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Novel Dirhodium Coordination Polymers: The Impact of Side Chains on View Article Online Cyclopropanation

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Abstract

Seven novel dirhodium coordination polymers (Rh₂-Ln) (n=1-7) are prepared by employing bitopic ligands to connect dirhodium nodes. The formation of the framework is confirmed by attenuated total reflectance Fourier transform infrared (ATR-FTIR) and ${}^{1}\text{H}\rightarrow{}^{13}\text{C}$ cross polarization magic angle spinning nuclear magnetic resonance (CP MAS NMR) spectroscopy. Defect sites resulting from incomplete ligand substitution are revealed by ${}^{19}\text{F}$ MAS NMR. The random stacking behavior of the frameworks in the obtained solid is analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The Rh₂/O interaction in neighboring layers is investigated by diffuse reflectance ultra-violet visible light (DR-UV-vis) spectroscopy and X-ray photoelectron spectroscopy (XPS). This interaction is relevant to understand the catalytic behavior of various Rh₂-Ln catalysts in the cyclopropanation of styrene with ethyl diazoacetate (EDA). In this context, the structure-reactivity relationship is discussed by taking into consideration both interlayer Rh₂/O interactions and steric effects of side chains.

Introduction

Homogeneous transition metal catalysts have strong advantages in the industrial scale production of fine chemicals owing to their high selectivity and activity, but their applications are prohibited owing to the often challenging recovery and recycling of the catalyst.^[1] Particularly in the synthesis of pharmaceutical products, even smallest metal contaminations have to be avoided both for medical and legal reasons. In certain cases, isolation of products such as pharmaceuticals,^[2] or of soluble polymer catalysts can be achieved via precipitation from reaction media.^[1a] Furthermore, heterogenization of organometallic catalysts is of

innovative interest,^[1b, 1c] where catalysts can be readily separated from reaction media. <u>vi39/C8CY01493K</u> filtration. Finally, fixed-bed reactors have been employed successfully in the production of pharmaceuticals to overcome separation issues.^[3]

Dirhodium (II) complexes are important examples of organometallic catalysts. They have drawn much attention as efficient catalysts for various carbene transfer reactions including cyclopropanation, C-H insertion, Si-H insertion.^[4] Over the last decades, major efforts have been devoted to develop recyclable heterogenized dirhodium catalyst by forming covalent bonds via equatorial^[5] or axial binding.^[6] Mainly functional silica materials and polymers were employed as carriers.^[4g, 5-6] Recently, some of us achieved two types of supported dirhodium catalysts using amine-carboxyl bi-functional SBA-15^[7] or cellulose nanocrystals^[8] as carriers, where the dirhodium unit was chemically bound via amine and/or carboxyl groups. While these immobilized catalysts preserve the selectivity of the homogeneous ones, their drawbacks cannot be ignored, namely the lower catalytic activities deriving from insufficient loading, mass transfer resistance and blocking of active sites by ligand coordination at axial position.^[9]

An alternative approach to the conventional immobilization of homogeneous catalysts, is the synthesis of self-supported catalysts, who emerged along with the development of coordination polymers or metal organic frameworks (MOFs).^[10] In the heterogenization process typically bitopic or polytopic ligand systems form a framework with metallic complexes. Such type of catalysts exhibits unique features, such as high density of catalytic sites, uniform distribution, high loadings and easy separability.^[11] Important examples, such as $[Cu(II)_3(BTC)_2]$,^[12] $[Cu(II)Er(III)_2(pdc)_2(Hpdc)(H_2O)_4] \cdot 2H_2O$,^[13] $[Cu(I)_2(4,4'-bpy)_2SO_4] \cdot 6(H_2O)$,^[14] and various polytopic bis(oxazoline)-based Cu(I) (or Cu(II)) coordination polymers^[15] were applied in cyclopropanation reactions. Moreover, Au(III) Schiff base^[12] and Ru(III)-salen^[16] were introduced into MOFs and employed as cyclopropanation catalysts.

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Dirhodium based coordination polymer catalysts were obtained via solvothermal synthesis or ligand exchange and applied in hydrogenation,^[17] H-D exchange reaction,^[17b] cyclopropanation reaction^[18] and photochemical reduction of water.^[19] Su et.al ^[20] prepared dirhodium metal-organic gels and applied them in coupling CO₂ with epoxides and intramolecular C-H amination of vinyl azides.

While most of these studies mainly focused on the synthesis of novel coordination polymers as catalysts, systematic investigations of the relationship between structure/chemical environment of the organometallic framework on the catalytic performance are rare. However, as two recent examples on Pd clusters and PdAu nanoparticles in MOFs showed, they are highly important for rational control of catalytic sites.^[21]

The present study illustrates the role of side chains in the layered dirhodium coordination polymers and related structure-reactivity relationship. These novel dirhodium coordination polymers Rh₂-Ln (n = 1-7) are prepared by ligand exchange employing ditopic ligands Ln (n = 1-7, Scheme 1) that are substituted with different side chains. ATR-FTIR, ¹H \rightarrow ¹³C CP MAS NMR and ¹⁹F MAS NMR are used to probe the local structure of these catalysts. DR-UV-vis and XPS are employed to investigate the interlayer Rh₂/O interaction in the dirhodium

coordination polymers. Finally, the obtained coordination polymers are applied in the model /C8CY01493K cyclopropanation between styrene and ethyl diazoacetate (EDA), and the impact of side chains on the catalytic performance is discussed.



Scheme 1. Ditopic ligand systems employed for the synthesis of novel dirhodium coordination polymers: H_2Ln (n = 1-5) represents modified terephthalic acids with ethers as side chains, H_2Ln (n = 6-7) represents modified terephthalic acids with ester side chains.

