This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
A Versatile Method for the Preparation of Carbon-Rhodium Hybrid Catalysts on Graphene and Carbon Black

Chin Min Wong, D. Barney Walker, Alexander H. Soeriyadi, J. Justin Gooding and Barbara A. Messerle

Strategies for combining the selectivity and efficiency of homogeneous organometallic catalysts with the versatility of heterogeneous catalysts are urgently needed. Herein a direct and modular methodology is presented that provides rapid access to well-defined carbon-rhodium hybrid catalysts. A pre-synthesized Rh(I) complex containing a carbene-triazole ligand was found to be stable for direct immobilization onto unactivated graphene, carbon black and glassy carbon electrodes. Characterization of the heterogeneous systems using X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), inductively coupled plasma-optical emission/mass spectrometry (ICP-OES/MS), Raman spectroscopy, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) confirmed the well-defined nature of the hybrid catalysts. The hybrid catalysts show excellent activity, comparable to that of the homogeneous system for the hydrosilylation of diphenylacetylene, with turnover numbers ranging from 5000 to 48000. These catalysts are the best reported to date for the hydrosilylation of diphenylacetylene. In common with conventional heterogeneous catalysts, high reusability, due to a lack of Rh metal leaching, was also observed for all carbon-rhodium complexes under investigation.

Introduction

The assembly of highly efficient and selective homogeneous systems onto heterogeneous solid materials is a facile route to the development of optimized and recyclable hybrid systems with well-defined active sites. A variety of catalysts covalently tethered to carbon based scaffolds (eg. activated carbon, graphene/graphene oxide and carbon nanotubes) and other well known supports (eg. aluminosilicates, organic resins and metal organic frameworks) have been reported, the fabrication of these hybrid systems is often complicated, requiring multiple reaction steps.

The development of hybrid catalysts consisting of well-defined organometallic complexes on solid supports can be established using both non-covalent interactions or covalent bonding. In terms of producing hybrid catalysts that are covalently bonded to the solid support, the synthesis route typically occurs via at least two steps, where initially a precursor ligand is attached to the surface then - in a second and separate step - a transition metal centre is introduced. The first step is normally dictated by the nature of the functional groups on the solid surface. For example, reactive Si-OH moieties on silica surfaces can be effectively used to initiate ligand immobilization. However, certain supports require additional surface activation in order to achieve the functional groups that are needed for ligand modification. This is a common strategy for functionalization of graphene surfaces, whereby pre-oxidation of graphene to graphene oxide (GO) is often necessary prior to functionalization with an appropriate ligand motif.

At times, reduction back to reduced GO is also performed after ligand immobilization and complexation with the metal precursor. This complicated multistep assembly to the hybrid system is not ideal for pristine materials, such as pure graphene, where it is desirable that its regular, conjugated surface is retained. The second step (complexation of metal with the immobilized ligand) in the stepwise assembly of hybrid catalysts could create an additional complication, as incomplete complexation of the immobilized ligand can occur. Furthermore, the common use of an excess of metal precursors increases the chance of nonspecific adsorption of metals onto the surface.

Scheme 1 Illustration of the direct attachment of catalyst to G, CB or GC without the need for oxidatively introduced functional groups.

In designing new hybrid catalysts, it would be highly desirable to have a simple, general method for attaching optimized metal complexes directly to a carbon support without the need for surface pre-activation or post-immobilization treatment with excess precious metal precursors. While direct functionalization of graphene is possible using aryl diazonium-based precursors, the harsh conditions required by this reaction are typically not compatible with finely tuned catalytically-active metal complexes. Herein we describe a modular protocol for the direct hybridization of
a pre-formed Rh(I) catalyst with the surface of unactivated carbon materials (Scheme 1). We demonstrate the potential widespread utility of this method by functionalizing a different high surface area carbon allotropes, graphene (G) and carbon black (CB) and show that these are highly efficient catalysts. Furthermore, it is demonstrated that even low surface area glassy carbon (GC) electrodes can be readily transformed into functionalized, recyclable catalytic systems using this efficient methodology.

**Results and discussion**

Here, we introduce our novel homogeneous catalyst, [2Rh(CO)₄]BPh₄ (Figure 1) onto the carbon supports by directly immobilizing the pre-synthesized Rh(I) complex containing an aniline-functionalized bidentate carbene-triazole ligand, [1Rh(COD)]BPh₄ (COD = cyclooctadiene) via the in situ generation of the diazonium moiety (Scheme 2). The aniline functionalized complex [1Rh(COD)]BPh₄ in an acidic solution of nitromethane and sodium nitrate was added to a GC electrode, or stirred with CB or G, for 24 h. The carbon materials were then washed repeatedly, and suspended in a mixture of dichloromethane and pentane under an atmosphere of CO. The GC electrode was washed thoroughly and dried under a gentle flow of nitrogen to give [GC-2Rh(CO)₄], [CB-2Rh(CO)₄] or [G-2Rh(CO)₄] were isolated as black powders after copious washing and drying under vacuum at 25 °C overnight.

![Scheme 2 Synthesis of [GC-2Rh(CO)₄], [CB-2Rh(CO)₄] and [G-2Rh(CO)₄].](image)

On application as a catalyst for hydroamination, our previously employed carbon supported *bis*-pyrazole system²⁹, ³⁰ (Fig. 1) delivered remarkably high turnover numbers²⁹ but underwent some leaching of the Rh metal centre over time. The novel Rh(I) catalyst attached to the carbon surface here contains a carbene-triazole ligand system that has a high binding affinity for the Rh ion in order to create recyclable hybrid catalysts that exhibit minimal metal leaching.

