Modular Construction of a Porous Organometallic Network Based on Rhodium Olefin Complexation

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S *Supporting Information*

ABSTRACT: We describe the rational design and synthesis of the first member of a new class of microporous materials. It is built from rhodium and a polyolefinic ligand featuring a rigid tetraphenylsilane backbone via metal olefin complexation, creating a truly organometallic network. The resulting framework, denoted as DUT-37 (Dresden University of Technology no. 37) exhibits considerable porosity and unprecedented stability under ambient conditions. Furthermore, it is catalytically active in transfer hydrogenation.

The design and synthesis of microporous materials ($d < 2$ nm) has been a subject of intense research in recent years because of the wide variety of possible areas of application, such as gas storage, separation, and catalysis.[1] In the last 20 years, decisive achievements in the development of new microporous materials incorporating organic molecules have been made. Linking single (transition) metal atoms or clusters through mostly rigid polyfunctional donor-heteroatom-containing organic molecules results in crystalline 3D connected microporous structures named porous coordination polymers (PCPs) or metal−organic frameworks (MOFs).[2] This modular approach has been translated into polymer chemistry by linking rigid organic molecules through multiple coupling reactions to create porous purely organic polymers.[3] A synthetic concept bridging the aforementioned approaches has been used to connect main-group elements such as tin and silicon through rigid organic molecules by means of strong covalent bonds yielding element−organic frameworks.[4]

As highly crystalline solids, MOFs are highly aesthetic and beneficial for detailed structural analyses. However, the rigid network architectures are often detrimental for catalytic applications because changes in coordination of the nodes cause network collapse. In this sense, to date it has been impossible to make use of the high catalytic activity of many organometallic complexes in extended networks such as MOFs. Moreover, the nodes in MOFs are traditional Werner-type complexes, and thus, their catalytic potential is limited compared with organometallic catalysts. Our interest was to generate such truly organometallic networks with intrinsic microporosity in order to integrate catalytically active nodes into an open porous structure. The latter requires a more flexible amorphous matrix that allows for local structural changes.

In this paper, we present the rational design and synthesis of a porous material generated from transition-metal−carbon bonds (olefin π-complexes), thus creating a truly organometallic framework. Although some examples of 3D coordination polymers utilizing metal−carbon bonds are known in the literature, they are neither based exclusively on a organometallic connecting motif nor permanently porous.[5]

Olefin ligands are ideal candidates to stabilize low oxidation states of transition metals. In particular, chelating diolefin ligands are highly stable. Since coordination of an olefin to a metal center leads to pyramidalization of the carbon atoms, pyramidalized molecules, such as highly strained bicyclo[2.2.1]-heptadienes, bind strongly to the metal centers.[6] Taking these considerations into account, we chose bicyclo[2.2.1]heptadiene (norbornadiene) as the connecting motif. Since a late transition metal such as rhodium will link only two norbornadiene moieties in a linear fashion, our objective was to design a polytopic and accordingly polyolefinic linker with a tetrahedral backbone. Starting from commercially available norbornadiene (**1**), we developed a short synthesis sequence that afforded a polyolefinic ligand with a tetraphenylsilane backbone (Scheme 1).

Readily available **1** was functionalized using CuBr and *tert*-butyl peroxybenzoate, resulting in 7-norbornadienyl *tert*-butyl ether (**2**). Although the yield appeared to be quite poor, the

Scheme 1. Synthesis of the TNPS Ligand
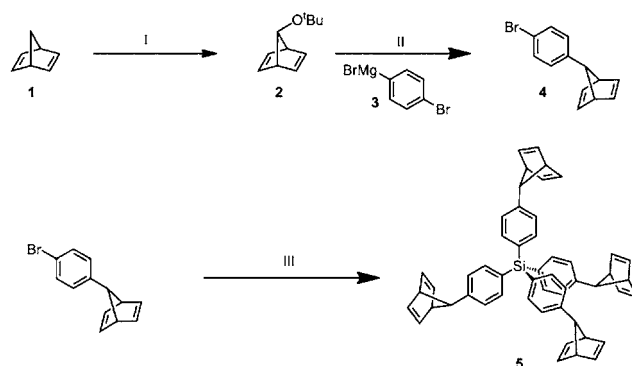
Reagents and conditions: (I) *tert*-butyl peroxybenzoate, CuBr, benzene, reflux, 2 h, 26%; (II) benzene, reflux, 2 days, 60%; (III) *t*-BuLi, THF, −90 °C, SiCl$_4$, 80%.