Experiment part

Synthesis of Coordination Polymers

General

Rhodium trifluoroacetate dimer (Rh₂(TFA)₄, Acros), 2,5-dihydroxyterephthalic acid (Sigma-Aldrich), diethyl 2,5-dihydroxyterephthalate (Sigma-Aldrich), iodomethane (Sigma-Aldrich), bromoethane (Sigma-Aldrich), 1-bromobutane (Alfa Aesar), 2-bromoethyl methyl ether (Merck), benzyl bromide (Merck), acetic anhydride (Sigma-Aldrich), butyric anhydride (Sigma-Aldrich), ethyl diazoacetate (EDA, Sigma-Aldrich) and styrene (Sigma-Aldrich) were purchased and utilized without further purification.

Linker synthesis

The linkers bearing ether side chains (H₂Ln, n = 1-5) were synthesized according to the work of the Fischer group,^[22] and the linkers bearing ester chains (H₂Ln, n = 6, 7) were prepared based on Yamada and Kitagawa's work (Scheme 2).^[23] ATR-FTIR spectra are displayed in ESI Figure S1. ¹H and ¹³C solution-state NMR spectra are displayed in ESI Figures S2 and S3, respectively.

H₂L1 (2,5-dimethoxyterephthalic acid)

For the preparation of H₂L1, 0.25 g diethyl 2,5-dihydroxyterephthalate (0.98 mmol), 0.40 g K_2CO_3 (3 eq.), and excess iodomethane (1 mL) were dissolved/suspended in acetonitrile (50 mL) in a 100 mL flask. The reaction was performed at 50 °C for 24 hours. After evaporating acetonitrile, 20 mL of water were added to the flask and the pH-value of the solution was

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adjusted to 1 by adding concentrated HCl (37%). The crude product diethyl-2,5-dimethoxy9/C8CY01493K 1,4-benzenedicarboxylate was obtained by extracting with ethyl acetate three times. Colorless powder was obtained after removing the ethyl acetate. Then, 50 g of a mixture of H₂O and EtOH (1:1, w:w) and 0.11 g (3 eq.) NaOH were introduced. The hydrolysis occurred at 50 °C for one day. After adjusting the pH to 1, the product (H₂L1) was obtained by extraction using ethyl acetate. The product was purified by dissolving it in a mixture of acetone and water. After evaporation of acetone at room temperature, the purified linker was filtrated and dried at 100 °C overnight.

¹H NMR (300 MHz, D₂O-DMF) δ 7.78 (2H, Ar-H), 4.26 (6H, OCH₃) ppm; ¹³C NMR (75.5 MHz, D₂O-DMF) δ 167.51, 152.16, 125.37, 115.16, 56.80 ppm. Elemental analysis: C% = 51.32, H% = 4.368

H₂L2 (2,5-diethoxyterephthalic acid)

 H_2L2 was synthesized similar to H_2L1 . Bromoethane (0.32 g, 3 eq.) was employed instead of iodomethane and the etherification reaction was carried out at reflux for 24 h.

¹H NMR (300 MHz, DMSO) δ 6.91 (2H, Ar-H), 3.95 (4H, OCH₂), 1.18 (6H, OCH₃) ppm; ¹³C NMR (75.5 MHz, D₂O) δ 175.57, 151.34, 130.57,124.36, 72.87, 70.96, 57.99 ppm. Elemental analysis: C% = 54.70, H% = 5.262

H₂L3 (2,5-dibutoxyterephthalic acid)

The preparation of H_2L3 was performed similar to H_2L2 . 1-bromobutane (0.40 g, 3 eq.) was employed instead of bromoethane.

¹H NMR (300 MHz, DMSO) δ 7.27 (s, 2H, Ar-H), 4.33-4.29 (m, 4H, OCH₂), 1.96-1.86 (m, 4H, CH₂), 1.59-1.46 (m, 4H, CH₂), 1.04-0.99 (m, 6H, CH₃) ppm; ¹³C NMR (75.5 MHz, CDCl₃) δ 164.06, 151.73, 122.67, 117.46, 71.01, 30.82, 19.05, 13.65 ppm. Elemental analysis: C% = 61.64, H% = 7.173

H₂L4 (2,5-bis(2-methoxyethoxy)terephthalic acid)

The preparation of H_2L4 was performed similar to H_2L2 . 2-bromoethyl methyl ether (0.41 g, 3 eq.) was employed instead of bromoethane.

¹H NMR (300 MHz, DMSO) δ 7.36 (s, 2H, Ar-H), 4.20-4.16 (m, 4H, OCH₂), 3.70-3.68 (m, 4H, OCH₂), 3.36 (s, 6H, OCH₃) ppm; ¹³C NMR (75.5 MHz, DMSO) δ 166.59, 150.52, 125.70, 116.10, 70.31, 69.18, 58.26 ppm. Elemental analysis: C% = 53.26, H% = 5.649

H₂L5 (2,5-bis(benzyloxy)terephthalic acid)

The preparation of H_2L5 was performed similar to H_2L2 . Benzyl bromide (0.50 g, 3 eq.) was employed instead of bromoethane.

¹H NMR (300 MHz, DMSO) δ 7.49-7.28 (m, 12H, Ar-H), 5.16 (m, 4H, OCH2); ¹³C NMR (75.5

MHz, DMSO) δ 165.76, 151.73, 136.94, 128.30, 127.66, 127.44, 125.60, 116.01, 70τ41: ppma9/C8CY01493K Elemental analysis: C% = 60.32, H% = 4.445

H₂L6 (2,5-diacetoxyterephthalic acid)

For preparation of H₂L6, 0.25 g 2,5-dihydroxyterephthalic acid (1.26 mmol) was dispersed in 5 mL acetic anhydride in a 10 mL glass bottle. Then, three drops of H₂SO₄ (98% wt) were added as catalyst. The reaction was stirred at room temperature overnight. The product (H₂L6) was obtained by filtering the reaction solution. To purify the product, a mixture of acetone and water was employed to dissolve the obtained raw product as described for the purification of H₂L1. ¹H NMR (300 MHz, DMSO) δ 7.69 (s, 2H, Ar-H), 2.26 (s, 6H, -CH₃) ppm; ¹³C NMR (75.5 MHz, DMSO) δ 169.13, 164.20, 146.94, 128.58, 126.38, 20.67 ppm. Elemental analysis: C% = 51.14, H% = 3.572

H₂L7 (2,5-bis(butyryloxy)terephthalic acid)

The preparation of H_2L7 was performed similar to H_2L6 . Butyric anhydride (5 mL) was employed instead of acetic anhydride.