![Fig. 1 Homogeneous Rh(I) complexes](image)

![Fig. 2 XP survey scan of [G-2Rh(CO)₄] and selected narrow scan of N1s and Rh3d.](image)

While [GC-2Rh(CO)₄] was characterized using X-ray photoelectron spectroscopy (XPS), [CB-2Rh(CO)₄] and [G-2Rh(CO)₄] were characterized using XPS, thermogravimetric analysis (TGA), inductively coupled plasma-optical emission/mass spectroscopy (ICP-OES/MS), Raman spectroscopy, scanning electron microscopy (SEM) and/or transmission electron microscopy (TEM).

In the XP spectra of [GC-2Rh(CO)₄] (Fig. 2), the appearance of the N1s peak at ca. 402 eV²⁹ and Rh3dₓ/₂ peak at ca. 310 eV were observed. N1s and Rh3d peaks at similar binding energies were observed in the XP spectra of [2Rh(CO)₄]BPh₄ and the unattached complex [2Rh(CO)₄]BPh₄ (see all XPS figures of hybrid complexes, unmodified carbon surfaces and homogeneous complex in the SI, section SI-2), consistent with analogous hybrid Rh(I) complexes on GC and CB reported previously.²⁹, ³⁰ The atomic ratio of N:Rh for [GC-2Rh(CO)₄] and [G-2Rh(CO)₄] was found to be close to 5:1 as expected, which statistically means that only individual complexes are immobilized on the surfaces. In the case of [CB-2Rh(CO)₄], the ratio of N:Rh was found to be 3:8:1 suggesting that there may be a small amount of adventitious physisorbed Rh on the CB surface.
The thermal stability of \([\text{CB-2Rh(CO)}_2]\) and \([\text{G-2Rh(CO)}_2]\) was analyzed against that of unmodified CB and G using TGA under an atmosphere of nitrogen (Fig. 3). The thermogram of \([\text{CB-2Rh(CO)}_2]\) displayed two weight loss processes at ca. 100-470 and 470-490 °C giving a total weight loss of 13% while the thermogram for \([\text{G-2Rh(CO)}_2]\) displayed one weight loss process between ca. 350-650 °C with a total weight loss of 7% (see SI, Section SI-3). Additionally, we observed that the thermogram of \([\text{2Rh(CO)}_2\text{BPh}_4]\) only and a mixture of \([\text{2Rh(CO)}_2\text{BPh}_4]\) and carbon black (see SI, Figure S12) showed a two weight loss trend from 100-380°C due to the metal complex similar to what was observed from the thermogram of \([\text{CB-2Rh(CO)}_2]\).

The quantitative amount of Rh on CB and G obtained using ICP-OES was found to be 2.5 wt% for \([\text{CB-2Rh(CO)}_2]\) and 0.84 wt% for \([\text{G-2Rh(CO)}_2]\). This corresponds well to the estimated amount of Rh in \([\text{CB-2Rh(CO)}_2]\) (2.6 wt%) and \([\text{G-2Rh(CO)}_2]\) (1.3 wt%), calculated from the total weight loss obtained from TGA. For \([\text{GC-2Rh(CO)}_2]\), cyclic voltammetry was used to determine the quantity of Rh complexes immobilized on the GC electrode to be 3.4 x 10^{-10} mol cm^{-2} or 1.2 x 10^{-10} mol cm^{-2} (see SI, section SI-5).

SEM and TEM images of \([\text{G-2Rh(CO)}_2]\) showed that the integrity and morphology of the 2D structure is retained after treatment for immobilization of the Rh complex, and is similar to images of unmodified G (see SI, section SI-8/9). The Raman spectra of \([\text{CB-2Rh(CO)}_2]\) and \([\text{G-2Rh(CO)}_2]\) showed a slight increase in the defects (D) band compared to the graphite (G) band following immobilization of the complex onto the surfaces (see SI, section SI-7), which indicates that both carbon-rhodium hybrids contains covalent linkages to the carbon black or graphite surface respectively, consistent with observations for similar covalent functionalization on carbon materials.13, 34 An increase in the defects (D) band compared to the graphite (G) band of the carbon samples can be observed when comparing the peak intensity ratio of the D to G band of unmodified graphene, which was 0.79. After immobilization to form \([\text{G-2Rh(CO)}_2]\), the peak intensity ratio of the D to G band increased to 0.82. Similarly, the peak intensity ratio of the D to G band for \([\text{CB-2Rh(CO)}_2]\) was 1.0 which was higher when compared to the peak intensity ratio of D to G band of the unmodified carbon black of 0.92.

To summarize the surface characterization, we have demonstrated a straight-forward and effective method for the direct immobilization of Rh(I) complexes containing a mixed bidentate carbene-triazole ligand system onto carbon surfaces. The well-defined complexes were covalently anchored on GC, CB and G, showing that this method is versatile enough to be performed on various carbon surfaces with different surface areas and properties.