reaction could be performed easily on a several hundred gram scale, thus setting no restrictions on the synthesis of the target molecule. Ether **2** was cleaved using *p*-dibromobenzene-derived Grignard reagent **3** to form 4-bromophenyl-substituted norbornadiene **4**. Careful lithiation of the aforementioned species and subsequent reaction with SiCl$_4$ generated the target molecule, *tetra*(4-(7-*norbornadienyl*)*phenyl*)*silane* (TNPS, **5**). The composition and structure of the ligand were confirmed by NMR data and single-crystal X-ray analysis [see section 2 in the Supporting Information (SI)].

The new organometallic network DUT-37 (Dresden University of Technology no. 37) was obtained in a ligand exchange reaction (Figures S18−S20 in the SI) using a suitable molecular precursor such as bis(norbornadiene)rhodium(I) tetrafluoroborate (**6**). A solution of the TNPS linker in dry dichloromethane (DCM) was combined with a solution of **6** in the same solvent at room temperature (Scheme 2). Upon

Scheme 2. Synthesis of DUT-37
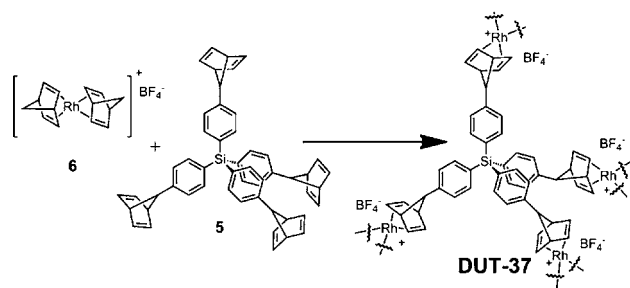
Reagents and conditions: DCM, room temperature, 2 h.

mixing, an orange precipitate was formed (Figure S12). When the precipitate was collected by filtration and dried in air, it suffered a drastic loss of volume. Subsequent physisorption experiments revealed no significant adsorption of either hydrogen or nitrogen at 77 K.

However, when the sample was dried using supercritical carbon dioxide, the resulting solid exhibited considerable porosity (Figure 1). The DUT-37 polymer had Brunauer−Emmett−Teller (BET) surface areas of up to 470 m^2/g, a micropore volume of 0.20 cm^3/g, and a total pore volume of 0.38 cm^3/g, which are comparable to textural data for zeolites. The nitrogen physisorption isotherm showed hysteresis over the entire range of relative pressures, which is typical for
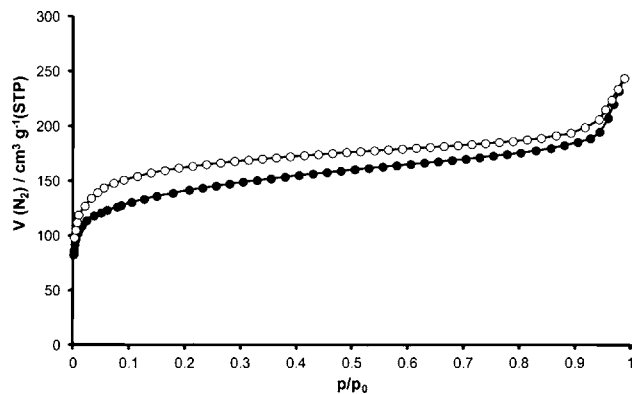

Figure 1. Nitrogen physisorption isotherm of DUT-37 at 77 K: (●) adsorption; (○) desorption.

nonordered porous polymers and is usually assigned to swelling induced by condensed adsorbate.[7] Despite its limited specific surface area, DUT-37 stored 1 wt % hydrogen at 77 K and 1 bar pressure (Figure S9). Attempts to synthesize a crystalline network have failed to date, probably as a result of the nonlinearity of the (7-norbornadienyl)phenyl moiety and the rotational flexibility of the norbornadienyl group due to the sp^3 hybridized bridge carbon atom.

In contrast to the air- and moisture-sensitive organometallic precursor complex **6**, the DUT-37 material showed unprecedented stability under ambient conditions. According to thermogravimetric analysis, DUT-37 was stable up to 493 K in air (Figure S2). When stored under normal laboratory conditions in an open jar for 1 month, no significant change in porosity could be found. Furthermore, the appearance did not change during that time. Formation of rhodium black or rhodium oxide species could not be observed visually or in powder X-ray diffraction patterns.