¹H NMR (300 MHz, DMSO) δ 7.67 (s, 2H, Ar-H), 2.58-2.50 (m, 4H, CH₂), 1.73-1.60 (m, 4H, CH₂), 1.00-0.95 (s, 6H, CH₃) ppm; ¹³C NMR (75.5 MHz, DMSO) δ 171.50, 164.26, 146.84, 128.68, 126.32, 35.17, 17.48, 13.38 ppm. Elemental analysis: C% = 59.19, H% = 5.903

Synthesis of dirhodium coordination polymers

The heterogeneous dirhodium coordination polymers were prepared by ligand exchange according to refs.^[18, 24] The C, H contents were determined by elemental analysis. The Rh content was determined by thermogravimetry (TG, see ESI Figure S4-S10) according to the method of Kaskel and co-workers.^[17d] The fluorine content was determined by quantitative analysis of the ¹⁹F MAS NMR spectra according to ref.^[8]

Rh_2 -L1

For preparation of Rh₂-L1, Rh₂(TFA)₄ (0.10 g, 0.1520 mmol), H₂L1 (0.10 g, 3 eq.) and 75 mL ethyl acetate was charged into a 100 mL flask. In a Soxhlet extractor, a mixture of K₂CO₃ and 4Å molecular sieves (SiO₂/Al₂O₃ \approx 2, Alfa Aesar) was loaded in a cellulose filter tube. The exchange reaction was conducted for 2 days. The precipitate was then filtered and washed in a Soxhlet extractor with ethyl acetate for another 2 days. Then, the solid was dried at 80°C under vacuum overnight to remove residual ethyl acetate.

Composition: C% = 32.93, H%= 3.225, Rh%(TGA) = 25.2 (nominal Rh% = 31.5), F% = 4.1 (2.14 mmol·g⁻¹)

Rh_2 -L2

Rh₂-L2 was synthesized similar to Rh₂-L1 employing H₂L2 (0.11 g, 3 eq.) as ligand. Composition: C% = 37.29, H%= 3.747, Rh%(TGA) = 28.4 (nominal Rh% = 29.0), F% = 9.2 (4.85 mmol·g⁻¹)

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Rh_2 -L3

Rh₂-L3 was synthesized similar to Rh₂-L1 employing H₂L3 (0.14 g, 3 eq.) as ligand. Composition: C% = 45.74, H%= 5.115, Rh%(TGA) = 23.7 (nominal Rh% = 24.9), F% = 0.5 (0.22 mmol·g⁻¹)

Rh_2 -L4

Rh₂-L4 was synthesized similar to Rh₂-L1 employing H₂L4 (0.14 g, 3 eq.) as ligand. Composition: C% = 38.92, H%= 4.180, Rh%(TGA) = 24.2 (nominal Rh% = 24.8), F% = 1.0 (0.52 mmol·g⁻¹)

Rh_2 -L5

Rh₂-L5 was synthesized similar to Rh₂-L1 employing H₂L5 (0.17 g, 3 eq.) as ligand. Composition: C% = 53.86, H%= 3.732, Rh%(TGA) = 20.8 (nominal Rh% = 22.7), F% = 1.2 (0.61 mmol·g⁻¹)

Rh_2 -L6

Rh₂-L6 was synthesized similar to Rh₂-L1 employing H₂L6 (0.13 g, 3 eq.) as ligand. Composition: C% = 32.17, H%= 2.976, Rh%(TGA) = 31.0 (nominal Rh% = 26.9), F% = 0.8 (0.40 mmol·g⁻¹)

Rh_2 -L7

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Rh₂-L7 was synthesized similar to Rh₂-L1 employing H₂L7 (0.15 g, 3 eq.) as ligand. Composition: C% = 39.54, H%= 3.836, Rh%(TGA) = 25.2 (nominal Rh% = 23.5), F% = 0.2 (0.12 mmol·g⁻¹)

Catalytic Cyclopropanation

The cyclopropanation between styrene and ethyl diazoacetate (EDA) was applied to evaluate the performance of the heterogenized dirhodium catalysts. Generally, an appropriate amount of Rh₂-Ln (i.e., 6.1 mg of Rh₂-L1, 6.7 mg of Rh₂-L2, 7.7 mg of Rh₂-L3, 7.8 mg of Rh₂-L4, 9.0 mg of Rh₂-L5, 7.2 mg of Rh₂-L6, or 8.2 mg of Rh₂-L7), which corresponds in each case to ca. 9.3 µmol Rh₂ assuming an ideal composition (no defect sites and complete ligand exchange) of the coordination polymer, was loaded into a 25 mL glass bottle sealed with a septum. Then, 0.52 g (5 mmol) styrene in 13.4 g dichloromethane (CH₂Cl₂) were added. This mixture was dispersed by ultrasonication for 15 min. Then 0.057 g (0.5 mmol) EDA in 4.0 g CH₂Cl₂ were introduced via a syringe. Samples were taken after 1 min, 2.5 min, 5 min, 7.5 min, 10 min, 15 min, 20 min, 25 min, 30 min, 60 min and 120 min of reaction. The clear filtered solutions were analyzed by GC (Agilent Technologies 7820A), which was equipped with a HP-5 (30m × 0.32mm × 0.25µm) column and FID detector.