**Catalysis**

Following characterization of the hybrid catalysts, the efficiency of homogeneous complex \([\text{2Rh(CO)}_2\text{BPh}_4]\) and hybrid complexes \([\text{GC-2Rh(CO)}_2]\), \([\text{CB-2Rh(CO)}_2]\) and \([\text{G-2Rh(CO)}_2]\) were evaluated as catalysts for the hydrosilylation of diphenylacetylene (4) and triethylsilane at 50 °C and/or 25 °C using 0.02 mol% of Rh relative to the quantity of 4 (Scheme 3).35 Transition metal-catalyzed hydrosilylation of alkynes allows the formation of alkynesilanes in a straightforward, atom efficient and convenient method. Alkynesilanes are versatile organosilicon compounds that can be used for further transformations in many organic synthesis reactions.

\[
\text{Scheme 3 Hydrosilylation reaction of diphenylacetylene 4 and triethylsilane.}
\]

At 50 °C, \([\text{CB-2Rh(CO)}_2]\) and \([\text{2Rh(CO)}_2\text{BPh}_4]\) were both highly efficient catalysts, with the reaction reaching complete conversion of substrate 4 to product 5 in just 0.25 h (Fig. 4). While \([\text{G-2Rh(CO)}_2]\) was slightly less efficient compared to \([\text{CB-2Rh(CO)}_2]\) and \([\text{2Rh(CO)}_2\text{BPh}_4]\), the reaction still reached 56% conversion in 0.5 h and complete conversion in 1 h. The hydrosilylation reaction was repeated at 25 °C (to decrease the reaction rate to a more readily monitored rate) with \([\text{2Rh(CO)}_2\text{BPh}_4]\) and \([\text{CB-2Rh(CO)}_2]\) for better comparison. \([\text{CB-2Rh(CO)}_2]\) and \([\text{2Rh(CO)}_2\text{BPh}_4]\) each displayed very similar efficiency as catalysts for the reaction (Fig. 4). The reaction using \([\text{CB-2Rh(CO)}_2]\) as catalyst was slightly slower, reaching 77% conversion to product 5 in 1 h compared to the complete conversion obtained using \([\text{2Rh(CO)}_2\text{BPh}_4]\) in the same time frame. This slightly lower efficiency of \([\text{CB-2Rh(CO)}_2]\) could be due to the time required for diffusion of substrate to the carbon black support compared to the direct mixing of the two in the homogeneous reaction mixture. On completion, all reactions had turnover numbers (TON) close to 5000 (see SI, Table S14). These catalysts are the most efficient reported to date for the hydrosilylation of disubstituted alkynyl, both homogeneous and heterogeneous.11-45

On immobilizing the complex on a GC support ([(G-C-2Rh(CO))]), it was found that although the reaction was slow and showed only 8% conversion to product 5 in 48 h (Fig. 4), the TON for this reaction reached the very high value of 48000 in that time. This correlates well with the fact that the GC electrode has a plate-like flat structure with a limited surface area (2.4 cm²) and hence holds only a small number of moles of immobilized catalyst relative to the substrate whereas there was a much higher mole ratio of catalyst to substrate immobilized on the high surface area CB and G. The high TON observed here for \([\text{GC-2Rh(CO)}_2]\) is very similar to the turnover numbers we reported previously for GC supported catalysts.29
Fig. 4 Graph depicting the % conversion at times 0.25, 0.5, 1, 2 and 48 h for the hydrosilylation reaction using [2Rh(CO)]BPh₄, [CB-2Rh(CO)]₂, [G-2Rh(CO)]₂ and [GC-2Rh(CO)]₂ at 50 °C or 25 °C.

Table 3. Control experiments for the hydrosilylation reaction.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Conv. (%) [a]</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Unmodified CB only</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>2 Unmodified G only</td>
<td>0</td>
<td>24</td>
</tr>
<tr>
<td>3 G + [2Rh(COD)]BPh₄ after synthesis treatment</td>
<td>0.08</td>
<td>24</td>
</tr>
<tr>
<td>4 No catalyst</td>
<td>0</td>
<td>24</td>
</tr>
</tbody>
</table>

[a] Determined using ¹H NMR spectroscopy

In a series of control experiments at 50 °C, when using no catalyst or unmodified CB and G as the catalyst, the hydrosilylation reaction did not proceed even after 24 h (Table 3). In order to confirm that the carbon surfaces are covalently attached to the Rh(I) complexes, the homogeneous complex [2Rh(COD)]BPh₄, which lacks the aniline functional group that [1Rh(COD)]BPh₄ contains for the purpose of attachment, was mixed together with some unmodified G. The mixture was then treated using the same approach used to synthesize the hybrid catalysts, and the isolated G powder was tested for the hydrosilylation reaction. There was <0.08% conversion observed after 24 h, confirming that without the aniline functionalized group on the ligand, a covalent hybrid catalyst could not be assembled using the established synthesis.