For a quantitative analysis of the water affinity, water vapor physisorption isotherms were measured (Figure S8). The degree of pore filling by water (calculated by comparison of the total pore volumes obtained from the nitrogen physisorption data and the pore volumes calculated from water physisorption) was only 30%. This figure characterizes the material as fairly hydrophobic, which is essential for stabilization against hydrolysis.

The rhodium content of the material varied between 9.7 and 11.4 wt % (based on a data set of 17 independently prepared samples; see Table S2 in the SI). The Rh/Si ratio varied from 2.1 to 3. The values for an ideal infinite polymeric framework would be 19.12 wt % for the rhodium content and 2 for the Rh/Si ratio (Table S3). On the other hand, the Rh/B ratio was equal to 1, the same as in the ideal framework, supporting the assumed idealized reaction in Scheme 2.

The connecting motif of DUT-37 in Scheme 2 (see Figure S12) is a 16-electron complex, leaving an open coordination site. When the material was exposed to a solvent with a coordinating donor atom (e.g., alcohols, nitriles, ethers), the color of the as-made material changed from red-orange to yellow (Figure S11), suggesting coordination to the free site and leading the way to a potential application as an indicator material. In addition, a carbon monoxide sorption experiment at 298 K using the activated material revealed coordination of at least one molecule of CO to the rhodium center, as confirmed by IR spectroscopy (Figure S3). Further support for this CO chemisorption mechanism was obtained from the shape of the sorption isotherm at 298 K (Figure S10). To get a more thorough picture of the actual binding situation in amorphous DUT-37, X-ray absorption spectroscopy (XAS) measurements of the rhodium K-edge on as-made samples dried under argon were performed. Fitting the measured data on a molecular model complex led to acceptable quality factors (e.g., *R* factor of 2.34%). The data suggest a mononuclear rhodium species surrounded by two norbornadiene ligands, thus supporting our hypothesis depicted in Scheme 2.

These observations demonstrate the accessibility of the metal and the fact that the norbornadiene groups have both relatively low dissociation energies and high flexibility caused by the sp^3-hybridized bridge carbon atom, which make the material a good candidate for heterogeneous catalysis. DUT-37 catalyzes transfer hydrogenation reactions (Figure 2); in this case, cyclohexanone was reduced to cyclohexanol. Almost complete conversion was achieved within 12 h with a yield of 96%. To
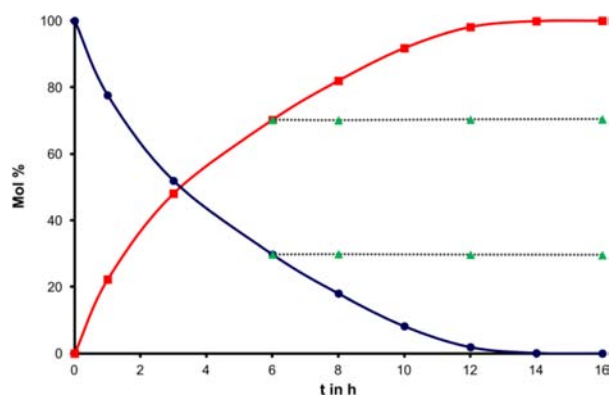
Figure 2. Formation of cyclohexanol (red ■), conversion of cyclohexanone (blue ●), and heterogeneity test after 6 h (green ▲).

rule out homogeneous side reactions and prove the heterogeneity, 1 mL of the reaction mixture was removed after 6 h using a syringe and filtered using a syringe filter (pore width 200 nm). The clear solution was subjected to the same conditions as the initial reaction mixture. No further conversion was observed, thus confirming the heterogeneous mechanism of the reaction. This proves the concept of truly organometallic networks and their use in catalytic conversions. The lack of crystallinity is advantageous in guaranteeing node accessibility without causing framework collapse. Further catalytic tests are currently under investigation to demonstrate broader applicability of DUT-37 as a first representative of porous organometallic networks.

In summary, we have reported the first truly organometallic microporous network, DUT-37. The material displays an unprecedented stability under ambient conditions. Moreover, DUT-37 is catalytically active in transfer hydrogenation and a promising candidate for further catalytic studies.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

Synthesis and general characterizations (additional adsorption data, TGA curve, and EA data), crystallographic data of **5** in CIF format, and additional structural figures. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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