Characterization techniques

The C and H contents were determined on an Elemental Analyzer Vario EL III working in CHN

mode.

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Thermogravimetry analyses (TGA) were carried out under oxygen atmosphere (75 ml·min⁻¹) using the simultaneous thermal analyzer Netzsch STA 429. The temperature was ramped up with a rate of 10°C /min in the range between 20-800°C. The Rh contents were calculated from the TGA according to the procedure described by Kaskel and co-workers.^[17d] The theoretical Rh contents were calculated from the fraction of Rh in $[Rh_2(Ln)_2]_x$ (n = 1-7) where each TFA ligand of the parent Rh₂(TFA)₄ is replaced by ditopic ligands Ln.

Solution NMR spectra of the synthesized ligands were recorded on a Bruker Avance II spectrometer at a frequency of 300 MHz for ¹H and 75.5 MHz for ¹³C. H₂L1 was dissolved in DMF with 1-2 drops of D₂O, while H₂Ln (n=2-7) were dissolved in DMSO-d₆.

The attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were recorded on a Perkin Elmer Spectrum spotlight 200 FT-IR spectrometer with an UATR unit and 4 cm⁻¹ resolution in the range between 4000-650 cm⁻¹.

X-ray Powder diffraction (XRD) patterns were recorded on a X-ray powder diffractometer (STADIP, Stoe & Cie GmbH, Darmstadt) in transmission geometry employing Cu K α_1 radiation (Ge[111]-monochromator, λ =1.54060 Å). The sample was placed on a flat sample holder and measured in the 2 θ range of 4 - 60°.

Scanning electron microscopy (SEM) was performed on a Philips XL30 S-FEG microscope to probe the microstructure of the coordination polymers with 200 K magnification under electron beam of 25 kV.

¹H \rightarrow ¹³C CP MAS NMR spectra were measured at room temperature on a 7 Tesla Bruker Avance III HD spectrometer equipped with a 4 mm broadband double-resonance probe at a frequency of 75.47 MHz for ¹³C and 300.13 MHz for ¹H. Cross polarization (CP) experiments were performed using a ¹H excitation pulse of 3.5µs and a contact time of 3 ms for polarization transfer at a spinning rate of 6 kHz. Spectra were recorded with a recycle delay of 1.5 s and 6000-48000 scans. Two-pulse phase modulation decoupling employing 15° phase jumps (tppm15)^[25] was employed during data aquistion. Spectra were referenced to tetramethylsilane (TMS, $\delta = 0$ ppm) employing adamantane ($\delta_{CH2} = 38.5$ ppm) as external standard.

¹⁹F MAS NMR spectra were recorded at 14 Tesla with a Bruker Avance III spectrometer at a frequency of 564.2 MHz employing a 1.3 mm MAS probe. Spectra were measured at a spinning frequency of 40 kHz and 256 transients with a recycle delay of 5 s. The ¹⁹F chemical shift scale was referenced to CFCl₃ ($\delta = 0$ ppm), and trifluoroacetic acid ($\delta = -76.5$ ppm) was employed as external standard. Quantitative analysis of ¹⁹F MAS NMR was carried out according to ref.^[8]

The diffusion reflection ultraviolet-visible spectrum (DR-UV-vis) was recorded on a Shimadzu UV 2450 spectrophotometer, and BaSO₄ was employed as reference.

The X-ray photoelectron spectroscopy (XPS) was measured on a ULVAC PHI PHI5000 Versa Probe using the Al K α radiation source. The binding energy of the C1*s* peak at 284.8 eV was employed to reference the spectra.

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Result and discussion

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Preparation and basic characterization

Seven novel dirhodium coordination polymers were prepared by ligand substitution between $Rh_2(TFA)_4$ and H_2Ln (n = 1-7) (Scheme 2).^[18, 24] In a basic characterization step their compositions were investigated. The differences between experimental rhodium contents and theoretical ones are less than 20 %, depending on the ligand system employed in the synthesis. This suggests the presence of guest molecules and/or incomplete ligand exchange.^[17c, 17d, 18] The occurrence of fluorine containing species in the obtained dirhodium coordination polymers, such as remaining trifluoroacetate coordinating the dirhodium units, is confirmed by the ¹⁹F MAS spectra (Figure 3) of H₂Ln (n = 1-7), which allow a quantitative analysis of the fluorine content. Additionally, partial hydrolysis of ester groups of the ditopic ligands is assumed for Rh₂-L6 and Rh₂-L7. Such a hydrolysis of ester groups was also observed by Yamada et al. during the preparation of hydroxyl functional MOFs.^[23]



Scheme 2. Preparation of modified terephthalic acids with ether (or ester) side chains and synthesis of dirhodium coordination polymers.

The morphology of the Rh₂-Ln frameworks was investigated by scanning electron microscopy (SEM) and X-ray powder diffraction (XRD). All catalysts exhibit a layered structure as shown in the SEM images (ESI Figure S11). The XRD patterns (ESI Figure S12) do not show sharp Bragg reflections, indicating a lack of long range order in the material, caused by a random stacking of the dirhodium-ligand framework layers. This observation is similar to our previous one for the Rh₂-bdc (bdc = benzene-1,4-dicarboxylate) coordination polymer, where also a disordered stacking of the layers was obtained.^[18]

ATR-FTIR, ¹H→¹³C CP MAS NMR and ¹⁹F MAS NMR

The ATR-FTIR spectra of Rh₂-Ln (n = 1-7) are displayed in Figure 1. The adsorption bands at 3064 ($v^{s}_{=CH}$), at 1635 and 1499 (skeletal vibrations of phenyl ring $v_{C=C}$), as well as at 850 cm⁻¹ (out-of plane C-H bending $\delta_{=CH}$) confirm the presence of the phenyl ring in the terephthalate

backbone. The bands at 1582 (v^{s}) and 1405 (v^{as}) refer to symmetric and asymmetric vibrations/C8CY01493K of COO⁻.^[18, 22a, 26] Bands for COOH in the parent acid (ESI Figure S1) have disappeared after ligand substitution, such as the broad band of O-H stretching (3200-2700 cm⁻¹), the overtone or

combination band of C-O (2700-2300 cm⁻¹) and the C=O stretching band of COOH (1677 cm⁻¹). These observations clearly indicate the success of ligand substitution between $Rh_2(TFA)_4$ precursor and the bitopic linkers.