Recyclability of hybrid catalysts

Initially, [GC-2Rh(CO)]₂ was investigated for the hydrosilylation reaction over the course of three reaction cycles. After each run, the GC electrode was analyzed by XPS. The ratio of N:Rh on the surface of the GC remained constant at ca. 4.5:1 (see SI, Table S1S), and this confirmed that the Rh complex remained on the GC surface even after multiple runs. The low level of conversion to product 5 (<11%) obtained over an extended reaction time (48 h) when using [GC-2Rh(CO)]₂ led to the investigation of the efficiency of hybrid catalysts on G and CB. In the recycling experiments for [CB-2Rh(CO)]₂ (1.6 mol%) and [G-2Rh(CO)]₂ (0.3 mol%), the hybrid catalysts were recycled over three 24 h cycles, and the filtrate and washings after each run were analyzed by ICP-MS to determine the Rh content. Both [G-2Rh(CO)]₂ and [CB-2Rh(CO)]₂ had excellent recycling ability (Fig. 5 (a)), with complete conversion to product 5 after each run. The excellent recyclability was reinforced by ICP-MS analysis of the washings (Fig. 5 (b)). When using [G-2Rh(CO)]₂ as the catalyst, the ICP-MS showed hardly any leaching after each run, with less than 6% loss of Rh from the G surface after three runs. When using [CB-2Rh(CO)]₂ as catalyst instead, an initial 12% loss of Rh from the CB surface was observed after the first cycle (Fig. 5(b)), consistent with the initial loss of the physisorbed Rh. This physisorbed Rh could not be removed prior to catalysis by normal washing procedures, and most likely requires the reaction conditions of the catalysis reaction to enable its removal. After the second and third cycle, there was only a total of 3% loss of Rh observed. Again, such results confirm the stability of the immobilized Rh complex on the CB surface. These results also suggest that the use of the mixed bidentate carbene-triazole ligand system allows an enhanced capacity to recycle the Rh(I) complexes compared to our previously described hybrid system.

Fig. 5 Graphs depicting: (a) the % conversions of the hydrosilylation reaction for three reaction cycles when using [CB-2Rh(CO)]₂ and [G-2Rh(CO)]₂, which are shown on the same graph and (b) the % Rhodium remaining on the carbon surfaces after each reaction cycle.

Fig. 6 Graphs depicting: (a) the % conversions of the hydrosilylation reaction for 10 reaction cycles when using [CB-2Rh(CO)]₂ and (b) the % conversions of the hydrosilylation reaction for 10 reaction cycles when using [G-2Rh(CO)]₂. 
To further investigate the recyclability of the hybrid catalysts on G and CB, \([\text{CB-2Rh(CO)}_3]\) and \([\text{G-2Rh(CO)}_3]\) were reused over 10 cycles of the catalysis reaction. Each cycle was tested after 4h at 25 °C (Fig. 6). \([\text{G-2Rh(CO)}_3]\) was found to be an extremely recyclable heterogeneous catalyst and complete (≥98%) conversions were obtained for all 10 cycles (Fig. 6 (b)). When recycling \([\text{CB-2Rh(CO)}_3]\), complete conversion (≥98%) of the reaction was obtained for the first 7 cycles. Over the following 8-10 cycles, there was a slight 10-20% reduction in product formation (Fig. 6 (b)), which suggests that \([\text{CB-2Rh(CO)}_3]\) is slightly less recyclable compared to \([\text{G-2Rh(CO)}_3]\). The high recyclability of the hybrid catalysts shown here supports the benefit of immobilizing the highly efficient and well-defined homogeneous catalyst \([\text{2Rh(CO)}_3]\)BPH_4 on the surface. \([\text{2Rh(CO)}_3]\)BPH_4 is also shown to be a highly efficient homogeneous catalyst for the hydrosilylation of diphenylacetylene as it can catalyze up to 5 cycles of extra substrate addition before reaching a saturation point in the reaction mixture (see SI, Figure S2). The development of the hybrid catalysts from the optimized homogeneous catalyst allows us to exploit the reusability of the homogeneous catalyst, providing us with highly recyclable hybrid catalyst that also allows for easy product separation.

Conclusions

In conclusion, investigations of a series of hybrid complexes on G, CB and GC as catalyst for the hydrosilylation of diphenylacetylene, it was found that \([\text{CB-2Rh(CO)}_3]\) was the most efficient catalyst and \([\text{G-2Rh(CO)}_3]\) was slightly less efficient than \([\text{CB-2Rh(CO)}_3]\). While \([\text{GC-2Rh(CO)}_3]\) did not reach the same conversion levels over time, the very highTON achieved demonstrated excellent efficiency of this catalyst as well. The results also showed hybrid complex \([\text{CB-2Rh(CO)}_3]\) was as efficient as the homogeneous complex \([\text{2Rh(CO)}_3]\)BPH_4 in catalyzing this reaction. The catalysts investigated here could be utilized in very small amounts to give high TONs ranging from 5000 to 48000. These catalysts are the most efficient of the homogeneous and heterogeneous catalysts reported to date for promoting the hydrosilylation of disubstituted alkyne. Finally, the recycling experiments also showed that the hybrid catalysts could be recycled for at least 10 times with hardly any loss of Rh from the surface. \([\text{G-2Rh(CO)}_3]\) was found to be slightly more recyclable compared to \([\text{CB-2Rh(CO)}_3]\). All the results demonstrate the stability and reusability of the rhodium Rhl complexes containing the carbene-triazole mixed bidentate ligand system.

