# **ORGANOMETALLICS**

# Carboxyl Graphene as a Superior Support for Bulky Ruthenium-**Based Olefin Metathesis Catalyst**

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**S** Supporting Information



ABSTRACT: A Hoveyda-type catalyst decorated with two quaternary ammonium tags was synthesized and noncovalently grafted on SiO<sub>2</sub>, SBA-15, and on carboxyl graphene. A comparative study showed that the efficiency of the dual-anchored heterogeneous catalysts was highly dependent on the properties of the supporting material with graphene outperforming silicate supports. The graphene-immobilized complex exhibited excellent efficiency reflected in turnover numbers obtained in ringclosing metathesis and in self-metathesis of 1-decene. Importantly, the solid-supported catalyst assured increased recyclability with no ruthenium leaching as confirmed by inductively coupled plasma mass spectrometry.

# INTRODUCTION

Olefin metathesis is a powerful, efficient, and versatile method allowing formation of carbon-carbon double bonds. It has been widely used for the preparation of a great variety of organic compounds including natural products and specialty polymers.<sup>1,2</sup> Development in the field of olefin metathesis resulted in a range of ruthenium-based complexes that can satisfy nearly any metathetic transformation.<sup>3</sup> Many of these catalysts are now commercially available, facilitating metathesis technology application in both academia and industry.<sup>4</sup>

Olefin metathesis catalyst performance directly relates to their lifetime under applied reaction conditions with the stability depending greatly on the structure of the coordinating ligands. While optimization maneuvers in the catalyst architecture can minimize some decomposition pathways such as C-H activation of ortho N-aryl substituents,<sup>5</sup> catalyst immobilization can prevent undesired bimetallic decomposition.<sup>6</sup> Moreover, immobilization of soluble metal catalysts on solid supports offers additional potential advantages such as recyclability of these precious reagents, minimized metal contamination, or process simplification. Despite many potential benefits, efficiency of heterogeneous systems thus

far developed is limited as turnover number (TON) and turnover frequency (TOF) usually drop with immobilization, or are similar to those of the soluble catalysts.<sup>7a</sup> Taking low efficiency and immobilization costs into consideration, Hübner et al. concluded that immobilized transition metal complexes are not industrially applied as catalysts because they do not offer any advantage over traditional soluble catalysts.<sup>7a</sup> Indeed, there is much space for improvement, and multiple research groups continue their work in addressing encountered challenges. Diversity of ruthenium catalyst immobilization strategies is provided in comprehensive review articles published over the years and includes immobilization through phosphine or benzylidene ligands (Chart 1, catalyst 2),<sup>7</sup> anionic ligands (Chart 1, catalyst 3),<sup>7,8</sup> or N-heterocyclic ligands (NHC) (Chart 1, catalysts 4 and 5).<sup>7,9</sup>

Anchoring ruthenium olefin metathesis (pre)catalysts via a modified benzylidene ligand creates a system where actual metathesis reaction is catalyzed homogeneously. In the catalytic turnover, upon olefinic substrate association, the 14e active

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# Chart 1. Exemplary Solid-Supported Olefin Metathesis Catalysts



species is released into the reaction mixture. The (pre)catalyst regenerates by the uptake of the active catalyst forms by the supported alkylidene ligand (so-called boomerang mechanism).<sup>10</sup> While immobilization via ligands that do not dissociate throughout the catalytic cycle allows the active species to remain on the solid support, this approach in most of the cases did not sufficiently increase stability of the methylidene complex to yield high turnover number (TON).<sup>7</sup>

We have previously reported complex **5** with bulky ortho substituents in the aromatic rings of the NHC ligand showing dramatic stabilization of the ruthenium methylidenes when the (pre)catalyst was noncovalently immobilized on SBA-15.<sup>9a</sup>A TON of 35500 obtained in a batch setup in ring-closing metathesis (RCM) of diallyl tosylamide established it as one of the most efficient heterogeneous olefin metathesis catalyst to date. Moreover, catalyst stabilization was observed in continuous flow mode when a catalytic amount of 2-isopropoxy-styrene was added to the reaction mixture. This observation, consistent with the above-mentioned boomerang effect, encouraged us to investigate further the described system.

Consequently, we envisioned that combining two noncovalent tags, i.e., quaternary ammonium groups, one in the NHC ligand and one in the benzylidene ligand, would ensure additional catalyst stabilization by allowing continuous regeneration of the (pre)catalyst, thus elongating its lifetime and stability. The literature precedence by Allen et al. reported dual-anchored catalysts covalently grafted on silica.<sup>9b,11</sup> The studies confirmed increased performance of the bis-coupled catalysts compared to the corresponding monocoupled ones. In alkenolysis of natural seed oil derivatives, TONs for production of methyl 9-decenoate reached 40000 for the dual-anchored

catalyst. Impressive efficiency of the covalently coupled catalysts comes at a price of its challenging preparation where solid-support grafting may dramatically increase the manufacturing costs. On the contrary, noncovalent linker free catalyst deposition makes the immobilization step trivial, allowing easy variations of the catalyst loading on the solid support. In his pioneering work, Jacobs et al.<sup>12</sup> prepared a truly heterogeneous catalyst by simple mixing of Hoveyda-Grubbs second generation catalyst and silica. Although the nature of the interaction between the Ru complex and the support has not been understood completely, the importance of surface OH groups for the formation of this rather firm bond was recognized soon<sup>13</sup> and the participation of hydrogen bonds was suggested. When a Hoveyda-Grubbs-type catalyst with a tetraalkylammonium tag was immobilized on siliceous molecular sieves, the elemental analysis found that Cl<sup>-</sup> counteranion was bound to the silica surface probably with a participation of surface OH groups.<sup>14a</sup> A comprehensive review reflecting on noncovalent immobilization of ruthenium metathesis complexes has been recently presented by Dewaele et al.<sup>70</sup>