The presence of side chains is revealed by the following adsorption bands. For Rh₂-Ln (n = 1-7), the bands between 2938 and 2834 cm⁻¹ refer to the stretching vibrations (v^{as}_{CH} and v^{s}_{CH}) of -CH₃ and -CH₂, while their scissoring vibrations (δ_{CH3} and δ_{CH2}) appear at around 1450 and 1354 cm⁻¹. For Rh₂-Ln (n = 1-5) containing ether side chains, the peaks at ca.1197 and 1127 cm⁻¹ assign the asymmetric and symmetric vibrations of C-O-C in the ether side chains. In the case of Rh₂-Ln (n =6, 7), the bands at 1754 and 1744 cm⁻¹ refer to C=O vibrations in the ester side chains. Finally, the adsorption band between 1200 and 1160 cm⁻¹ are attributed to the asymmetric vibration of the C-C(=O)-O groups.



Figure 1. ATR-FTIR spectra of dirhodium coordination polymers, Rh₂-L1 (a), Rh₂-L2 (b), Rh₂-L3 (c), Rh₂-L4 (d), Rh₂-L5 (e), Rh₂-L6 (f) and Rh₂-L7 (g). Note: No adsorption bands were observed between 2600 and 1800 cm⁻¹.

The ¹H \rightarrow ¹³C CP MAS NMR spectra of the various Rh₂-Ln (n = 1-7) coordination polymers are shown in Figure 2. The chemical shift at 185 ppm, which is visible in all spectra, is assigned to COO⁻ groups, coordinated to the dirhodium unit.^[18] The signals at 116 and 127 ppm are characteristic for the phenyl ring of the terephthalate backbone. These results corroborate the

ATR-FTIR data and verify the presence of the terephthalate backbone, which coordinates the /C8CY01493K dirhodium units via the carboxylate groups in all obtained dirhodium coordination polymers.

Additionally, a signal at ca. 172 ppm is visible in the spectra of Rh₂-Ln (n = 1=4, Figure 2a-d), which most probably stems from the carboxylate group of the trifluoroacetate.^[7b, 18] This is a further indication of incomplete ligand substitution during the synthesis.

Information on the ether side chains of Rh₂-Ln (n = 1-5) are obtained in the ¹H \rightarrow ¹³C CP MAS spectra. In detail, the signals at ca. 151 ppm (Figure 2a-e) refer to the phenolic carbon involved in the ether group (C_{Ph}-O-). The chemical shift at 55 ppm (Rh₂-L1, Figure 2a) is attributed to - O-CH₃. Signals at 65 ppm (Rh₂-L2, Figure 2b), 70 ppm (Rh₂-L3, Figure 2c), 70 and 58 ppm (Rh₂-L4, Figure 2d), and 70 ppm (Rh₂-L5, Figure 2e) refer to -O-CH₂- groups. Since in Rh₂-L4, the ether side chain (-O-(CH₂)₂-O-CH₃) contains two ether groups, two different resonance peaks (70 and 58 ppm) appear in the spectrum. The resonance at 14 ppm in the spectrum of Rh₂-L2 (Figure 2b) is clearly assigned to methyl carbons in the -OCH₂CH₃ side chain. In the aliphatic region of Rh₂-L3 (Figure 2c), the signals at 31, 19 and 13 ppm are attributed to β -methylene, γ -methylene and methyl carbons in the side chain appear at 136 and 127 ppm with corresponding spinning side bands. The latter one overlaps with the signal of the phenyl carbon in the terephthalate backbone but can be clearly identified via the spinning side bands marked with +.

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Figure 2. ${}^{1}H \rightarrow {}^{13}C$ CP MAS NMR spectra of dirhodium coordination polymers, Rh₂-L1 (a), Rh₂-L2 (b), Rh₂-L3 (c), Rh₂-L4 (d), Rh₂-L5 (e), Rh₂-L6 (f) and Rh₂-L7 (g).

Note: The peaks marked with # and + are spinning side bands of the phenyl group (136 and 127 ppm) in the ester side chain of Rh₂-L5. The spectra do not indicate signals from ethyl acetate. Spectra are not normalized on the number of scans to enable the visibility of signals also in cases of lower S/N ratio.

In the case of dirhodium coordination polymers containing ester side chains (Figure 2f-g), Rh₂-L6 and Rh₂-L7 exhibit the typical -(C=O)-O- signal at ca. 174 ppm. The phenolic carbon signals in the ester group (C_{Ph}-O-) emerge at 146 ppm. In addition, two small peaks at ca. 140 and 156 ppm are visible in these spectra, also referring to phenolic carbon. This underlines our assumption that the ester bond was partly hydrolyzed, which changes the symmetry of the phenyl ring of the terephthalate backbone. Such a symmetry break of the terephthalate is also reflected by the broad signal in the region of 116-127 ppm. In the case of Rh₂-L6, an additional signal appears at 193 ppm, which indicates the presence of adsorbed acetic acid or coordinated acetate.^[7a, 18] This further strengthens the hypothesis of the partial decomposition of the ester side chains during the catalyst synthesis.

