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

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Content

1. ATR-FTIR of synthesized ditopic ligands

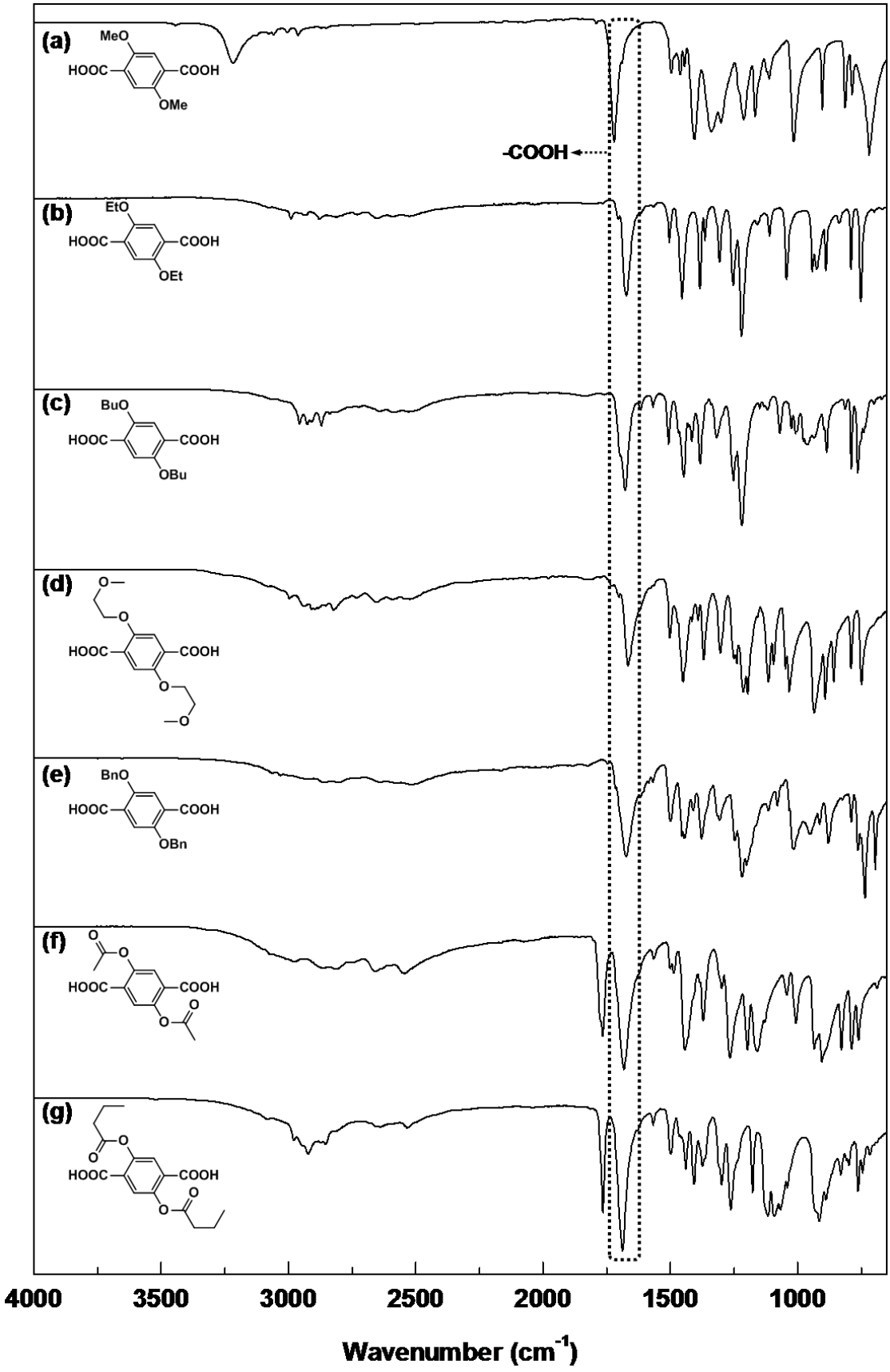

Figure S1. ATR-FTIR of H_2L1(a), H_2L2(b), H_2L3(c), H_2L4(d), H_2L5(e), H_2L6(f) and H_2L7(g).