Suitable solid supports should enable fast diffusions of reactants to and from the catalytic centers and should be characterized by large surface area for proper site isolation of the active species to minimize bimetallic catalyst decomposition. In our previous research,<sup>9a,14</sup> we used silica and siliceous mesoporous molecular sieves with different pore sizes as supports for ruthenium catalysts. Generally, the activity of the heterogeneous catalysts was found to increase with an increase in pore size of the used support, with the best results observed for the SBA-15-supported catalyst.<sup>14a</sup> Recently, Balcar et al. reported that the layered structure of MCM-22 and MCM-56 can provide better access of reactants to the catalytically active centers in comparison with SBA-15-based heterogeneous catalysts.<sup>15</sup>

Another material that drew our attention was graphene, a sp<sup>2</sup> hybridized carbon-based material with a hexagonal (benzene ring) monolayer network.<sup>16</sup> The network creates a unique twodimensional structure with huge surface area, which together with other excellent properties makes it a convenient support in heterogeneous catalysis. Graphene and reduced graphene oxide surfaces materials have been described as promising supports for many metallic nanocatalysts.<sup>17</sup> Examples of catalysts enhancement, particularly recyclability of heterogenized Pd catalysts and Ru NHC complexes,<sup>17</sup> encouraged us to investigate their impact on Hoveyda–Grubbs-type complexes.

Graphene's unique properties with its sheet-shaped surface may turn beneficial for bulky ruthenium complexes immobilization by matching required physical properties to accommodate association of olefinic substrates to the catalytic centers and olefin metathesis initiation. Recently, pyrene-tagged Hoveyda– Grubbs-type ruthenium complexes were immobilized on a graphene support via noncovalent  $\pi-\pi$  interactions delivering recyclable metathesis catalysts.<sup>18</sup> In our present study, we





describe the synthesis of bis(quaternary ammonium)-tagged ruthenium complex 1 and its subsequent immobilization on carboxyl graphene and silica supports (SiO<sub>2</sub>, SBA-15), with employment of OH and COOH interaction (as supposed). In a set of comparative experiments, the utility of the supported analogues as heterogeneous catalysts is evaluated.

# RESULTS AND DISCUSSION

The desired ligand 12 was obtained in 6 steps using well-known chemical transformations (Scheme 1). The substitution pattern was selected with an aim of limiting potential steric clashes with the bulky NHC substituent present in the final catalyst. Consequently, para rather than meta substitution with respect to the propenyl group in 12 was preferred for the linker positioning. A nine carbon atom long and flexible alkyl chain was chosen for connecting the quaternary ammonium immobilization handle in order to span a range of conformations and increase chances of finding most optimal ligand positioning on the solid supports.

The NHC ligand precursor 13 was prepared according to the literature procedure (Scheme 2).<sup>19</sup> NHC was generated in situ

Scheme 2. Synthesis of 1 - Ruthenium Catalyst with Two Quaternary Ammonium Tags



by deprotonation of salt 13 and reacted with first generation indenylidene catalyst 14, followed by the addition of ligand 12 to form tertiary amine-tagged catalyst 15. The quaternization of 15 with methyl chloride provided catalyst 1 in 61% isolated yield.

With the double-tagged catalyst 1 in hand, we proceeded with its deposition on  $SiO_2$ , SBA-15, and carboxyl graphene. Addition of 1 to the suspension of a selected support in dichloromethane resulted in a fast and quantitative deposition of the catalyst and provided, after removal of the solvent, a light-green solid  $1/SiO_2$ , 1/SBA-15, and black 1/Graphene-COOH containing 1 wt % of the supported ruthenium complex. Catalyst quantitative deposition on the supports was confirmed by inductively coupled plasma mass spectrometry (ICP-MS) ruthenium screening of filtrates from immobilized catalysts washes.

Texture parameters of the obtained materials were analyzed by means of nitrogen adsorption/desorption isotherms and are summarized in Table 1. The  $N_2$  adsorption/desorption isotherms (Figure S2) of all samples under study were classified as type IV isotherm according to IUPAC classification,<sup>20</sup> typical for mesoporous adsorbents. All samples were characterized by different shape of hysteresis loops reflecting the size and shape of pores. SBA-15 exhibited a type H1 loop observed in materials with a narrow range of uniform mesopores. SiO<sub>2</sub> was characterized by a H2a loop given by the complex pore structure, while grapheneCOOH by a type H3 loop typical for aggregates of plate-like particles giving rise to slit-shaped pores. These characteristics nicely correspond to the obtained results (Figure S3). SBA-15 was characterized by a narrow distribution of pores with a maximum at 6.8 nm, whereas the standard silica, SiO<sub>2</sub>, exhibited a broad pore size distribution centered at 6.4 nm, which are typical values for these materials. Graphene-COOH showed a very broad distribution of mesopores without any distinct maximum. The sharp peak centered around 4 nm does not reflect the exact porous properties of the material, but is caused by the nature of the adsorptive and so-called tensile strength effect.<sup>21</sup> All supports had similar surface area  $(S_{BET})$  in the range of  $335-398 \text{ m}^2/\text{g}$ . The use of the NLDFT method revealed no micropores in their structures. Compared to SiO<sub>2</sub>  $(38 \text{ m}^2/\text{g})$  and SBA-15 (94 m<sup>2</sup>/g), the external surface area  $(S_{\text{EXT}})$  represented practically the total surface area for grapheneCOOH (245  $m^2/g$ ). The attachment of the ruthenium complex resulted in a decrease of both S<sub>BET</sub> and  $V_{\text{TOT}}$ , being in line with previous studies.<sup>14a</sup>

To investigate the efficiency of the catalysts, we selected a well-studied ring-closing metathesis example with N,N-diallyl tosylamide **16** at low, 25 ppm catalyst loading (Table 2).

The results indicated superior catalytic properties of the hybrid materials as the observed reaction conversions surpassed significantly the reaction outcomes obtained with their homogeneous counterparts (Table 2, conversions obtained in

Table 1. Textural Parameters of the Supports and Solid-Supported Catalysts

sample	$S_{\rm BET}^{a}$ (m <sup>2</sup> /g)	$S_{\rm EXT}^{b} ({\rm m}^2/{\rm g})$	$V_{\rm MI}^{d}$ (cm <sup>3</sup> /g)	$V_{\rm ME}^{e} (\rm cm^3/g)$	$V_{\rm TOT}^{c} (\rm cm^3/g)$	$D_{\rm ME}^{e,f}$ (nm)
SBA-15	398	94	0	0.63	0.65	6.8
1/SBA-15	357	58	0	0.60	0.61	6.6
SiO <sub>2</sub>	338	38	0	0.56	0.56	6.4
$1/SiO_2$	321	34	0	0.51	0.51	5.8
GrapheneCOOH	335	317	0	1.59	1.71	b.d.
1/GrapheneCOOH	245	245	0	0.84	1.14	b.d.