Experimental

General Experimental and Materials

Unless otherwise stated, all manipulations were carried out under inert or argon-filled Braun glovebox. All reagents were purchased from Aldrich Chemical Company Inc. or Alfa Aesar Inc. and used as received unless otherwise noted. Graphene was contributed by Professor John Stride (UNSW). Glassy carbon electrodes (1 x 1 x 0.1 cm^3) were purchased from Goodfellow. Carbon black (XC-72R) was supplied by Cabot Corporation. RhCl_3·xH_2O was purchased from Precious Metals Online P/L. For the purposes of air sensitive manipulations and in the preparation of air sensitive metal complexes, tetrahydrofuran, dichloromethane, acetonitrile and pentane were dispensed from a Purasolv solvent purification system. Methanol was distilled from magnesium methoxide under an atmosphere of nitrogen or argon. The bulk compressed gases argon (>99.999%) and carbon monoxide (>99.5%) were obtained from Air Liquide and used as received. Nitrogen gas for Schlenk line operation comes from in-house liquid nitrogen boil-off. 1-azido-4-nitrobenzene, [Rh(COD)Cl]_2, 1-mesityl-3-(prop-2-yn-1-yl)-1H-imidazol-3-iium bromide and 1-mesityl-3-[(1-phenyl-1H-1,2,3-triazol-4-yl)methyl]-1H-imidazol-3-iium tetraphenylborate were synthesized using literature procedures. 1H and 13C(1H) NMR spectra were recorded on Bruker DMAX400, DMAX500 and DMAX600 spectrometers operating at 400, 500 and 600 MHz (1H) respectively and 100, 125 and 150 MHz (13C) respectively. 1H and 13C NMR chemical shifts were referenced internally to residual solvent resonances. Unless otherwise stated, spectra were recorded at 298 K and chemical shifts (δ), with uncertainties ±0.01 Hz for 1H and ±0.05 Hz for 13C, are quoted in parts per million, ppm. Coupling constants (J) are quoted in Hz and have uncertainties of ±0.05 Hz for 1H and ±0.05 Hz for 13C. 1H and 13C-1B. Numbering and figures corresponding to NMR characterization data are located in the SI, Table S1. Deuterated solvents were purchased from Cambridge Stable Isotopes and used as received. Air sensitive NMR samples were prepared in an inert gas glovebox or by vacuum transfer of deuterated solvents into NMR tubes fitted with a Young’s teflon valve. For air sensitive NMR samples, dicloromethane-d_2 and chloroform-d were distilled over calcium hydride. Microanalyses were carried out at the Campbell Micro-analytical Laboratory, University of Otago, New Zealand or at the Research School of Chemistry, The Australian National University, Canberra, Australia. Mass spectra were acquired using a Thermo LTQ Orbitrap XL located in the Bioanalytical Mass Spectrometry Facility (BMSF) in UNSW. M is defined as the molecular weight of the compound of interest or cationic fragment for cationic metal complexes.

1-mesityl-3-[(1-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl)methyl]-1H-imidazol-3-iium bromide, nitro functionalized ligand precursor to ligand 1
red crystals. (712 mg, 46%) \(^1\)H NMR (400 MHz, CDCl₃): δ 10.31 (br s, 1H, Im-H2), 9.63 (s, 1H, Tz-H5), 8.38 (d, \(^3\)J = 9.3 Hz, 2H, m-CH of ArNO₂), 8.13 (d, \(^3\)J = 9.3 Hz, 2H, o-CH of ArNO₂), 8.08 (t, \(^3\)J = 1.5 Hz, 1H, Im-H3), 7.14 (t, \(^3\)J = 1.5 Hz, 1H, Im-H4), 6.98 (s, 2H, m-CH of Mes), 6.22 (s, 2H, CH₂), 2.32 (s, 3H, p-CH₃ of Mes), 2.04 (s, 6H, o-CH₃ of Mes) ppm; \(^13\)C\(^{[\text{H}]}\) NMR (100 MHz, CDCl₃): 147.5 (C of PhNO₂), 142.0 (Tz-C'), 141.7 (p-CH₃ of Mes), 140.9 (ipso-C to NH₂ of PhNH₂), 138.1 (Im-C2), 134.2 (o-CH₃ of Mes), 130.6 (ipso-C of Mes), 130.0 (m-CH of Mes), 125.6 (m-CH of ArNO₂), 124.9 (Tz-C'), 123.4 (Im-C5), 123.3 (Im-C4), 120.9 (o-CH of ArNO₂), 44.5 (CH₃), 21.2 (p-CH₃ of Mes), 17.8 (o-CH₃ of Mes) ppm; HRMS (ESI\(^{+}\), MeOH): m/z (%): calculated for \(\text{C}_{12}\text{H}_{14}\text{N}_2\text{O}_2\) \([\text{M}^+\] = \(\text{M}^+\) = 197.1721; found \([\text{M}^+\] = 197.1718 (100 %) amu; **Elemental Analysis:** Found C, 51.85; H, 4.68; N, 17.21; Calculated for \(\text{C}_{12}\text{H}_{23}\text{BrN}_2\text{O}_2\); 0.25CH₂Cl₂; C, 52.03; H, 4.42; N, 17.13 %.