2. Solution-state NMR of synthesized ditopic ligands

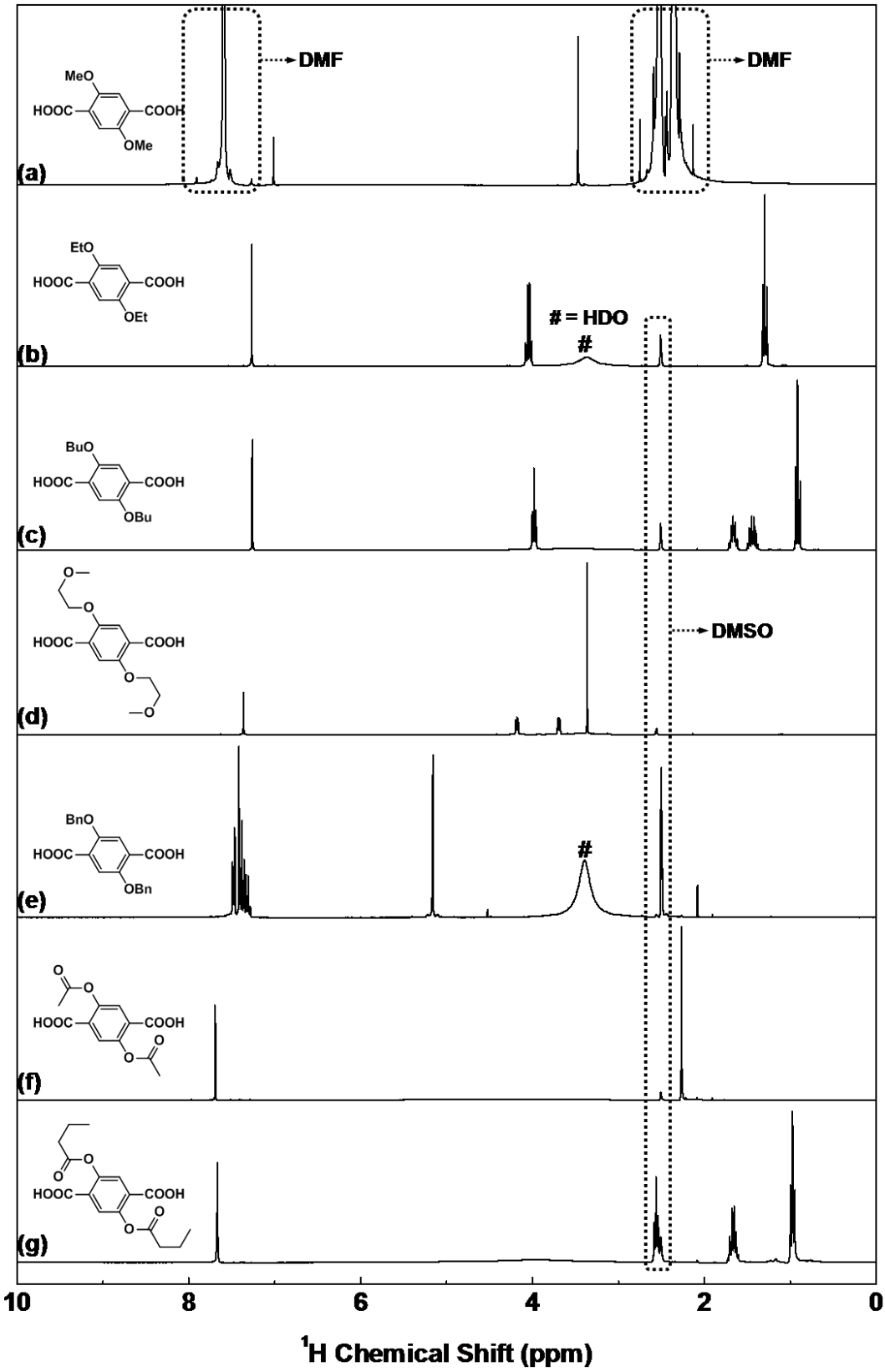

Figure S2. ^{1}H solution-state NMR of H_2L1(a), H_2L2(b), H_2L3(c), H_2L4(d), H_2L5(e), H_2L6(f) and H_2L7(g).

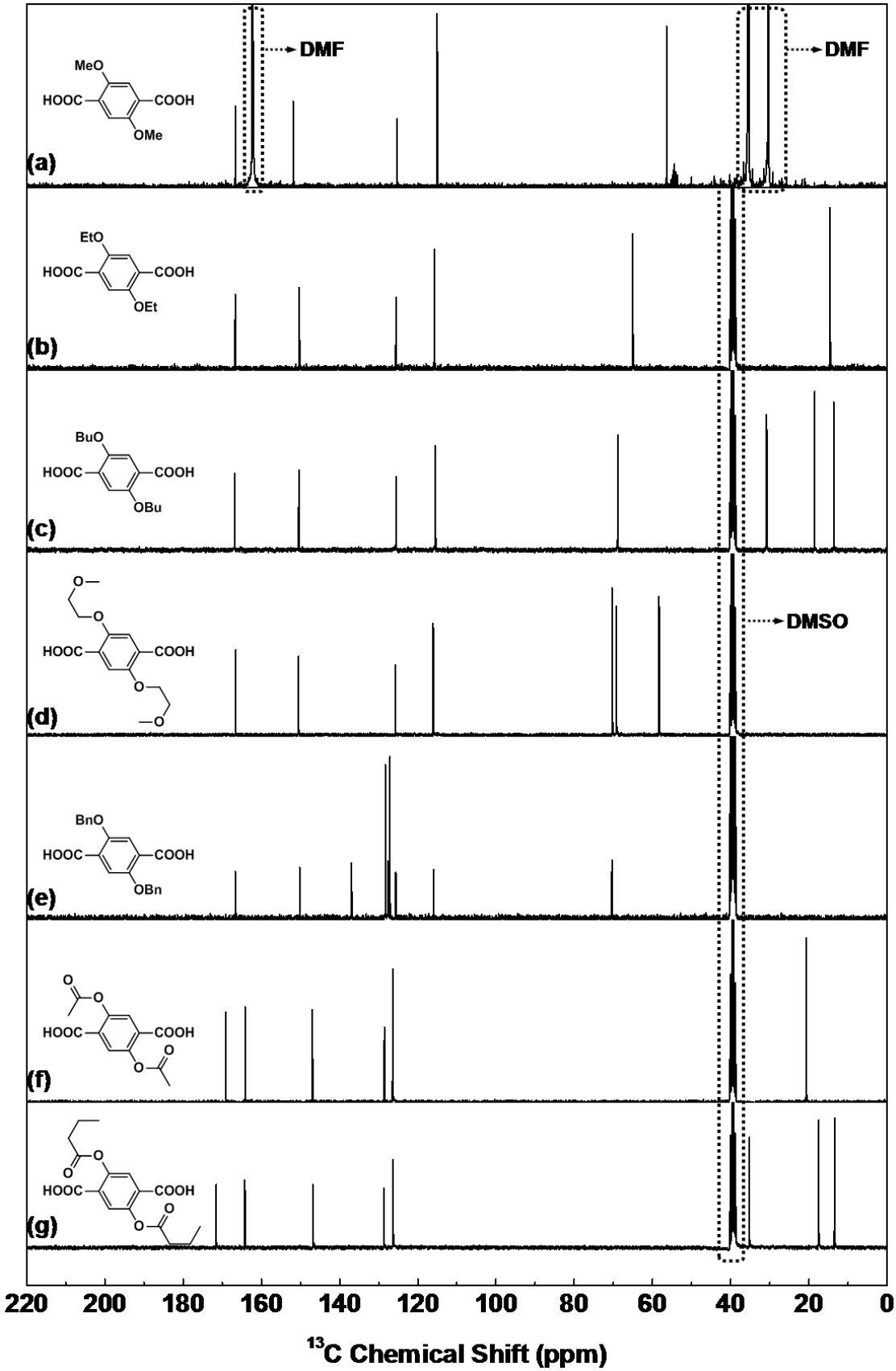

Figure S3. ^{13}C solution-state NMR of H_2L1(a), H_2L2(b), H_2L3(c), H_2L4(d), H_2L5(e), H_2L6(f) and H_2L7(g). Note: H_2L1 was dissolved in DMF with 1–2 drops of D_2O, while H_2Ln (n = 2–7) were dissolved in DMSO-d_6.