 ${}^{a}S_{BET}$  – surface area  $(p/p_0 = 0.05-0.20)$ .  ${}^{b}S_{EXT}$  – external surface area (*t*-plot method).  ${}^{c}V_{TOT}$  – total pore volume (at  $p/p_0 = 0.99$ ).  ${}^{d}V_{MI}$  – micropore volume (NLDFT method).  ${}^{c}V_{ME}$ ,  $D_{ME}$  – mesopore volume and the average mesopore diameter (BJH method).  ${}^{f}$ b.d. – broad distribution.

Ts N 16	Catalyst 25 0.0025 m	5 ppm Ts hol%	
catalyst	solvent	temp. (°C)	GC yield (%)
1	DCM	40	23
1	1,2-DCE	80	9
1	toluene	80	5
1/SBA-15	toluene	40	9
1/SBA-15	toluene	80	28
1/SiO <sub>2</sub>	toluene	40	2
1/SiO <sub>2</sub>	toluene	80	9
1/GrapheneCOOH	toluene	40	41
1/GrapheneCOOH	toluene	80	65
FixCat/GrapheneCOOH	toluene	80	3
<sup>a</sup> Conversion measured after	r 3 h.		

toluene at 80 °C). As expected, the SBA-15-supported version yielded better results compared to the SiO<sub>2</sub>-based catalyst. We were also pleased to see an outstanding effect of graphene on the reaction conversion. While reasonable activity was registered at 40 °C, the efficiency increased at elevated temperatures, yielding 65% conversion at 80 °C (Table 2 and Figure S1). The initial turnover frequencies (TOFs) (calculated from the conversion at 30 min) were 8.44 s<sup>-1</sup>, 1.55 s<sup>-1</sup>, 0.89 s<sup>-1</sup> for 1/GrapheneCOOH, 1/SBA-15, and 1/SiO<sub>2</sub>, respectively. The superior behavior of graphene-supported 1 over silicatebased 1/SBA-15 and 1/SiO<sub>2</sub> in this reaction was most likely related to the bulkiness of 1. When the catalyst was immobilized on SBA-15 or SiO<sub>2</sub>, the pore blocking phenomena could occur, limiting the availability of the active sites. In the case of carboxyl graphene with the sheet-like texture, the catalytic center accessibility was greatly increased. Consequently, 1/GrapheneCOOH catalyzed tested RCM reaction with 5 times higher initial TOF and over 2-fold greater final conversion compared to 1 deposited on mesoporous SBA-15. To our surprise FixCat/GrapheneCOOH performed very poorly in RCM of 16, giving only traces of the product (<3%). We hypothesized that, after the release of the untagged benzylidene ligand, the active form generated from FixCat needs stabilization offered by pores of SBA-15 (very good lifetime of active species generated from 5 (FixCat/SBA-15) after treatment with ethylene was previously reported by our group<sup>9a</sup>) but not by sheet-shaped graphene.

The results obtained for catalyst 1 and its heterogeneous versions summarized in Table 1 address some of the concerns raised by Hübner et al. as they indicate that immobilization of an inefficient homogeneous catalyst may improve TON by locking the dissociative ligand in the proximity of the catalytic center.<sup>7a</sup>

Interestingly, in our previous study performed on the same reaction, we observed TOF values of 26.5 s<sup>-1</sup> for catalyst **5** immobilized on SBA-15.<sup>9a</sup> This dramatic decrease of TOF noted for solid-supported **1** suggests fast reuptake of the benzylidene ligand which stays in a close proximity to the catalytically active species. However, this phenomenon can be beneficial in reactions which require long catalyst lifetime. To test this hypothesis, we performed a reusing experiment with **1**/ GrapheneCOOH (Figure 1). RCM of **16** was run in toluene (0.2 M) at 30 °C with only 0.1 mol % of the catalyst. After





**Figure 1.** Reusing of 0.1 mol % 1/GrapheneCOOH in ring-closing metathesis of *N*,*N*-diallyl tosylamide 16; reaction times: runs 1-8, 30 min; run 9, 45 min; runs 10-30, 1 h; run 31, 7 h; run 32, 12 h; run 33, 4 h; run 34, 11 h; run 35; 4 h) (also see Table S1).

every run, the catalyst was separated by filtration, washed with toluene and new portions of toluene, and N,N-diallyl tosylamide 16 were added. As shown in Figure 1, 1/GrapheneCOOH exhibited excellent recyclability and provided an average conversion of 62% over 35 cycles which corresponds to a cumulative TON of 21560. A noticeable drop in conversion (from 98% to 90%) was observed from the second reusing cycle and went down to 70% at runs 8 and 9. The gradual conversion decrease could be compensated by elongating the reaction time in each cycle (Figure 1, conversion spikes observed at runs 10 and 31-33; see also Table S1 in the Supporting Information). This indicates limited catalyst 1 stability and deactivation of a portion of the catalytically active centers by competing degradation pathways. Multiple factors certainly play a role in the catalyst deactivation, including catalyst handling in between every run (handled on air), traces of impurities in the wash and reaction solvents deactivating the catalyst, or not optimal length and positioning of the catalyst's immobilization handle. Despite the conversion decrease, this result represents a significant improvement when compared to the one previously measured for 5/SBA-15 (TON 15180).<sup>9</sup>

To examine the robustness of 1/GrapheneCOOH, we carried out a set of ring-closing metathesis reactions and selfmetathesis of 1-decene as presented in Table 3. The substrates selected for the evaluation are among the most favorite models used in the field; however, direct comparison of the outcome is somehow challenging. Many literature experiments are performed with an excess of catalysts, yielding maximum conversions but not allowing to register actual catalyst productivity. For example, RCM of 16 was studied by Allen et al. with 0.4 mol % of covalently immobilized ruthenium catalysts resulting in >96% conversion.<sup>9b</sup> Morge-Marcet et al. obtained full conversions ( $\geq$ 99%) in RCM of 16 and 18 with a silica-supported catalyst at loadings of 2 mol %.<sup>22</sup> Our initial RCM tests with substrate 16 at 0.1 mol % 1/GrapheneCOOH led to 95% conversions within 1 h reaction time.

