried. The resin was then transferred in a vial and the remaining solvent removed

under vacuum to yield yellow beads of the polymer-supported alkoxycarbonylcyclopentadienyl rhodium(I) (**4**) (0.309 g) which was analyzed by inductively coupled plasma optical emission spectroscopy. ICP-OES analysis of the beads showed a grafting of ca. 3.2% (wt/wt) rhodium on the beads, equivalent to 0.311 mmol/g loading of complex which corresponds to 43% yield (based on loading of the starting Wang resin). IR (refl./abs.) of imidazolide carbamates functionalized resin: $v = 3158–2850$ (s, br); 1944 (w); 1870 (w); 1764 (s, OC(O)Im); 1613 (s); 1586 (m); 1515 (s); 1491 (s); 1454 (s); 1399 (s); 1364 (s); 1314 (s); 1289 (s); 1242 (s); 1169 (s); 1115 (w); 1094 (m); 1060 (w); 1000 (s); 943 (w); 910 (m); 830 (s); 771 (s); 709 (s) cm^{-1}. IR (refl./abs.) of **4**: $v = 3103–2846$ (s, br); 1944 (w); 1878 (w); 1747 (s, (OC(O)O)); 1708 (s, (C=O, CpCO$_2$–)); 1608 (s); 1583 (w); 1512 (s); 1491 (s); 1450 (s); 1393 (m); 1373 (m); 1262 (s, br); 1174 (s); 1133 (m); 1061 (w); 1016 (m, br); 609 (w); 877 (w); 822 (m); 760 (s); 705 (s) cm^{-1}.

3.4. NMR tube reaction of [Rh{C$_5$H$_4$CO$_2$(CH$_2$)$_2$OH}-(NBD)] (1) with NaH and THF-d$_8$

In an NMR tube **1** (8.2 mg, 0.02 mmol) was dissolved in a slurry of NaH (excess) and THF-d_8 (0.5 mL). ^{1}H NMR after 10 min at room temperature showed the formation of [Rh{C$_5$H$_4$CO$_2$(CH$_2$)$_2$O}(NBD)]$^-$ (**7**). ^{1}H NMR (300.1 MHz, THF-d_8): $\delta = 5.55$ (AA′BB′, ^3J(H,H) = 1.8 Hz, 2H; Cp), 5.31 (AA′BB′X, ^3J(H,H) = 2.1 Hz, J(H,Rh) = 0.9 Hz, 2H; Cp), 4.18 (AA′XX′, ^3J(H,H) = 6.6 Hz, 2H; CO$_2$CH$_2$), 3.69 (AA′XX′, ^3J(H,H) = 5.3 Hz, 2H; CH$_2$OH), 3.30 (m, 6H, CH; NBD), 0.96 (m, 2H, CH$_2$; NBD). After 6 h at room temperature, ^{1}H NMR showed the quantitative formation of [Rh$_2${µ-(C$_5$H$_4$CO$_2$CH$_2$)$_2$}(NBD)$_2$] (**5**) ^{1}H NMR (300.1 MHz, THF-d_8): $\delta = 5.55$ (AA′BB′X, ^3J(H,H) = 2.1 Hz, J(H,Rh) = 0.6 Hz, 4H; Cp), 5.33 (AA′BB′X, ^3J(H,H) = 2.0 Hz, J(H,Rh) = 0.9 Hz, 4H; Cp), 4.40 (s, 4H; CO$_2$CH$_2$), 3.31 (m, 12H; NBD), 0.95 (t, ^3J(H,H) = 1.2 Hz, 4H, NBD); ^{13}C–{^{1}H} NMR (75.5 MHz, THF-d_8 major peaks): $\delta = 90.1$ (d, J(C,Rh) = 4.9 Hz, CH; Cp), 88.5 (d, J(C,Rh) = 3.7 Hz, CH; Cp), 64.1 (CO$_2$CH$_2$), 57.4 (d, J(C,Rh) = 7.3 Hz, C$_7$, NBD), 49.0 (d, J(C,Rh) = 2.5 Hz, C$_{1,4}$; NBD), 33.9 (d, J(C,Rh) = 9.7 Hz, C$_{2,3,5,6}$; NBD) and the insoluble white co-product NaOCH$_2$CH$_2$ONa disodium salt of ethyleneglycol **6** identified after alkylation with an excess of MeI to dimethoxyethane. The gas evolved during the experiment was identified as H$_2$ (m/z (%): 2 (variable 0–100)).

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