Experimental Details:

^{1}H and ^{13}C solution-state NMR spectra were recorded on a 7 T Bruker Avance II 300 spectrometer corresponding to frequencies of 299.91 MHz for ^{1}H and 75.41 MHz for ^{13}C. Typically, ^{1}H spectra were recorded with single pulse excitation employing a 30° excitation pulse of ca. 4.4 μs, a relaxation delay of 1 s and 32-64 scans. ^{13}C spectra were recorded with single pulse excitation employing a 30° excitation pulse of ca. 3.1 μs, a relaxation delay of 0.5 s and 600-1500 scans. Protons were decoupled during data acquisition employing the waltz16 [1] sequence.

3. TG-DTA analyses

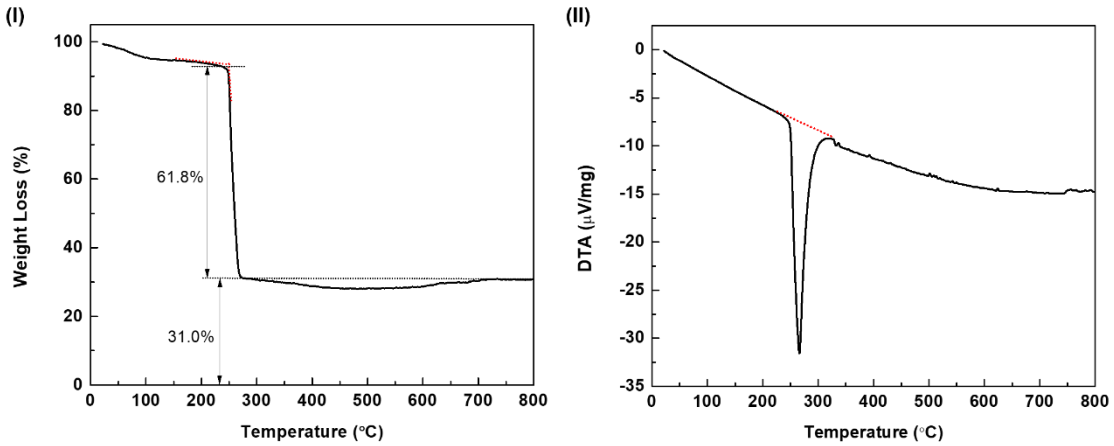

Figure S4. TG curve (I) and DTA curve (II) of Rh_2-L1 under O_2 atmosphere.

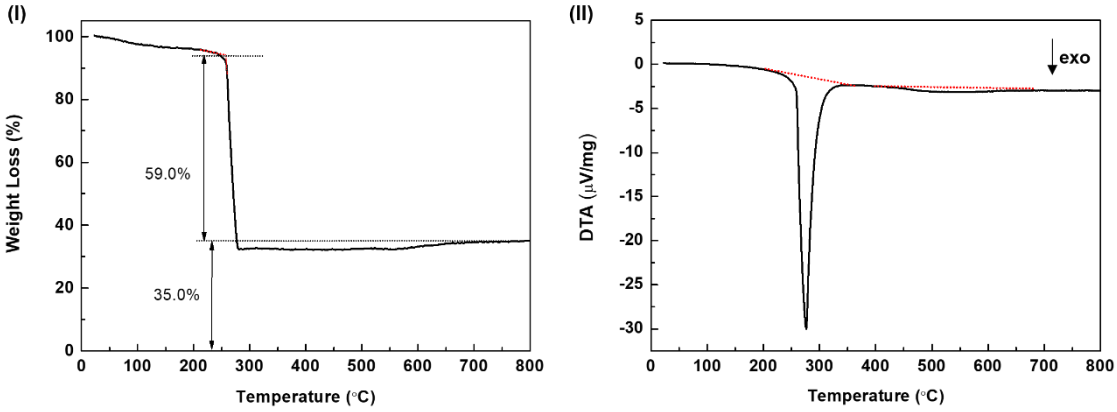

Figure S5. TG curve (I) and DTA curve (II) of Rh_2-L2 under O_2 atmosphere.

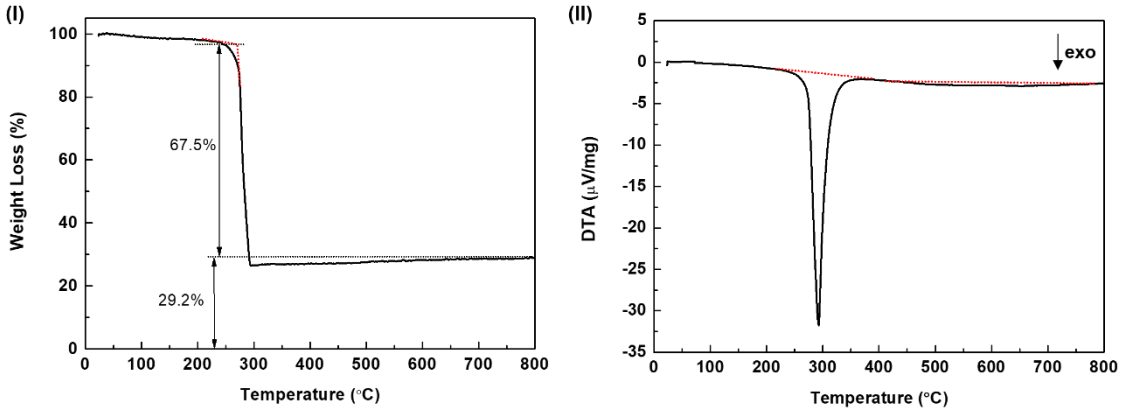

Figure S6. TG curve (I) and DTA curve (II) of Rh_2-L3 under O_2 atmosphere.