**3-[(1-(4-aminophenyl)-1H-1,2,3-triazol-4-yl)methyl]-1-mesityl-1H-imidazol-3-ium bromide, (1)**

The nitro functionalized ligand precursor above (605 mg, 1.29 mmol) was dissolved in methanol (30 mL). Pd/C (10% w/w, 54.4 mg, 0.0511 mmol, 4 mol%) was then added to the orange solution. After stirring for 5 minutes, hydrize hydrate (1.3 mL, 26.8 mmol) was added slowly to the reaction mixture. The red-black mixture was heated at reflux under argon overnight. The mixture was filtered through celite\(^{\text{c}}\) which was washed thoroughly with excess acetone. The solvent was removed in vacuo and the crude product was dissolved in dichloromethane (15 mL). NaBH₄ (147 mg, 0.430 mmol) was added and white solid precipitates immediately. The reaction mixture was stirred vigorously at room temperature for 45 minutes to ensure complete reaction. The mixture was filtered through celite\(^{\text{c}}\) which was washed thoroughly with dichloromethane. The solution was concentrated in vacuo to ca. 2 mL which was added slowly dropwise to a vigorously stirred solution of pentane (30 mL) in an ice bath. Yellow precipitate forms immediately. After five minutes of stirring, the solvent was filtered and the precipitate dried under vacuum to give \[\text{[Rh(COD)]BPh₄}\] as a bright yellow solid. (323 mg, 85%) \(^1\)H NMR (400 MHz, CD₂Cl₂): δ 7.40 (m, 8H o-CH of BPh₄), 7.24 (d, \(^3\)J\text{HH} = 0.9 Hz, 2H, o-CH of ArNH₂), 7.04 (m, 2H, m-CH of Mes overlapped with Tz-H'), 7.04 (s, 1H, Tz-H overlapped with m-CH of Mes), 7.00 (t, \(^3\)J\text{HH} = 7.5 Hz, 8H, m-CH of BPh₄), 6.89 (d, \(^3\)J\text{HH} = 1.9 Hz, 1H, Im-H5), 6.85 (t, \(^3\)J\text{HH} = 7.1 Hz, 3H, p-CH of BPh₄), 6.75 (d, \(^3\)J\text{HH} = 1.9 Hz, 1H, Im-H4), 6.72 (d, \(^3\)J\text{HH} = 8.9 Hz, 2H, m-CH of ArNH₂), 4.92 (m, 2H, CH of COD), 4.76 (s, 2H, CH₂), 4.02 (s, 2H, NH₂), 3.64 (m, 2H, CH of COD), 2.37 (s, 3H, p-CH₃ of Mes), 2.25 (m, 2H, CH₂ of COD), 2.10 (s, 6H, o-CH₃ of Mes), 1.97 (m, 6H, CH₃ of COD) ppm; \(^13\)C\(^{[\text{H}]}\) NMR (100 MHz, CD₂Cl₂): δ 176.2 (d, \(^3\)J\text{HC} = 51.2 Hz, Im-C₂), 164.4 (q, \(^3\)J\text{HC} = 49.3 Hz, o-CH of BPh₄), 149.0 (C of ArNH₂), 140.1 (p-CH₃ of Mes), 140.0 (C of Tz), 136.3 (br s, o-CH of BPh₄), 135.9 (o-CH₃ of Mes), 135.5 (ipso-C of Mes), 129.5 (m-CH of Mes), 127.1 (ipso-C to NH₃ of ArNH₂), 126.2 (q, \(^3\)J\text{HH} = 2.6 Hz, m-CH of BPh₄), 123.1 (Im-C₄), 122.6 (o-CH of ArNH₂), 122.5 (im-C₅), 122.3 (p CH of BPh₄), 121.2 (Tz-C'), 115.3 (m-CH of ArNH₂), 96.7 (d, \(^3\)J\text{HH} = 7.9 Hz, 2C, CH of COD), 79.1 (d, \(^3\)J\text{HH} = 12.4 Hz, 2C, CH of COD), 45.1 (CH₃), 32.6 (2CH₂ of COD), 29.2 (2CH₃ of COD), 21.2 (p-CH₃ of Mes), 18.6 (o-CH₃ of Mes) ppm; HRMS (ESI\(^{+}\), MeOH): m/z (%): calculated for \(\text{C}_{21}\text{H}_{24}\text{N}_2\text{Rh}^+\) \([\text{M}^+\] = \(\text{M}^+\) = 569.1900; found \([\text{M}^+\] = 569.1893 (100 %); calculated for [M-C₄H₄Rh⁺] = 359.1979; found [M-C₄H₄Rh⁺] = 359.1977 (78%) amu; **Elemental Analysis:** Found C, 71.62; H, 6.09; N, 9.44; Calculated for \(\text{C}_{12}\text{H}_{23}\text{BrN}_2\text{Rh}\); C, 71.62; H, 6.12; N, 9.46 %.

**[2Rh(COD)]BPh₄**

Sodium ethoxide (14.7 mg, 0.225 mmol) was added to a stirred suspension of \([\text{RhCOD}]^+\) (53.5 mg, 0.109 mmol) in ethanol (10 mL). The orange-yellow mixture was stirred at room temperature for 10 minutes. A solution of 1-mesityl-3-[(1-phenyl-1H-1,2,3-triazol-4-yl)methyl]-1H-imidazol-3-ium tetraphenylborate \(^{[\text{d}]}\) (144 mg, 0.217 mmol) in tetrahydrofuran (20 mL) was added slowly dropwise into the stirred suspension. The reaction mixture was stirred at room temperature for three hours. The solvent was removed in vacuo to give the crude product as a bright yellow solid. The crude product was dissolved in dichloromethane and filtered through celite\(^{c}\) which was washed thoroughly with excess dichloromethane. The solvent was concentrated to ca. 2 mL. Pentane (25 mL) was then added slowly and a bright yellow solid