We then proceeded with lowering catalyst loadings to operate with reactions that do not go to completion. After the adjustment, standard measurements of the catalysts productivity, turnover numbers, allowed us to register fine performance differences in the selected catalytic systems. Among tested RCM reactions, five-membered rings were assembled most

Table 3. RCM Reaction	(Toluene 1 M,	80 °C, 3 h	) Promoted by	y 1/GrapheneCOOH
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Substrate	Product	Catalyst loading, ppm/mol%	Conversion (%)	TON	Ru (ppm)
Ts N 16	, N N N	25/0.0025	65	26000	0.6
Ts N N 17	N <sup>Ts</sup>	200/0.02	63	3150	0.9
<sup>Ts</sup> N_↓ 18	, N N	100/0.01	28	2800	<dl<sup>a</dl<sup>
Ts N 19	, , , , , , , , , , , , , ,	100/0.01	68	6800	0.5
<i>€</i> 6 20	$f_{6}$	100/0.01	82	8200	<dl<sup>a</dl<sup>

<sup>*a*</sup>dl stands for detection limit.

efficiently, yielding a TON of 26000 in the reaction of 16. In this case, 25 ppm catalyst loading sufficed to convert 65% of terminal diene 16, while RCM of 19 bearing one internal double bond required a 4-fold loading increase to achieve a comparable conversion level. Seven-membered ring formation via RCM of 17 proved more challenging, and 200 ppm of the catalyst was needed for the conversion range observed in the above-mentioned examples. A relatively poor result was obtained with trisubstituted olefin 18 which is most probably due to the slow propagation rate originating from the bulkiness of the ligands and an efficient benzylidene ligand reuptake in the heterogeneous system. Self-metathesis of 1-decene proceeded smoothly with 100 ppm of 1/GrapheneCOOH. In all tested metathesis reactions, after filtration of the reaction mixtures through a Schott funnel and removal of solvents, the residual ruthenium in crude products was in low ppm level (below 1 ppm), reflecting no catalyst/ruthenium leaching from the support (Table 3).

# CONCLUSIONS

Ruthenium olefin metathesis catalyst 1 bearing two quaternary ammonium groups inserted in the N-heterocyclic and benzylidene ligands was synthesized and immobilized on three different support materials, namely, SiO<sub>2</sub>, SBA-15, and carboxyl graphene. Deposition on carboxyl graphene led to a dramatic increase in initial TOFs and to excellent efficiencies expressed in TONs in ring-closing metathesis and in selfmetathesis of 1-decene. The superior behavior of 1/GrapheneCOOH over its silicate analogues could be explained by graphene's large surface area and its unique sheet-like topology. These properties allowed accommodating the bulky structure of 1 and enabled fast diffusion of reactants to and from the catalytic centers of 1/GrapheneCOOH. No ruthenium leaching was observed, allowing the catalyst (at loadings of only 0.1 mol %) to be recycled and reused 35 times with the accumulative TON of 21560.

# EXPERIMENTAL SECTION

**Materials and Methods.** NMR spectra were collected on a Bruker Avance 500 MHz spectrometer, and the chemical shifts were referenced to residual protons of the deuterated solvent. MS was carried out with a Synapt G2-S HDMS (Waters Inc.) mass spectrometer equipped with an electrospray ion source and q-TOF type mass analyzer. The instrument was controlled and recorded data were processed using the MassLynx V4.1 software package (Waters Inc.). ICP-MS analysis was performed on the model NexION 300D, PerkinElmer, USA. All GC analyses were performed on a Trace GC Ultra, Thermo Electron Corporation, that was equipped with an HP-5 column capillary column. Textural parameters of the supports and the catalysts were determined using nitrogen adsorption isotherms at  $-196\ ^\circ C$  with a Micromeritics ASAP 2020 instrument.

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Toluene was washed with citric acid (1 M in water) and deionized water, dried with sodium sulfate, and distilled over Na. Dry solvent was transferred under argon and stored over MS 4A. Dichloromethane was distilled on air, dried with MS 4A (at least for 24 h prior to use), and degassed by purging with argon for 30 min prior to use. SiO<sub>2</sub> was purchased from Sigma and carboxyl graphene from ACS Materials. SBA-15 was synthesized according to the literature method.<sup>12</sup> All metathesis substrates and products have been previously described. Their identity was confirmed by comparison of retention times (GC) with samples previously authenticated by NMR. The substrates were treated by workup with activated alumina prior to use. All glassware was oven-dried prior to use. All manipulations were carried out under argon using standard Schlenk techniques unless otherwise noted.

**Experimental Procedures.** 4-(*tert-Butyldiphenylsilyl*)*oxy*)-2-*hydroxybenzaldehyde* 7. Imidazole (1.43 g, 21.0 mmol, 1.05 equiv) was added to a solution of *tert*-butyl(chloro)diphenylsilane (5.77 g, 21.0 mmol, 1.05 equiv) in DCM (80 mL), and the mixture was stirred at rt for 15 min. The flask was placed in an ice bath and stirred for an additional 15 min. 2,4-Dihydroxybenzaldehyde (2.76 g, 20.0 mmol, 1 equiv) was added in one portion, and the stirring continued for 30 min at 0 °C, followed by 1 h at rt. The solids were filtered off, the solvents were removed in vacuo, and the product was isolated by chromatography on silica gel with cyclohexane/ethyl acetate (95/5 v/v) as eluent (white solid, 7.03 g, 93% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  11.24 (s, 1H), 9.67 (s, 1H), 7.74–7.69 (m, 3H), 7.50–7.44 (m, 2H), 7.44–7.38 (m, 5H), 7.28–7.28 (d, <sup>5</sup>J<sub>HH</sub> = 1.0 Hz, 1H), 6.40–6.35 (m, 2H), 1.12 (s, 9H).