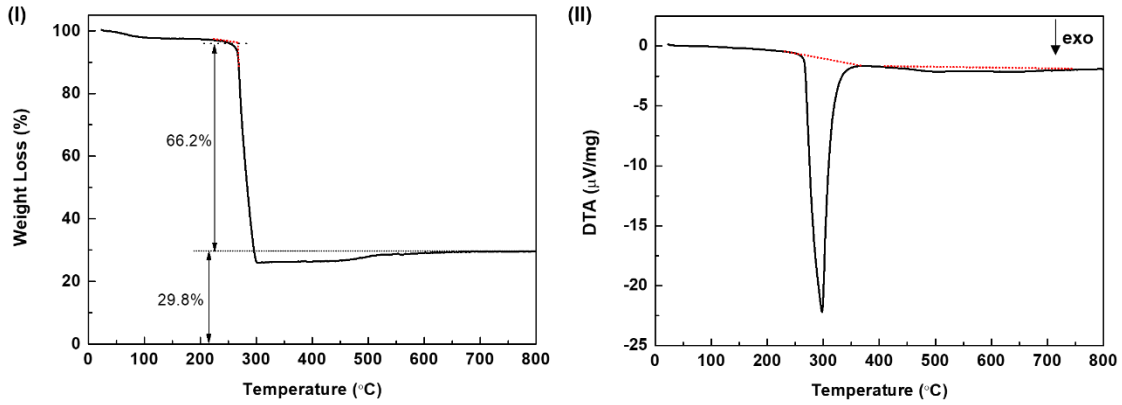

Figure S7. TG curve (I) and DTA curve (II) of Rh_2-L4 under O_2 atmosphere.

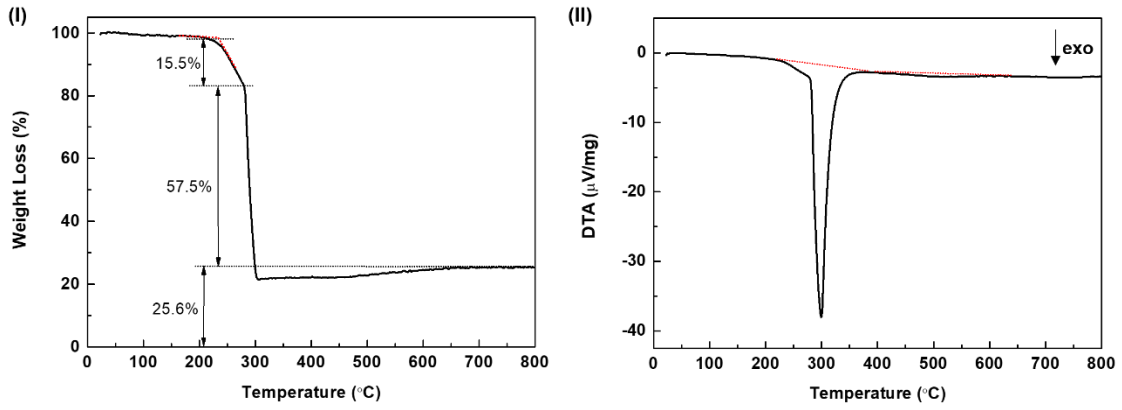

Figure S8. TG curve (I) and DTA curve (II) of Rh_2-L5 under O_2 atmosphere.

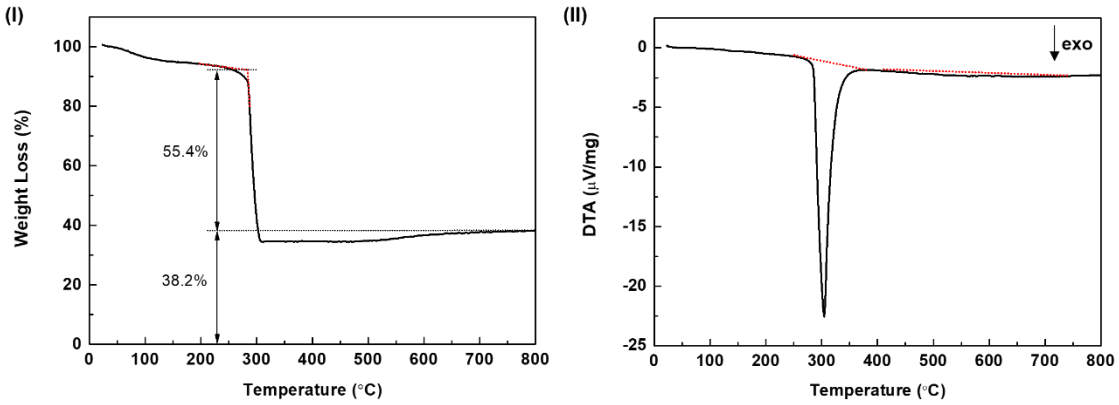

Figure S9. TG curve (I) and DTA curve (II) of Rh_2-L6 under O_2 atmosphere.

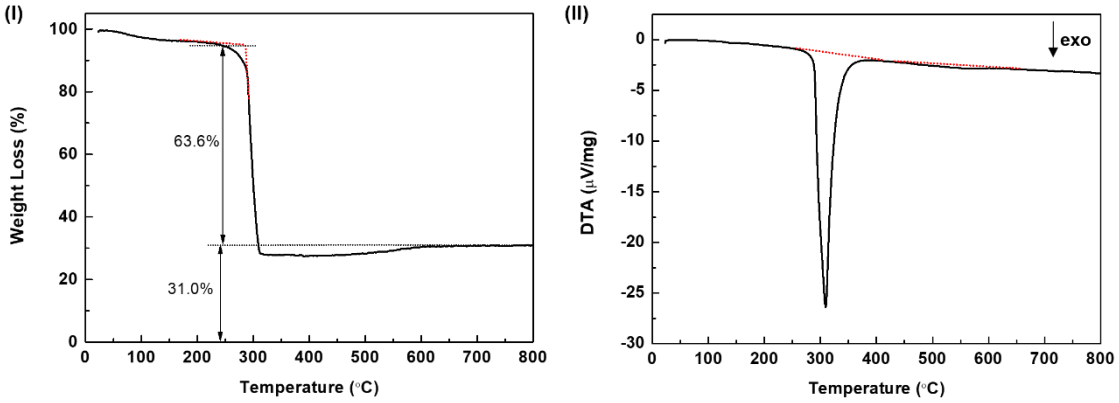

Figure S10. TG curve (I) and DTA curve (II) of Rh_2-L7 under O_2 atmosphere.