---

\(^{[\text{a}]}\) This journal is © The Royal Society of Chemistry 20xx

---

**ARTICLE**

Journal Name

---

Page 6 of 9
precipitates. The solvent was filtered off and the solid was dried under vacuum to yield [2Rh(COD)]BPh₄ as a bright yellow solid. (126 mg, 64%)[^6] ¹H NMR (400 MHz, CDCl₃): δ 7.55 (m, 8H, o-CH of BPh₄), 7.48 (m, 3H, o- and p-CH of Ph), 7.38 (m, 2H, m-CH of Ph), 7.02 (s, 2H, m-CH of Mes overlapped with m-CH of BPh₄), 7.00 (t, J_H-H = 7.2 Hz, 8H, m-CH of BPh₄ overlapped with m-CH of Mes), 6.84 (t, J_H-H = 7.3 Hz, 4H, p-CH of BPh₄), 6.76 (d, J_H-H = 1.8 Hz, 1H, Im-H₄), 6.65 (d, J_H-H = 1.8 Hz, 1H, Im-H₄), 6.58 (s, 1H, Tz-₄), 4.89 (m, 2H, CH₂ of COD), 4.44 (s, 2H, CH₂), 3.63 (m, 2H, CH of COD), 2.38 (s, 3H, o-CH₃ of Mes), 2.25 (m, 2H, CH₂ of COD), 2.09 (s, 6H, p-CH₃ of Mes), 1.96 (m, 6H, CH₂ of COD ppm); ¹³C(¹H) NMR (100 MHz, CDCl₃): δ 175.3 (d, J_C-H = 52.7 Hz, 3C, ipso-C of Ph), 164.4 (q, J_C-H = 49.6 Hz, ipso-C of BPh₄), 140.1 (C of Tz), 139.8 (p-CCH₃ of Mes), 136.3 (br s, o-CH of BPh₄), 135.8 (o-CCH₃ of Mes), 135.6 (ipso-C of Ph), 135.2 (ipso-C of Mes), 130.1 (p-CH of Ph), 130.0 (o-CH of Ph), 129.4 (m-CH of Ph), 126.0 (q, J_C-H = 2.8 Hz, m-CH of BPh₄), 122.8 (im-C₃), 122.6 (im-C₄), 122.1 (p-CH of BPh₄), 121.8 (Tz-₄), 120.8 (m-CH of Ph), 96.3 (d, J_C-H = 7.8 Hz, 2C, CH of COD), 78.9 (d, J_C-H = 12.5 Hz, 2C, CH of COD), 44.6 (CH₂), 32.4 (2CH₂, CH of COD), 29.0 (2CH₂, CH of COD), 21.2 (p-CH₃ of Mes), 18.6 (o-CH₃ of Mes) ppm; HRMS (ESI, MeOH): m/z (%) calculated for [C₉H₇N₂RhH]⁺ = [M⁺] = 554.1786, found [M⁺] = 554.1776 (100 %) element; Analytical Data: Found C, 69.76; H, 6.19 and N, 7.80; Calculated for C₉H₇B₄N₂Rh.O.5CH₂Cl₂: C, 70.13; H, 5.94 and N, 7.64 %.

[2Rh(COD)]BPh₄

[2Rh(COD)]BPh₄ (117 mg, 0.133 mmol) was dissolved in dichloromethane (15 mL). The yellow solution was degassed via three cycles of freeze-pump-thaw. The reaction mixture was placed under an atmosphere of carbon monoxide gas in a balloon. The solution turned pale yellow in colour after stirring at room temperature for one hour. Pentane (45 mL) was added and yellow solid precipitates in solution with vigorous stirring. The solvent was filtered and the solid was washed with pentane (2 x 2 mL). The precipitate was dried in vacuo to yield [2Rh(COD)]BPh₄ as a pale yellow solid. (75.6 mg, 70%)[^6] ¹H NMR (500 MHz, CDCl₃): δ 7.59 (m, 3H, 3H, o-CH of Ph), 7.53 (m, m-CH of Ph), 7.44 (m, 8H, o-CH of BPh₄), 7.06 (s, 2H, m-CH of Mes), 6.98 (t, J_H-H = 7.5 Hz, 8H, m-CH of BPh₄ overlapped with Im-H₄), 6.97 (d, J_H-H = 1.8 Hz, 1H, Im-H₄ overlapped with m-CH of BPh₄), 6.93 (d, J_H-H = 1.8 Hz, 1H, Im-H₄), 6.82 (t, J_H-H = 7.2 Hz, 4H, p-CH of BPh₄), 6.70 (s, 1H, Tz-H₄), 4.41 (s, 2H, CH₂), 2.38 (s, 3H, p-CH₃ of BPh₄), 2.06 (s, 0H, o-CH₃ of BPh₄); ¹³C(¹H) NMR (125 MHz, CDCl₃): δ 184.7 (d, J_C-H = 55.9 Hz, CO), 184.6 (d, J_C-H = 70.6 Hz, CO), 172.1 (d, J_C-H = 46.9 Hz, Im-C₂), 164.5 (q, J_C-H = 49.3 Hz, ipso-C of BPh₄), 141.2 (p-CCH₃ of Mes), 140.8 (C of Tz), 136.2 (br s, o-CH of BPh₄), 136.1 (o-CCH₃), 135.7 (ipso-C of Ph), 135.2 (ipso-C of BPh₄), 131.1 (p-CH of Ph), 130.5 (o-CH of Ph), 129.9 (m-CH of Mes), 126.4 (q, J_C-H = 2.6 Hz, m-CH of BPh₄), 124.1 (im-C₃), 123.4 (im-C₄), 122.5 (m-CH of BPh₄), 122.3 (Tz-C₄), 121.4 (m-CH of Ph), 44.6 (CH₂), 21.3 (p-CH₃ of Mes), 18.4 (o-CH₃ of Mes) ppm; HRMS (ESI, MeOH): m/z (%): calculated for [C₉H₇N₂O₂RhH]⁺ = [M⁺] = 502.0750, found [M⁺] = 502.0703 (100 %) amu; FTIR (solid) νCO = 2083, 2019 (s cm⁻¹); Elemental Analysis: Found C, 66.42; H, 4.95; N, 8.49; Calculated for C₂₇H₃₄N₂O₂Rh.0.5CH₂Cl₂: C, 66.03; H, 4.90; N, 8.52 %.