4-((tert-Butyldiphenylsilyl)oxy)-2-isopropoxybenzaldehyde **8**. Silver(I) oxide (27.7 g, 120 mmol, 2.5 equiv), anhydrous magnesium sulfate (28.8 g, 239 mmol, 5 equiv), and isopropyl iodide (23.9 mL, 239 mmol, 5 equiv) were added to a solution of 4-((tertbutyldiphenylsilyl)oxy)-2-hydroxybenzaldehyde (18.0 g, 47.8 g, 1 equiv) in dry dichloromethane (180 mL). The flask was sealed and stirred in the dark at rt for 48 h. The solids were filtered off, the solvents were removed in vacuo, and the product was isolated by chromatography on silica gel with cyclohexane/ethyl acetate (98/2– 90/10 v/v) as eluent (yellow oil, 16 g, 80% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.23 (s, 1H), 7.74–7.68 (m, 4H), 7.65 (d,  ${}^{3}J_{HH} = 8.6$ Hz, 1H), 7.48–7.43 (m, 2H), 7.42–7.36 (m, 4H), 6.47 (ddd,  $J_{HH} = 8.6$ , 2.2, 0.7 Hz, 1H), 6.18 (d,  ${}^{4}J_{HH} = 2.1$  Hz, 1H), 4.08 (sept,  ${}^{3}J_{HH} = 6.1$  Hz, 1H), 1.12 (s, 9H), 1.12 (d,  ${}^{3}J_{HH} = 6.0$  Hz, 6H).  ${}^{13}$ C NMR (126 MHz, CDCl<sub>3</sub>) δ 188.9, 162.6, 162.1, 135.5, 132.3, 130.4, 129.9, 128.2, 120.1, 112.9, 105.2, 71.0, 26.6, 21.8. HRMS (ESI - TOF) m/z: [M + Na]<sup>+</sup> Calculated for C<sub>26</sub>H<sub>30</sub>O<sub>3</sub>NaSi 441.1862; Found 441.1851.

tert-Butyl(3-isopropoxy-4-(prop-1-en-1-yl)phenoxy)diphenylsilane 9. Potassium tert-pentoxide solution in toluene (35.3 mL, 1.7 M, 59.9 mmol, 1.3 equiv) was added dropwise to a mixture of 4-((tertbutyldiphenylsilyl)oxy)-2-isopropoxybenzaldehyde (19.3 g, 46.1 mmol, 1 equiv) and ethyltriphenylphosphonium bromide (23.1 g, 62.2 mmol, 1.3 equiv) in toluene (230 mL) at -20 °C over 30 min. The mixture was brought to rt and stirred for an additional 30 min. After removal of the solvents in vacuo, water was added (100 mL) and the mixture was extracted with cyclohexane  $(3 \times 60 \text{ mL})$ . Combined organic phases were dried over sodium sulfate, filtered, and concentrated in vacuo. The product was isolated by chromatography on silica gel with cyclohexane/ethyl acetate (95/5 v/v) as eluent (white solid, 11.1 g, 56% yield). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.77-7.71 (m, 4H), 7.60-7.20 (m, 6H), 7.15 (d,  ${}^{3}J_{HH}$  = 8.5 Hz, 0.4H), 7.05 (d,  ${}^{3}J_{HH}$  = 8.3 Hz, 0.6H), 6.59-6.52 (m, 0.3H), 6.44-6.36 (m, 1.6H), 6.28-6.17 (m, 1H), 6.11–5.95 (m, 0.4H), 5.71–5.63 (m, 0.6H), 4.04 (sept,  ${}^{3}J_{HH} =$ 6.0 Hz, 1H), 1.84 (dd,  $J_{\rm HH}$  = 6.6, 1.7 Hz, 1H), 1.79 (dd,  $J_{\rm HH}$  = 7.1, 1.8 Hz, 2H), 1.14–1.09 (m, 15H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  156.2, 155.5, 135.8, 135.7, 135.7, 135.4, 133.3, 130.4, 130.0, 130.0, 129.4, 127.9, 127.4, 125.2, 124.9, 120.7, 111.3, 106.3, 70.6, 26.7, 22.1, 14.9. HRMS (ESI - TOF) m/z:  $[M + H]^+$  Calculated for  $C_{28}H_{35}O_2Si$ 431.2406; Found 431.2395.

3-lsopropoxy-4-(prop-1-en-1-yl)phenol 10. Potassium carbonate (7.1 g, 51.6 mmol, 2 equiv) was added to a solution of *tert*-butyl(3-isopropoxy-4-(prop-1-en-1-yl)phenoxy)diphenylsilane (11.1 g, 25.8 mmol, 1 equiv) in acetonitrile/water (115 mL, 10% water), and the mixture was stirred at 70 °C for 4 h. The suspension was diluted with water, and acidified with 5% HCl, and the mixture was extracted with dichloromethane (3  $\times$  50 mL). Combined organic phases were dried over sodium sulfate, filtered, and concentrated in vacuo. The product (3.0 g, yellow oil, 61% yield, unstable) was purified by chromatography on silica gel with cyclohexane/ethyl acetate (10–30%) as eluent and used immediately in the following step.