4. SEM and XRD

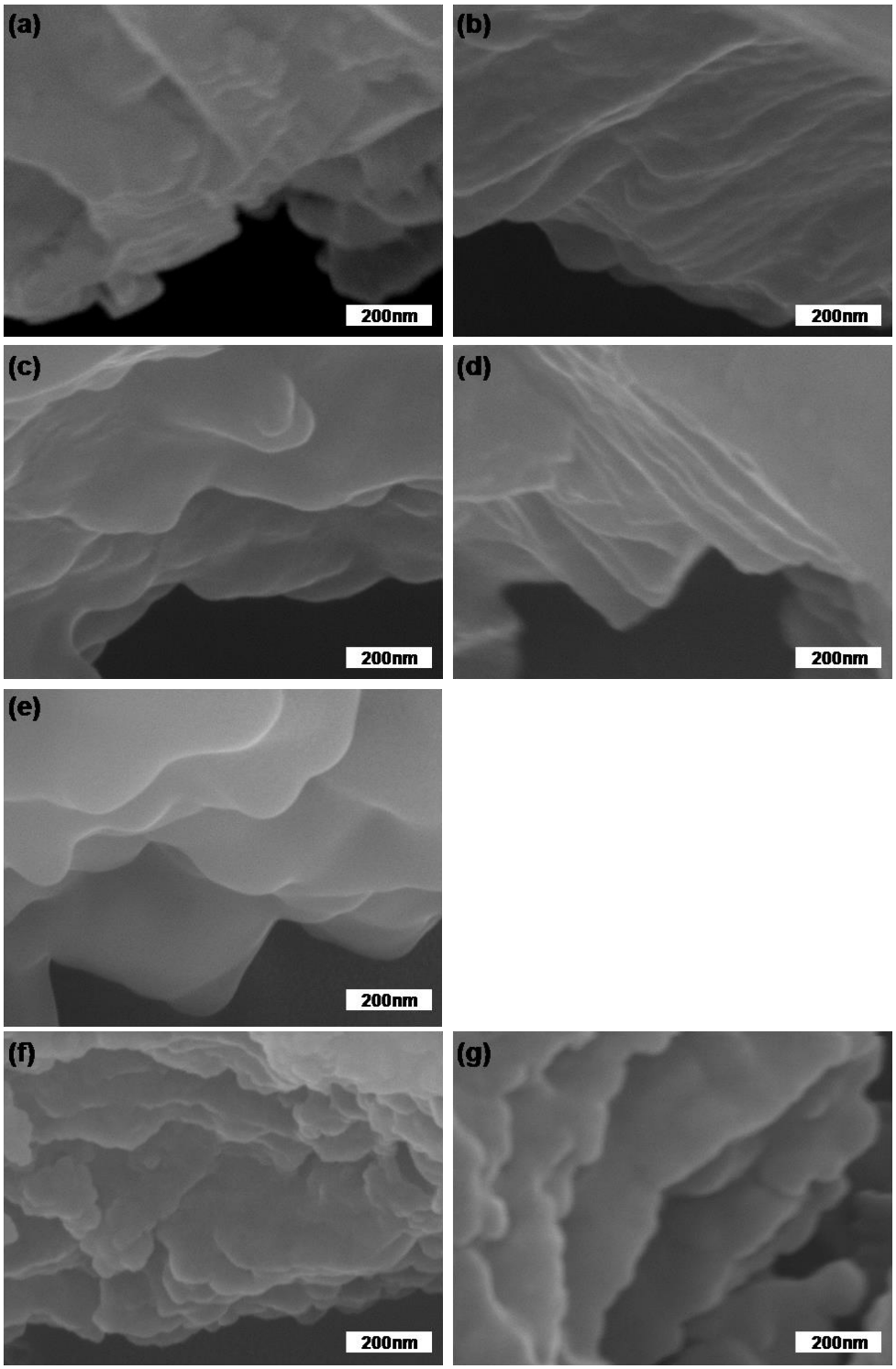

Figure S11. SEM of Rh_2-L1(a), Rh_2-L2(b), Rh_2-L3(c), Rh_2-L4(d), Rh_2-L5(e), Rh_2-L6(f) and Rh_2-L7(g).

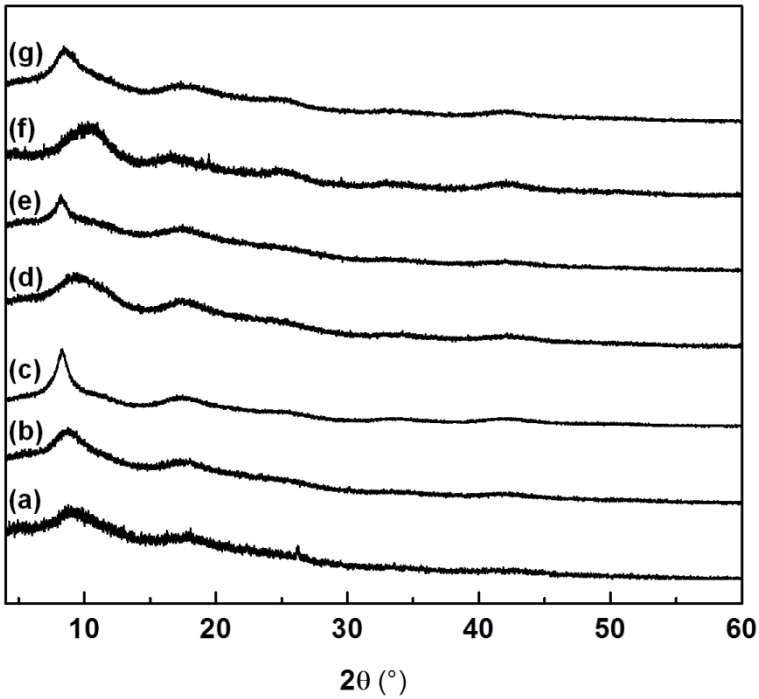

Figure S12. XRD patterns of Rh_2-L1(a), Rh_2-L2(b), Rh_2-L3(c), Rh_2-L4(d), Rh_2-L5(e), Rh_2-L6(f) and Rh_2-L7(g).