¹⁹F MAS NMR (Figure 3(I)) provides information on fluorine containing defect sites occurring in the dirhodium coordination polymers. For Rh₂-L1 and Rh₂-L2, a ¹⁹F signal centered at ca. -78 ppm is obtained, which contains a weak shoulder peak at -75.5 ppm. The former signal most probably refers to a TFA group located at a position *trans*- to a ditopic linker molecule (Figure 3(IIa)), while the latter signal refers to a TFA group located at *trans*-position to another TFA group (Figure 3(IIb)).^[18]

There are some small differences in the chemical shift values of the ¹⁹F MAS NMR signals. For Rh₂-Ln (n = 3-7) coordination polymers, only a single, symmetric ¹⁹F signal centered between -76 and -78 ppm is obtained. For the Rh₂-Ln (n = 1, 2) coordination polymers a superposition of two lines is observed. A weak signal centered at 76 ppm and a strong signal centered at 77.5 ppm. The most probably reason for this difference are heavy atom effects, similar to the γ -gauche effect,^[27] which cause a stronger shielding of the fluorine nuclei in the coordination polymers with the more bulky side chains Rh₂-Ln (n = 3-7).

A quantitative analysis of the ¹⁹F MAS spectra was carried out to determine the amount of TFA defect sites in the coordination polymers. In comparison, the content of fluorine in the coordination polymers Rh_2Ln (n = 3-7) (in the range between 0.1-0.7 mmol/g) is much lower than that in Rh_2 -Ln (n = 1, 2) (2.1-4.9 mmol/g). This let us assume that TFA groups are more easily replaced by terephthalate derivatives containing bulky side chains. To verify this hypothesis, advanced experimental and theoretical efforts are required to understand the kinetics of the ligand exchange as function of side chain, which are beyond the scope of the present work.

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Figure 3. (I) ¹⁹F MAS NMR spectra of dirhodium coordination polymers, Rh₂-L1 (a), Rh₂-L2 (b), Rh₂-L3 (c), Rh₂-L4 (d), Rh₂-L5 (e), Rh₂-L6 (f) and Rh₂-L7 (g). Spectra were referenced to CFCl₃ employing trifluoroacetic acid (δ = -76.5 ppm) as external standard. (II) Illustration of defect sites: (a) TFA group located at a position *trans*- to a ditopic linker and (b) TFA group located at *trans*-position to another TFA group.

DR-UV-vis and XPS

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To investigate the chemical environment of the dirhodium units in the obtained coordination polymers, diffuse reflectance ultraviolet-visible (DR-UV-vis) spectra for Rh₂-Ln (n=1-7) were recorded (Figure 4). All spectra show two bands which are centered at 605 or 620 nm (band I) and ca. 450 nm (band II), respectively. While band I represents Rh-Rh $\pi^* \rightarrow$ Rh-Rh σ^* transitions, band II refers to Rh-Rh $\pi^* \rightarrow$ Rh-O σ^* transitions, according to ref.^[26c] These results confirm that the dirhodium unit is maintained during the ligand exchange process. More interestingly, the position of band I depends on the ligand system employed in the synthesis. In detail, band I in Rh₂-L1, Rh₂-L4, Rh₂-L6 and Rh₂-L7 is centered at about 605 nm, while those in Rh₂-L2, Rh₂-L3 and Rh₂-L5 appear at ca. 620 nm.

To understand this observation, simple model systems were investigated (see ESI Figure S13-16). The solution-state UV-vis spectrum of parent $Rh_2(TFA)_4$ was recorded in dichloromethane, a weak coordinating solvent. Various amounts of ethyl ether (Et₂O) were introduced yielding different molar ratios of $Rh_2(TFA)_4/Et_2O$ (see ESI Figure S13). For this model, a 15 nm blue shift of band I is observed along adding of Et₂O. Similar observations are found for the oxygenadducts of $Rh_2(TFA)_4$ with ethanol (29 nm blue shift, see ESI Figure S14), acetone (25 nm blue shift, see ESI Figure S15), ethyl acetate (15 nm blue shift, see ESI Figure S16 and ref. ^[18]) These observations in solution lead to the assumption that the interaction between Rh_2 unit and oxygen atom of the ligand system influences the position of band I in the spectra of the dirhodium coordination polymers, and vice versa the position of band I represents the

interaction between the Rh₂ unit and oxygen atom of the ligand system.

According to the different positions of band I, the obtained dirhodium coordination polymers are classified into two groups, namely *Group 1* (Rh₂-L1, Rh₂-L4, Rh₂-L6 and Rh₂-L7) and *Group 2* (Rh₂-L2, Rh₂-L3 and Rh₂-L5). When increasing the length of the ether side chain from methoxy (Rh₂-L1, *Group 1*) to ethoxy (Rh₂-L2, *Group 2*) and then to n-butyloxy (Rh₂-L3, *Group 2*), their corresponding band I shifts from 605 nm (Figure 4a) to 620 nm (Figure 4b,c). On the contrary, band I shifts back to 605 nm by replacing the n-butyloxy group (Rh₂-L3, *Group 2*) with the 1-methoxy-2-ethoxy (CH₃-O-(CH₂)₂-O-) group (Rh₂-L4, *Group 1*). This implies that the wave length of band I is related to the position of the O atom in the ether side chain. Terminal methoxy groups (in Rh₂-L1 and Rh₂-L4, *Group 1*) cause a blue shift of band I. In contrast, terminal aliphatic (ethyl, n-butyl) or aromatic (phenyl) groups (Rh₂-L2, Rh₂-L3 and Rh₂-L5) cause a red shift of band I, which represents reduced Rh₂/O interlayer interactions in these catalyst systems.

For Rh₂-L6 and Rh₂-L7 (*Group 1*), the partial hydrolysis of the ester groups leads to phenolic hydroxyl groups that interact with the dirhodium moieties in the neighboring layers, which is underlined by the blue shift of band I for these catalysts.