4-((9-Bromononyl)oxy)-2-isopropoxy-1-(prop-1-en-1-yl)benzene 11. Diisopropyl azodicarboxylate (3.72 mL, 18.9 mmol, 1.1 equiv) was added dropwise at -20 °C to a mixture of 3-isopropoxy-4-(prop-1-en-1-yl)phenol (3.30 g, 17.2 mmol, 1.0 equiv), 9-bromo-1-nonanol (4.02 g, 18.0 mmol, 1.05 equiv), and triphenylphosphine (4.95 g, 18.9 mmol, 1.1 equiv) in dry dichloromethane (80 mL). After 1 h, the reaction mixture was allowed to warm up to room temperature and stirred for 1 h, then concentrated. Water (50 mL) was added, and the mixture was extracted with cyclohexane  $(3 \times 50 \text{ mL})$ . Combined organic phases were dried over sodium sulfate and filtered. After evaporation of the solvents, the crude product was purified by column chromatography (silica gel, cyclohexane/ethyl acetate, 98/2 v/v) to give the product as a colorless oil (3.9 g, 57%). <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.21-7.17 (m, 1H), 6.51–6.36 (m, 3H), 5.76–5.62 (m, 1H), 4.48 (sept,  ${}^{3}J_{HH} =$ 6.0 Hz, 1H), 4.02-3.85 (m, 2H), 3.44-3.37 (m, 2H), 1.91-1.81 (m, 5H), 1.81–1.71 (m, 2H), 1.49–1.41 (m, 4H), 1.38–1.30 (m, 12H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.2, 156.7, 130.6, 125.3, 124.9, 120.5, 105.0, 102.0, 71.0, 68.1, 34.1, 33.0, 29.5, 29.5, 29.4, 28.8, 28.3, 26.2, 22.4, 14.9. HRMS (ESI - TOF) m/z: [M + H]<sup>+</sup> Calculated for C<sub>21</sub>H<sub>34</sub>O<sub>2</sub>Br 397.1742; Found 397.1729.

1-(9-(3-lsopropoxy-4-(prop-1-en-1-yl)phenoxy)nonyl)-4-methylpiperazine 12. Potassium carbonate (0.142 g, 1.02 mmol, 1.1 equiv)and 1-methylpiperazine (0.187 g, 1.86 mmol, 2.0 equiv) were added toa solution of 4-((9-bromononyl)oxy)-2-isopropoxy-1-(prop-1-en-1yl)benzene (0.370 g, 0.93 mmol, 1.0 equiv) in acetonitrile (4.8 mL).The suspension was stirred at 80 °C for 4 h, then cooled to rt. Thesolvents were removed in vacuo, and the residue was resuspended indichloromethane (10 mL) and filtered through a Schott funnel. Themixture was concentrated in a rotary evaporator and purified bycolumn chromatography (silica gel, DCM/MeOH gradient up to 70/ 30 v/v) to give the product as a colorless oil (0.35 g, 90%). <sup>1</sup>H NMR (601 MHz, CDCl<sub>3</sub>)  $\delta$  7.20–7.13 (m, 1H), 6.50–6.38 (m, 3H), 5.74–5.63 (m, 1H), 4.47 (sept, <sup>3</sup>J<sub>HH</sub> = 6.0 Hz, 1H), 3.93 (t, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 2H), 2.75–2.46 (bs, 6H), 2.45–2.39 (m, 2H), 2.35 (s, 3H), 1.87–1.79 (dd, J<sub>HH</sub> = 7.1, 1.8 Hz, 3H), 1.79–1.69 (m, 2H), 1.59–1.50 (m, 2H), 1.48–1.39 (m, 2H), 1.35–1.24 (m, 16H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>)  $\delta$  159.2, 156.7, 130.6, 125.3, 124.9, 120.5, 105.0, 102.0, 71.0, 68.2, 58.9, 55.1, 53.2, 46.1, 29.6, 29.5, 29.5, 27.7, 26.9, 26.2, 22.3, 14.9. HRMS (ESI - TOF) *m/z*: [M + H]<sup>+</sup> Calculated for C<sub>26</sub>H<sub>45</sub>N<sub>2</sub>O<sub>2</sub> 417.3481; Found 417.3478.

Complex 15. Potassium tert-pentoxide solution in toluene (1.7 M, 1.4 mL, 1.1 equiv) was added to a suspension of 1,3-bis(2,6diisopropylphenyl)-4-((4-ethylpiperazin-1-yl)methyl)-4,5-dihydro-1Himidazol-3-ium tetrafluoroborate salt (1.5 g, 2.48 mmol, 1.15 equiv) in toluene (27 mL) and stirred for 30 min at rt under argon. The suspension was heated up to 80 °C and stirred for 10 min. Umicore M10TM (1.91 g, 2.15 mmol, 1 equiv) was added, and the reaction mixture was stirred at 80 °C for an additional 20 min. Then the mixture was cooled down to 60 °C and 1-(9-(3-isopropoxy-4-(prop-1en-1-yl)phenoxy)nonyl)-4-methylpiperazine (0.81 g, 1.9 mmol, 0.9 equiv) was added, followed by addition of copper(I) chloride (0.53 g, 5.4 mmol, 2.5 equiv). The resulting mixture was stirred for an additional 20 min at 60 °C. The mixture was cooled to room temperature and filtered through silica gel with cyclohexane/ethyl acetate (80:20 v/v), followed by ethyl acetate/trimethylamine (98:2 v/ v). The green filtrate was concentrated in vacuo to yield 0.49 g of the product (green solid, 21% yield). Due to its limited stability, the product was used immediately in the following step. TLC (SiO<sub>2</sub>)  $R_f$  = 0.25, AcOEt/TEA 98:2 v/v. <sup>1</sup>H NMR (500 MHz,  $CD_2Cl_2$ )  $\delta$  15.92 (s, 1H, Ru = C<u>H</u>), 7.60–7.57 (m, 1H), 7.48–7.45 (m, 1H), 7.41–7.39 (m, 2H), 7.35-7.32 (m, 2H), 6.71 (d,  ${}^{3}J_{HH} = 8.0$  Hz, 1H), 6.40-6.37(m, 2H), 4.84 (sept,  ${}^{3}J_{HH} = 6.0$  Hz, 1H, (CH<sub>3</sub>)<sub>2</sub>CH-O), 4.47–4.37 (m, 1H, ArNCH), 4.32-4.28 (m, 1H, ArNCH), 4.19-4.15 (m, 1H, ArNCH), 3.91 (t,  ${}^{3}J_{HH} = 6.5$  Hz, 2H, CHCH<sub>2</sub>N), 3.81–3.69 (bs, 1H, (CH<sub>3</sub>)<sub>2</sub>CHAr), 3.68–3.57 (bs, 1H, (CH<sub>3</sub>)<sub>2</sub>CHAr), 3.53–3.38 (m, 1H,  $(CH_3)_2CHAr)$ , 3.29 (sept,  ${}^{3}J_{HH} = 6.5$  Hz,  $1H(CH_3)_2CHAr)$ , 2.71 (t,  ${}^{3}J_{\rm HH} = 11.5$  Hz, 1H), 2.60–2.25 (m, 20H), 2.21 (s, 3H), 1.76–1.71 (m, 2H), 1.48- 1.38 (m, 10H), 1.35-1.20 (m, 30H), 1.12-1.04 (m, 2H), 0.98 (t,  ${}^{3}J_{HH}$  = 6.5, 3H), 0.92–0.86 (m, 2H).  ${}^{13}C$  NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 288.5, 217.1, 161.8, 154.7, 150.0, 139.7, 130.2, 130.0, 125.5, 123.9, 107.3, 101.5, 75.7, 69.2, 61.3, 60.5, 59.2, 55.8, 53.8, 53.3, 52.7, 46.4, 30.1, 29.8, 29.7, 28.4, 28.1, 27.5, 26.5, 25.9, 22.2, 22.0, 12.4.