5. UV-vis spectroscopy

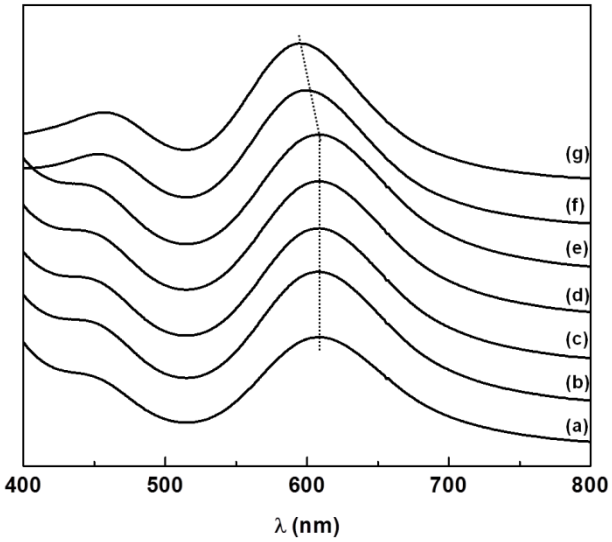

Figure S13. UV-vis spectrum of $Rh_2(TFA)_4$ CH_2Cl_2 solution by adding ethyl ether (EtOEt) probe molecule with $Rh_2(TFA)_4$/EtOEt molar ratio of 1/0 (a), 1/1 (b), 1/2 (c), 1/6 (d), 1/10 (e),1/1800 (f) and 1/3600 (g).

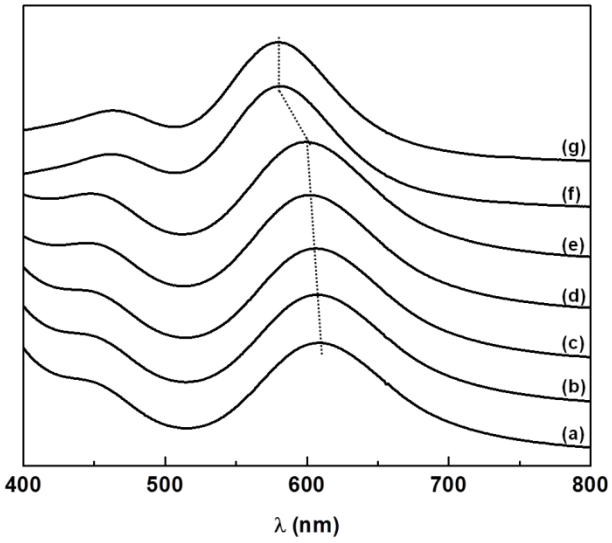

Figure S14. UV-vis spectrum of $Rh_2(TFA)_4$ CH_2Cl_2 solution by adding ethanol (EtOH) probe molecule with $Rh_2(TFA)_4$/EtOH molar ratio of 1/0 (a), 1/1 (b), 1/2 (c), 1/6 (d), 1/10 (e), 1/1800 (f) and 1/3600 (g).

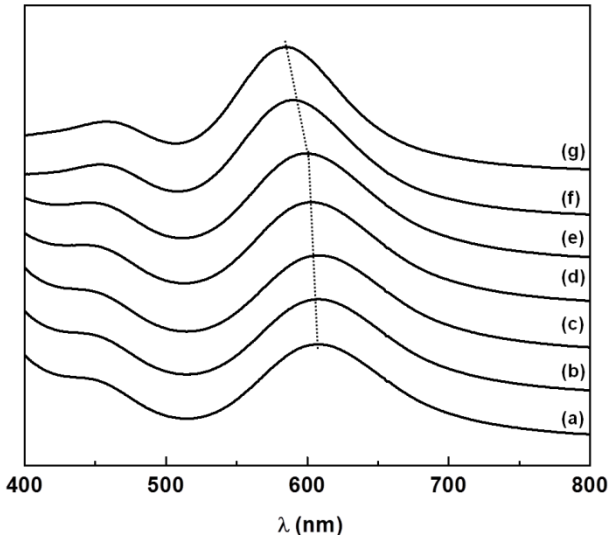

Figure S15. UV-vis spectrum of $Rh_2(TFA)_4$ CH_2Cl_2 solution by adding acetone probe molecule with $Rh_2(TFA)_4$/acetone molar ratio of 1/0 (a), 1/1 (b), 1/2 (c), 1/6 (d), 1/10 (e), 1/1800 (f) and 1/3600 (g).

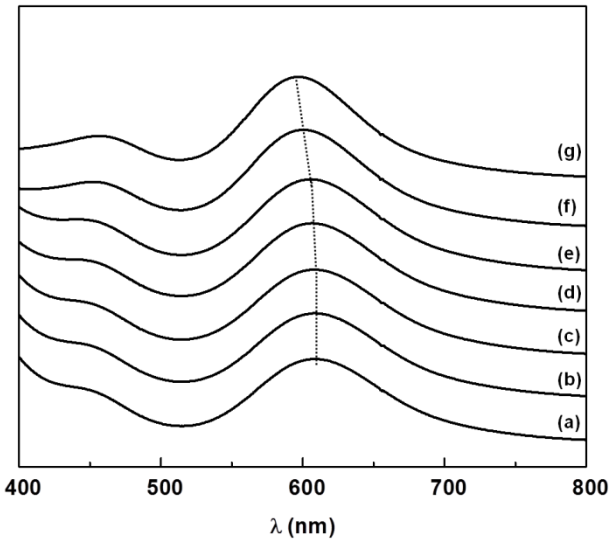

Figure S16. UV-vis spectrum of $Rh_2(TFA)_4$ CH_2Cl_2 solution by adding ethyl acetate (EtOAc) probe molecule with $Rh_2(TFA)_4$/EtOAc molar ratio of 1/0 (a), 1/1 (b), 1/2 (c), 1/6 (d), 1/10 (e), 1/1800 (f) and 1/3600 (g). Note: These spectra were reproduced from our previous work (see ref [2]).

Experiment details:

The solution was prepared by dissolving 0.0155 g (23.5 μmol) of $Rh_2(TFA)_4$ into 25 mL CH_2Cl_2 resulting in a concentration of 0.94 mmol·L^{-1}. All liquid samples were recorded on a TIDAS 100 MCS spectrometer (J&M Analytik AG). For each measurement, 0.6 mL solution was added into ca. 1 mL quartz cuvette (10.00 mm QS Hellma Analytics).