Figure 4. DR-UV-vis spectra of dirhodium coordination polymers, Rh₂-L1 (a), Rh₂-L2 (b), Rh₂-L3 (c), Rh₂-L4 (d), Rh₂-L5 (e), Rh₂-L6 (f) and Rh₂-L7 (g).

As a second approach to investigate the chemical environment of the dirhodium units in the obtained dirhodium coordination polymers, high-resolution XPS spectra in the region of 305-320 eV were recorded (Figure 5). In all samples, the electron binding energies for Rh3 $d_{5/2}$ are in the range between 308.9 - 309.2 eV and those for Rh3 $d_{3/2}$ are in the range of 313.8 - 314.0 eV. These values clearly indicate that the oxidation state of the dirhodium unit is +2.^[18, 26c] Together with the above discussed DR-UV-vis data, these results reveal that the dirhodium moieties stayed intact during the ligand replacement process. For comparison, the high-resolution XPS spectrum of the parent Rh₂(TFA)₄ was measured (see ESI Figure S18).^[18] The obtained binding energies for Rh3 $d_{5/2}$ and Rh3 $d_{5/2}$ are 310.2 eV and 314.9 eV, respectively.

These values are lower by 0.9-1.3 eV compared to those of the dirhodium coordination /C8CY01493K polymers. This is a further indication for the ligand exchange that occurred during the synthesis of the coordination polymers.

The electron binding energy is sensitive to the chemical environment of the dirhodium units as shown for the different dirhodium coordination polymers in Figure 5. In detail, the Rh3*d*_{5/2} binding energy of Rh₂-L1, Rh₂-L4, Rh₂-L6 and Rh₂-L7 (*Group 1*) is 308.9 eV, which is 0.3 eV lower than that of Rh₂-L2, Rh₂-L3 and Rh₂-L5 (*Group 2*). The Rh3*d*_{3/2} binding energy of the former ones is ca. 313.8 eV, which is 0.2 eV lower than that of the latter ones. These observations underline that the chemical environment of the dirhodium unit is influenced by the side chain of the bitopic ligand in the dirhodium coordination polymers. Interestingly, the obtained tendency is in excellent agreement with the DR-UV-vis data. The Rh3*d*_{5/2} and Rh3*d*_{3/2} binding energies can be used to study the Rh₂/O interaction as well. The electron density of the rhodium atom increases upon interaction with an O atom of the ether groups that act as electron donor which is the case for the Rh₂-Ln (n = 1, 4, 6, 7, *Group 1*, black line in Figure 5) coordination polymers. On the other hand, the side chains of Rh₂-L3 and Rh₂-L5 (*Group 2*, red line in Figure 5) shield the O atom from the dirhodium unit in the neighboring layers and thus lower the electron density. This yields a higher binding energy of the dirhodium unit.



Figure 5. XPS of dirhodium coordination polymers in high-resolution mode, Rh₂-L1 (a), Rh₂-L2 (b), Rh₂-L3 (c), Rh₂-L4 (d), Rh₂-L5 (e), Rh₂-L6 (f) and Rh₂-L7 (g).

Catalytic Tests

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The cyclopropanation between styrene and EDA (Figure 6 (I)) was employed to evaluate the catalytic performances of the seven novel dirhodium coordination polymers. Employing an excess of the substrate styrene, as major products *cis*- and *trans*-1-ethoxycarbonyl-2-phenylcyclopropane are formed and the amount of side products of this reaction such as fumarates is less than 7%. The diastereoselectivities (*cis/(cis+trans)*) are listed in Table 1. For all catalysts insignificant diastereoselectivity is obtained, which is not very surprising since the homogeneous Rh₂(TFA)₄ catalyst shows also no diastereoselective control.^[7-8, 18] Nevertheless,

small deviations of the diastereoselectivities were observed for dirhodium coordinations/C8CY01493K polymers bearing various side chains. As the electrophilicity of the dirhodium unit affects the diastereoselectivity,^[4a] the impact of electron properties of side chains on the dirhodium unit may account for these tiny variations of diastereoselectivity for the different dirhodium coordination polymers.

The catalytic performance of dirhodium coordination polymers are compared in Figure 6 (II), and product yields at a reaction time of 120 min are summarized in Table 1. The corresponding turnover frequencies (TOFs), calculated from the TGA determined Rh₂-amounts (Rh% TGA), are collected in the ESI (Table S1). The catalytic activity shows the following trend: $Rh_2-L_2 > 2$ $Rh_2-L3 > Rh_2-L6 > Rh_2-L5 >> Rh_2-L1 \approx Rh_2-L4 \approx Rh_2-L7$. For dirhodium coordination polymers containing ether side chains, this trend illustrates that the catalysts in Group 2 (Rh₂-Ln; n = 2, 3, 5) exhibit higher activity than the catalysts in *Group 1* (Rh₂-L1 and Rh₂-L4). In detail, by replacing the methoxy side chains (in Rh₂-L1, Group 1) with the n-butyloxy groups (in Rh₂-L3, Group 2), the yield of products at 120 min increases from 11% to 75%. However, the yield drops down to 10% when substituting n-butyloxy groups (in Rh₂-L3, Group 2) with 1-methoxy-2-ethoxy (CH₃-O-(CH₂)₂-O-) groups (in Rh₂-L4, Group 1), although in both catalysts the length of side chains is comparable. This shows that the terminal groups in the side chains drastically influence the catalytic performance of the dirhodium coordination polymers. These obtained trends of catalytic performances are in excellent agreement with the interlayer Rh₂/O interactions in these catalysts discussed by DR-UV-vis and XPS. Strong interlayer Rh₂/O interactions result in low catalytic efficiency. Related catalysts models are illustrated in Figure 7. According to the catalytic mechanism proposed in ref. ^[4a], an intermediate rhodium carbenoid has to be formed after axial coordination of the substrate to the dirhodium unit. Thus, it is feasible that the hindrance of forming this rhodium carbenoid by strong interlayer Rh/O interactions reduces the catalytic performance of the dirhodium coordination polymer. For dirhodium coordination polymers with ethers as side chains, Rh₂-L1 and Rh₂-L4 (Group 1) possessing strong interlayer Rh₂/O interactions (Figure 7, Model 1) exhibit the lowest catalytic performances. In contrast, Rh₂-L2, Rh₂-L3 and Rh₂-L5 (Group 2) show high catalytic efficiency, most probably due to their weak interlayer Rh₂/O interactions (Figure 7, Model 2 and 3).