HRMS: two independent, specialized laboratories were not able to measure the molecular ion for complex **15**. The best attempt allowed for measurement of a complex with a partially fragmented piperazine ring.

IR (film, cm<sup>-1</sup>) 2962, 2922, 2853, 2812, 2768, 1677, 1597, 1463, 1441, 1382, 1323, 1256, 1187, 1611, 1103, 1014, 803.

Catalyst 1. Ruthenium complex 15 (450 mg, 0,42 mmol, 1 equiv) was placed in a pressure reactor and dissolved in dry isopropanol (10 mL). Cooled -30 °C liquid chloromethane (4.21 g, 84.0 mmol, 200 equiv) was added, the tube was sealed, and the mixture was stirred at 50 °C for 48 h. The reaction mixture was concentrated in vacuo, and the crude residue was purified by filtration through neutral aluminum oxide with dichloromethane/methanol (90:10 v/v) as eluent. The product (green solid) was obtained in 61% yield. TLC (Al<sub>2</sub>O<sub>3</sub>)  $R_f$  = 0.2, DCM/MeOH 9:1 v/v.<sup>1</sup>H NMR (500 MHz,  $CD_2Cl_2$ )  $\delta$  15.86 (s, 1H, Ru=C<u>H</u>), 7.62–7.59 (m, 1H), 7.49–7.46 (m, 1H), 7.42–7.40 (m, 2H), 7.35–7.32 (m, 2H), 6.71 (d,  ${}^{3}J_{\text{HH}} = 8.0 \text{ Hz}$ , 1H), 6.40–6.37 (m, 2H), 4.84 (sept,  ${}^{3}J_{\text{HH}} = 6.0 \text{ Hz}$ , 1H, (CH<sub>3</sub>)<sub>2</sub>CH-O), 4.43–4.30 (m, CH<sub>3</sub>)<sub>2</sub>CH-O), 4.43–4.30 (m, CH<sub>3</sub>)<sub>3</sub>CH-O), 4.43–4.30 (m, CH<sub>3</sub>)<sub>3</sub>CH 2H, ArNCH<sub>2</sub>), 4.18 (t,  ${}^{3}J_{HH}$  = 9.0 Hz, 1H, ArNCH), 3.91 (t,  ${}^{3}J_{HH}$  = 6.5 Hz, 2H,CHCH<sub>2</sub>N), 3.84 (sept,  ${}^{3}J_{HH} = 6.5$  Hz, 2H, 2 × (CH<sub>3</sub>)<sub>2</sub>CHAr), 3.78-3.71 (m, 2H), 3.67-3.56 (m, 6H), 3,46 (s, 6H, N<sup>+</sup>(CH<sub>3</sub>)<sub>2</sub>), 3.37 (d,  ${}^{3}J_{HH} = 5.0$  Hz, 1 H), 3.32 (s, 3H, N<sup>+</sup>CH<sub>3</sub>), 3.26 (quint,  ${}^{3}J_{HH} = 6.5$ Hz, 1H), 2.84-2.59 (m, 10H), 2.43-2.40 (m, 2H), 1.76-1.70 (m, 2H), 1.47-1.39 (m, 7H), 1.37-1.17 (m, 35H), 1.11-1.01 (m, 3H), 0.93-0.75 (m, 2H). <sup>13</sup>C NMR (126 MHz, CD<sub>2</sub>Cl<sub>2</sub>) δ 288.7, 218.2, 161.8, 154.7, 149.7, 139.6, 130.3, 130.2, 125.6, 123.9, 107.3, 101.5, 75.8, 69.1, 62.6, 60.0, 57.9, 47.4, 29.9, 29.8, 29.7, 29.6, 28.3, 27.6, 27.1, 26.4, 25.9, 22.2, 21.9, 8.1.

HRMS (ESI - TOF) m/z: [M]<sup>2+</sup> Calculated for  $0.5 \times C_{60}H_{98}N_6O_2$ -Cl<sub>2</sub>Ru 553.3086; Found: 553.3089. Note: the formula corresponds to the positively charged catalyst structure without chlorine counterions.

IR (film, cm<sup>-1</sup>) 3376, 2927, 2861, 2604, 2498, 1595, 1465, 1442, 1384, 1324, 1244, 1187, 1103, 1037, 805, 729, 462.

Immobilization of Catalyst 1 on SiO<sub>2</sub>. SiO<sub>2</sub> was dried in a Schlenk tube under vacuum at 300 °C for 3 h to remove water adsorbed on the surface. Dry support (100 mg) was dissolved in dry dichloromethane (10 mL) under argon, and a solution of 1 in dry dichloromethane (10 mg in 0.2 mL) was added dropwise. The resulting suspension was stirred for 1 h at room temperature. After evaporation of dichloromethane, the product was dried under high vacuum to give  $1/SiO_2$ , 1% (w/w) as a light green solid. In order to confirm the catalyst's quantitative deposition on the support, a sample of the immobilized catalyst (50 mg) was resuspended in dichloromethane (5 mL) and stirred at room temperature for 30 min. The solids were filtered off, the filtrate was concentrated in vacuo, and obtained traces were dissolved in methanol (0.5 mL) and analyzed by ICP-MS. The ruthenium content in the filtrate was below the detection limit.