6. XPS

The compositions of obtained dirhodium coordination polymers can be reflected via wide scan X-ray photoelectron spectra (ESI Figure S17). The electron binding energies obtained at 531 eV (O1*s*), 522 eV (Rh3$p_{1/2}$), 497 eV (Rh3$p_{3/2}$), 312-308 eV (Rh3$d_{3/2}$ and Rh3$d_{5/2}$) and 284 eV (C1*s*) reflect the main composition of dirhodium coordination polymers.[3] The appearance of an electron binding energy at 688 eV, assigns to F1*s* which underlines the occurrence of trifluoroacetate residues in the obtained dirhodium coordination polymers.[3a] This observation further supports the incomplete ligand exchange as suggested by the ^{13}C CP MAS NMR (Figure 2 in main text) and ^{19}F MAS NMR spectra (Figure 3 in main text).

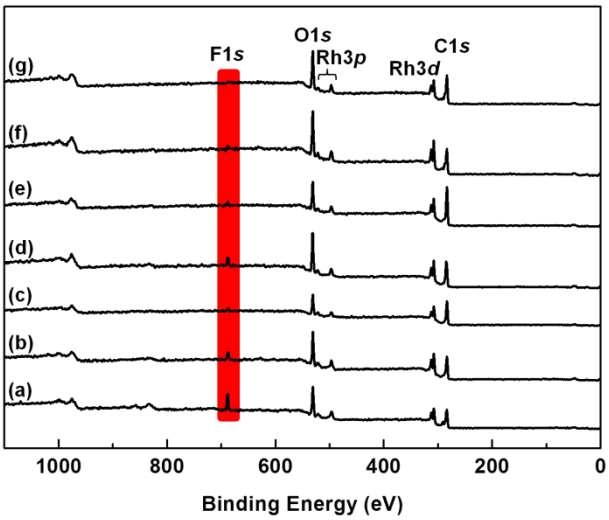

Figure S17. XPS of dirhodium coordination polymers in wide scan mode, Rh_2-L1(a), Rh_2-L2(b), Rh_2-L3(c), Rh_2-L4(d), Rh_2-L5(e), Rh_2-L6(f) and Rh_2-L7(g).

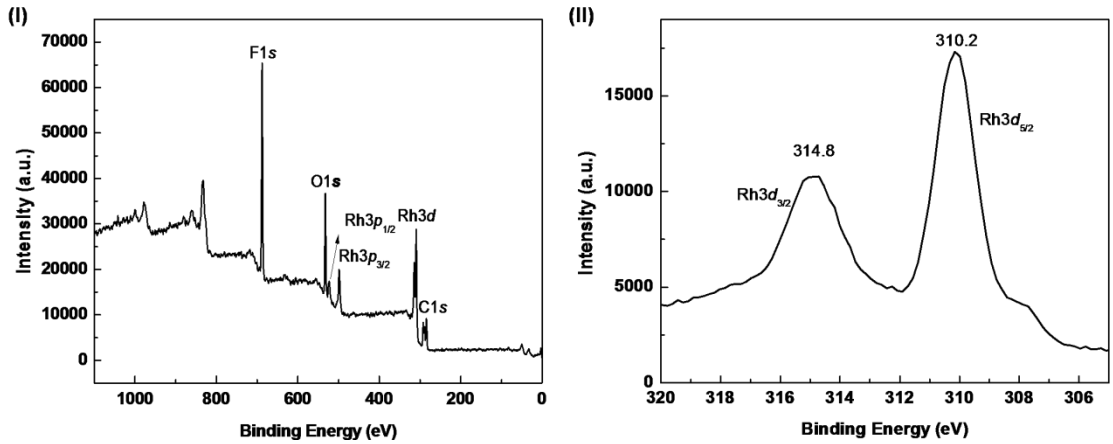

Figure S18. XPS of $Rh_2(TFA)_4$ in (I) wide scan mode and (II) high resolution mode. Note: The figure was reproduced from our previous work (see electronic supporting information of ref.[2])

7. Leaching test

To prove the heterogeneous nature of the dirhodium coordination polymers, Rh_2-L2 was chosen for a case study (ESI Figure S19). The catalyst Rh_2-L2 was filtrated at 15 min and the product yields in the filtered solution stayed around 35% along the reaction time until 120 min, even for extended reaction time (240 min). Furthermore, the filtrated reaction medium was collected for ICP-MS measurement to determine the rhodium contain. As can be seen in Table S1, the rhodium fraction was found to be ca. 160 ppb. Similar to our previous work,[2] both chemical confinement and separation of binding sites from the catalytic sites (Figure S19b) seem to be responsible for the negligible release of active sites during the cyclopropanation.

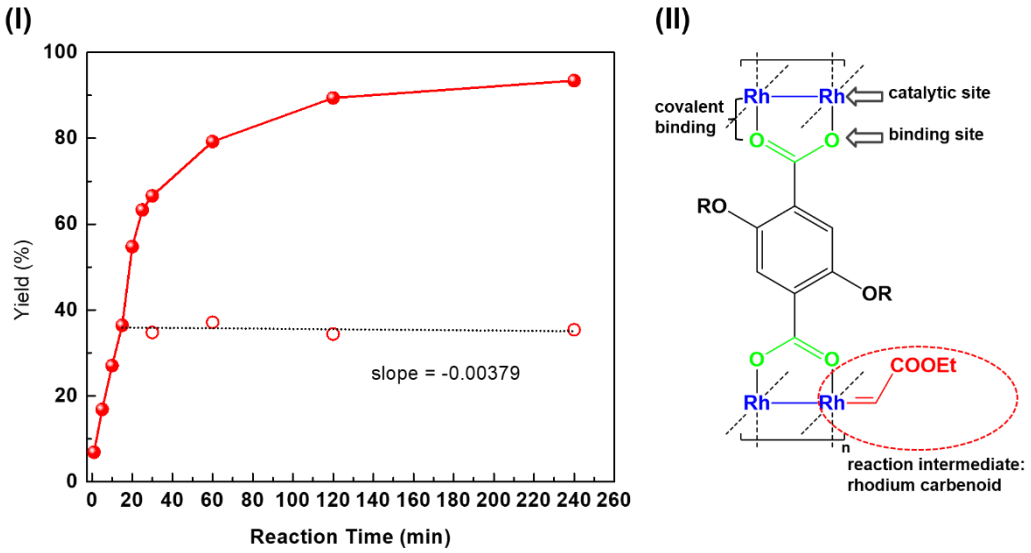

Figure S19 (I) Leaching test: reaction in the presence of Rh_2-L2 (b) and after removal of Rh_2-L2 (b'), and (II) schematic representation of binding site and catalytic site in dirhodium coordination polymers.