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Figure 6. (a) Schematic drawing of the model cyclopropanation of styrene with EDA. (II) Time dependent total yield of *cis*- and *trans*-isomer obtained with the Rh₂-Ln (n = 1-7) coordination polymers. Rh₂-L1 (a), Rh₂-L2 (b), Rh₂-L3 (c), Rh₂-L4 (d), Rh₂-L5 (e), Rh₂-L6 (f) and Rh₂-L7 (g).

Among the catalysts in *Group 2* (Rh_2 -L2, Rh_2 -L3 and Rh_2 -L5), Rh_2 -L2 exhibits the highest efficiency while Rh_2 -L5 shows lowest performance. This may be explained by the additional steric effect of the side chain (Figure 7, Model 3). The bulky side chains (n-butyloxy in Rh_2 -L3 and benzyloxy in Rh_2 -L5) render the frameworks of the catalysts more crowded than that containing ethoxy side chains (Rh_2 -L2). This hinders the substrate to reach catalytic sites and lowers the catalytic performance.

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Catalysts	Yield ^[a] (%)	Diastereoselectivity ^[a] (<i>cis/(cis+trans</i>)) (%)	DR-UV-vis (band I) (nm)	XPS (Rh3 <i>d</i> 5/2) (eV)	Structure Model
Rh ₂ -L1	11	54	605 ^[b]	308.9 ^[b]	Model 1
Rh ₂ -L2	91	48	620 ^[c]	309.2 ^[c]	Model 2
Rh ₂ -L3	75	49	620 ^[c]	309.2 ^[c]	Model 3
Rh ₂ -L4	10	54	605 ^[b]	308.9 ^[b]	Model 1
Rh ₂ -L5	27	56	620 ^[c]	309.2 ^[c]	Model 3
Rh ₂ -L6	35	49	605 ^[b]	308.9 ^[b]	Model 1
Rh ₂ -L7	8	54	605 ^[b]	308.9 ^[b]	Model 1
^[a] Yield and diastereoselectivity obtained at a reaction time of 120 min for freshly prepared catalysts; ^[b] catalysts refer to <i>Group 1</i> ; ^[c] catalysts refer to <i>Group 2</i> .					

 Table 1. Comparison of the results obtained from UV-VIS and XPS with the catalytic performances of the coordination polymers.

The discussed models are in principle also suitable for the explanation of the reactivity of Rh₂-L7. In comparison with Rh₂-L2, Rh₂-L6 exhibits lower catalytic efficiency due to the strong interaction between the dirhodium node and phenolic oxygen atom which is a result of partial decomposition of the ester side chain during the catalyst preparation. The higher activity of Rh₂-L6 compared to Rh₂-L7 most probably refers to the steric of the ligand system, which is higher for Rh-L7 compared to Rh-L6.

A closer inspection of the catalytic yield of the three efficient catalysts (Rh₂-L2, Fig.6b; Rh₂-L3, Fig.6c and Rh₂-L6, Fig.6f) shows that they have practically the same initial conversion rate up to ca 10 minutes (slope of the curves). After this time the conversion rates of Rh₂-L3 and in particular Rh₂-L6 go down. There are two possible explanations of these observation, which are not mutually exclusive. On the one hand this effect can be caused by different degradation rates of the catalyst and on the other hand it can be caused by (partial) blocking of active sites or the access to the active sites by product molecules.

Finally, the heterogeneous nature of the coordination polymer catalysts was studied exemplarily for Rh₂-L2. ESI Figure S19(I) shows that after removal of the catalyst from the reaction mixture no conversion is obtained in the filtrated solution. Moreover, the rhodium content in this solution was found to be less than 0.2 ppm according to ICP-MS measurement (see ESI Table S1). Both outcomes clearly underline that the catalytic active rhodium species are bound in the coordination polymer and are not dissolved in the reaction medium.

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Figure 7. Schematic models to illustrate possible interlayer interactions in Rh₂-L_n (n = 1-7) catalysts induced by side chains: Model 1 is representative for Rh₂-L_n (n = 1, 4, 6, 7). Model 2 is representative for Rh₂-L_n (n = 2). Model 3 is representative for Rh₂-L_n (n = 3, 5). Note that a parallel layer stacking is used to simplify the representation of the interactions. For the real coordination polymer, a random orientation of the planes in the stack is deduced from the XRD data.

Conclusion

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A series of modified terephthalic acid derivatives containing either ether side chains or ester side chains, respectively, were obtained and employed to synthesize seven novel dirhodium coordination polymers (Rh₂-Ln). ATR-FTIR and ¹H \rightarrow ¹³C CP MAS NMR results confirmed the success of ligand exchange and coordination between the dirhodium unit and carboxylate group. Incomplete ligand substitution was verified via ¹H \rightarrow ¹³C CP MAS NMR, ¹⁹F MAS NMR and XPS. The random stacking of the Rh₂-Ln frameworks was revealed by SEM and XRD. The

relationship between catalytic activity and Rh₂/O interactions as well as steric effects of the /C8CY01493K

ligand systems were analyzed for the cyclopropanation of styrene with EDA. Reduced Rh_2/O interactions and steric effects were found to improve the catalytic performance of dirhodium coordination polymers. These results give essential insights on the influence of the ligand system on the catalytic performance of coordination polymers, which will help to design coordination polymers with efficient catalytic performance in future.

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