Immobilization of Catalyst 1 on SBA-15. SBA-15 was dried in a Schlenk tube under vacuum at 300 °C for 3 h to remove water adsorbed on the surface. Dry support (100 mg) was dissolved in dry dichloromethane (10 mL) under argon, and a solution of 1 in dry dichloromethane (1.0 mg in 0.2 mL) was added dropwise. The resulting suspension was stirred for 1 h at room temperature. After evaporation of dichloromethane, the product was dried under high vacuum to give 1/SBA-15, 1% (w/w) as a light green solid. In order to confirm the catalyst's quantitative deposition on the support, a sample of the immobilized catalyst (50 mg) was resuspended in dichloromethane (5 mL) and stirred at room temperature for 30 min. The solids were filtered off, the filtrate was concentrated in vacuo, and obtained traces were dissolved in methanol (0.5 mL) and analyzed by ICP-MS. The ruthenium content in the filtrate was below the detection limit.

Immobilization of Catalyst 1 on GrapheneCOOH. Graphene-COOH was dried in a Schlenk tube under vacuum at 90 °C for 3 h to remove water adsorbed on the surface. Dry support (99 mg) was suspended in dry dichloromethane (10 mL) under argon, and a solution of 1 in dry dichloromethane (10 mg in 0.2 mL) was added dropwise. The resulting suspension was stirred for 1 h at room temperature. After evaporation of dichloromethane, the product was dried under high vacuum to give 1/GrapheneCOOH, 1% (w/w), as a black, free-flowing powder. In order to confirm the catalyst's quantitative deposition on the support, a sample of the immobilized catalyst (50 mg) was resuspended in dichloromethane (5 mL) and stirred at room temperature for 30 min. The solids were filtered off, the filtrate was concentrated in vacuo, and obtained traces were dissolved in methanol (0.5 mL) and analyzed by ICP-MS. The ruthenium content in the filtrate was below the detection limit.

*Immobilization of FixCat on GrapheneCOOH.* The immobilization was performed as described above for catalyst 1/GrapheneCOOH.

General Procedure for Ring-Closing Metathesis. In a typical RCM experiment, 1/solid support (1 wt %, 10.7 mg, reaction catalyst loading of 25 ppm, 0.0025 mol %) was placed in a three-neck round-bottom flask, suspended in 3 mL of a solvent and equilibrated at a given temperature for 15 min under argon. Then, *N*,*N*-diallyl tosylamide (1.0 g, 4 mmol) in a selected solvent (1 mL) was added under stirring. Samples (0.1 mL of a reaction mixture quenched with ethyl vinyl ether) were analyzed at given time intervals by GC.

Determination of Ruthenium Content. Mineralization. Ruthenium content was determined by ICP-MS equipped with a sample introduction system which requires solubilized samples. Therefore, all samples were mineralized before ICP-MS analysis. The wet digestion procedures were carried out using a single reaction cell (SRC) microwave-assisted digestion unit (UltraWAVE, Milestone, Italy). Samples in milligram quantities were directly weighed inside the Teflon or quartz vessels. Two different combinations of acids were used depending on the samples nature: (i) 4 mL of 65% HNO<sub>3</sub> (Suprapur, Merck, Germany) and 0.125 mL of 70% HClO<sub>4</sub> (ultrapure, Chem-Lab NV, Belgium) or (ii) 2 mL of 65% HNO<sub>3</sub> and 0.2 mL of 40% HF (Suprapur, Merck, Germany) for samples containing silicates. The microwave program was set to 270  $^{\circ}$ C (for samples containing silicates 170  $^{\circ}$ C) for 15 min after 25 min heat up period at 120 bar and 1500 W. In most of the cases, a predigestion step was applied (equilibration in an acid mixture at room temperature prior to the microwave program). Final digests were diluted with water before introducing them into the ICP-MS spectrometer.

*ICP-MS*. The total Ru content was determined by an external calibration with standards in the range of  $0.001-0.200 \text{ mg L}^{-1}$  (ruthenium standard solution 1000 mg L<sup>-1</sup> in 20% HCl, VHG Laboratories, USA). The isotopes 102 and 104 were monitored. The purging time was set to 60 s between the samples measurements and 20 s before the first measurement out of three. The limit of detection (0.06 ppm) and quantification (0.08 ppm) was calculated from the results obtained for blanks undergoing the same mineralization procedures as the processed samples.

Measurements of Textural Parameters of the Supports and the Solid-Supported Catalysts. Adsorption measurements were performed with a Micromeritics ASAP 2020 volumetric instrument at -196 °C using a liquid bath of N<sub>2</sub>. In order to attain the necessary accuracy in the accumulation of the adsorption data, the instrument was equipped with three pressure transducers covering the 13.3 Pa, 1.33 and 133 kPa ranges. Prior to the sorption measurements, all samples were degassed under the turbomolecular pump vacuum. Starting at an ambient temperature, the samples were heated up to 80 °C (heating rate 0.5 °C/min) until the residual pressure of 1 Pa was achieved. After further heating at 80 °C for 1 h, the temperature was increased up to 110 °C (0.5 °C/min) and maintained for 6 h.

The surface area,  $S_{\rm BET}$ , was calculated using adsorption data in the range of relative pressures  $p/p_0 = 0.05-0.2$ . The adsorbed amount at  $p/p_0 = 0.99$  reflects the total adsorption capacity ( $V_{\rm TOT}$ ). The external surface area ( $S_{\rm EXT}$ ) was calculated using the *t*-plot method. Non-Local Density Functional Theory (NLDFT) using standard Micromeritics software on Carbon Slit Pores (graphene) and cylindrical pores on oxide surfaces (silica, SBA-15) for N<sub>2</sub> at -196 °C was applied to estimate the micropore volume ( $V_{\rm MI}$ ). The volume of mesopores ( $V_{\rm ME}$ ) together with the distribution of mesopores ( $D_{\rm ME}$ ) was calculated from the desorption branch of the hysteresis loop using the BJH algorithm with Halsey equation.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.8b00026.

Additional figures and tables, NMR characterization of synthesized materials (PDF)

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# Notes

The authors declare no competing financial interest.

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