Testing Report

Client Name	Liu Jiquan	Report No.	ICPMS-JC-20180708
Number of Samples	2	Testing date	2018/7/8
Unit	ppb	Instrument	ThermoFisher Scientificr X series ICP-MS
Analytical Center	The Laboratory of Mineralization and Dynamics, Chang'an University		

Testing element	Analytical No. / Sample No.						
	JQQ-b-1	LJQ-b-2					
	Rh_2-L2	Rh_2-L2					
Rh	160.5	161.8					

Table S1 The rhodium fraction in the reaction medium as determined by ICP-MS.

Experiment details

The Rhodium content was determined by a Thermofisher Scientific X series ICP-MS instrument (Waltham, MA, USA) in the Laboratory of Mineralization and Dynamics, Chang'an University. After removal of the Rh_2-L2 catalyst via centrifugation, the clear solution was collected and the solvent was removed at elevated temperature (50-100 ^oC). The residue was further treated at 500 ^oC under air for 6 h. After burning the organic species, the sample was shifted into a Teflon vessel, and 1.0 mL of concentrated HNO_3 (68% v/v, AR grade) was added. After continually heating at 130 ^oC for 2 h, the solution was evaporated until incipient dryness. Thereafter, the samples were diluted using 2% HNO_3 (v/v) to 13.0 mL calibrated mark. With the solutions filtrated through the filter paper (0.22 μm), the Rh levels were directly quantified by ICP-MS.

8. Calculation of turnover frequency (TOF)

The TOFs were calculated from the yield according to ref.[4] employing the following equation:

$$TOF = n_{(EDA)} * yield / n_{(catalyst, exp)} / t ,$$

where t is the reaction time, $n_{(EDA)}$ is the amount of EDA (0.5 mmol) and $n_{(catalyst, exp)}$ is the amount of dirhodium units calculated from the nominal concentration of the weighted samples, $n_{(catalyst, nom)}$, which is ca. 9.3 μmol for all coordination polymers, multiplied by the ratio of the nominal concentration (Rh%(nominal)) calculated for perfect stoichiometric exchange to the experimental Rh_2 concentration from TGA (Rh%(TGA)):

$$n_{(catalyst, exp)} = n_{(catalyst, nom)} * (Rh\%(nominal) / Rh\%(TGA)).$$

Table S1. Calculation of the TOF for each catalyst at each time point.

t (min)	Rh_2-L1		Rh_2-L2		Rh_2-L3		Rh_2-L4		Rh_2-L5		Rh_2-L6		Rh_2-L7	
	yield (%)	TOF (h^{-1})	yield (%)	TOF (h^{-1})	yield (%)	TOF (h^{-1})	yield (%)	TOF (h^{-1})	yield (%)	TOF (h^{-1})	yield (%)	TOF (h^{-1})	Yield (%)	TOF (h^{-1})
1	0.9	35.5	5.4	176.9	2.4	82.7	0.0	0.0	3.1	109.1	4.9	136.0	0.0	0.0
2.5	1.3	20.8	8.4	110.1	4.0	54.1	0.0	0.0	3.4	48.0	7.5	84.1	0.5	5.4
5	1.9	15.5	12.1	79.5	7.6	51.4	0.0	0.0	4.1	28.8	10.3	57.8	0.5	2.7
7.5	2.2	12.0	14.8	65.0	11.9	53.8	0.0	0.0	4.5	21.2	13.1	49.0	0.6	2.3
10	2.6	10.7	20.4	67.0	16.6	56.3	0.0	0.0	5.4	19.0	14.9	41.8	0.5	1.6
15	3.6	9.6	32.8	72.0	22.3	50.3	0.0	0.0	6.2	14.6	16.9	31.6	0.8	1.7
20	3.7	7.5	49.6	81.8	28.9	49.0	0.0	0.0	7.3	12.8	18.7	26.2	1.0	1.5
25	3.9	6.3	54.7	72.1	35.9	48.6	1.2	1.6	7.9	11.1	21.4	23.9	0.9	1.1
30	4.2	5.6	62.4	68.5	41.0	46.4	1.3	1.4	9.4	11.0	21.7	20.3	1.3	1.3
60	7.3	4.9	89.3	49.0	61.4	34.7	2.3	1.3	20.7	12.2	27.7	12.9	2.9	1.5
120	10.5	3.5	91.1	25.0	75.7	21.4	10.1	2.8	26.8	7.9	35.2	8.2	7.9	2.0

9. References

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[3] aH. J. Mathieu, *Auger Electron Spectroscopy*, John Wiley & Sons, Ltd, **2009**; bA. D. Hamer, D. G. Tisley, R. A. Walton, *Journal of the Chemical Society, Dalton Transactions* **1973**, 116-120; cA. M. Dennis, R. A. Howard, K. M. Kadish, J. L. Bear, J. Brace, N. Winograd, *Inorganica Chimica Acta* **1980**, *44*, L139-L141; dP. R. Bontcev, M. Miteva, E. Zhecheva, D. Mechandjiev, G. Pneumatikakis, C. Angelopoulos, *Inorganica Chimica Acta* **1988**, *152*, 107-110; eN. F. Gol'dshleger, B. I. Azbel, Y. I. Isakov, E. S. Shpiro, K. M. Minachev, *Journal of Molecular Catalysis A: Chemical* **1996**, *106*, 159-168.

[4] J. Liu, P. B. Groszewicz, Q. Wen, A. S. L. Thankamony, B. Zhang, U. Kunz, G. Sauer, Y. Xu, T. Gutmann, G. Buntkowsky, *The Journal of Physical Chemistry C* **2017**, *121*, 17409-17416.