Immolization of [CB-2Rh(CO)₃] and [G-2Rh(CO)₃]

The complex [1Rh(COD)]BPh₄ (24.8 mg, 0.0279 mmol) was dissolved in a degassed solution of nitromethane (10 mL). The mixture was cooled in an ice bath for 15 minutes before concentrated hydrochloric acid (0.5 mL, 0.5 M) was added dropwise into the stirred yellow solution while keeping the mixture between 0-5 °C. Sodium nitrate (1.90 mg, 0.0279 mmol) was then added and the mixture was stirred vigorously for 5 minutes. After taking the mixture out of the ice bath, carbon black or graphene (50 mg) was added while the mixture was stirred vigorously to ensure that the carbon powders was diffused in solution properly. The mixture was gradually warmed up to room temperature. The mixture was stirred under nitrogen at room temperature overnight. The modified carbon powder was separated from the reaction media via centrifugation (4000 rpm) for 5 minutes. It was consecutively washed and stirred vigorously with a methanol:MilliQ water (50:50, 20 mL) and methanol (5 x 10 mL) followed by centrifugation after each washing. The washed powder was dried under vacuum in a dessicator for 24 hours. The modified carbon powders was then dispersed with vigorous stirring in a dichloromethane:pentane solution (1:1, 20 mL). The mixture was degassed via three cycles of freeze-pump-thaw and then placed under an atmosphere of carbon monoxide in a balloon (1 atm). The mixture was left to react for one hour before the modified powder was separated from the reaction solvent via centrifugation. The modified powder was washed and stirred vigorously with pentane (3 x 10 mL) and methanol (3 x 10 mL) followed by centrifugation after each washing. The washed powder was then dried under vacuum in the dessicator for 24 hours to give with [CB-2Rh(CO)₃] (37.2 mg, 72%) and [G-2Rh(CO)₃] (32.0 mg, 68%).

Immolization of [GC-2Rh(CO)₃]

The glassy carbon electrode was polished sequentially in alumina slurries (distilled water suspension) of 1.0, 0.3 and 0.05 µm on micropolishing cloth (Buehler, IL, USA) and rinsed with distilled water between each step. It was then washed thoroughly with ethanol and soaked for 30 mins in dichloromethane. The complex [1Rh(COD)]BPh₄ (24.8 mg, 0.0279 mmol) was dissolved in a degassed solution of nitromethane (10 mL). The mixture was cooled in an ice bath for 5 minutes before concentrated hydrochloric acid (0.5 mL, 0.5 M) was added dropwise into the stirred yellow solution while keeping the mixture between 0-5 °C. Sodium nitrate (1.90 mg, 0.0279 mmol) was then added followed by the glassy carbon (GC) electrode. The mixture was left to sit in the ice bath for a further hour before allowing the mixture to gradually warm up to room temperature and remained at room temperature overnight. The modified GC electrodes was separated from the reaction media and washed with MilliQ water (5 mL). It was then consecutively washed with a methanol:MilliQ water
(50:50, 20 mL) and methanol (5 x 10 mL). The washed modified GC electrode was dried under a gentle flow of nitrogen. The modified GC electrode was then dispersed in a dichloromethane:pentane solution (1:1, 20 mL). The mixture was degassed via three cycles of freeze-pump-thaw and then carbon monoxide was slowly bubbled into the mixture for 15 minutes. The modified GC electrode was washed with pentane (3 x 10 mL) and then methanol (3 x 10 mL). The washed powder was then dried under a gentle flow of nitrogen to give with [GC-2Rh(CO)]

Procedure for hydrosilylation reaction using the homogeneous catalyst, glassy carbon (GC), carbon black (CB) and graphene (G) hybrid catalysts

The reactions were performed in glass v-vials fitted with a magnetic stirring bar and a Teflon screw-caps. For the glassy carbon hybrid catalyst, the electrode (1 x 1 x 0.1 cm), diphenylacetylene (0.1 M), triethysilane (0.2 M) and tetrahydrofuran (2 mL) were weighed into the glass vial in the glovebox. For the homogenous catalyst (0.3 mg), carbon black (0.8 mg) or graphene (0.5 mg) hybrid catalysts, the catalyst (0.02 mol% Rh relative to amount of diphenylacetylene) and diphenylacetylene (3.3 M) were weighed in air into the vial. The vials were then brought into the glovebox and triethylsilane (6.6 M) and tetrahydrofuran (0.06-0.6 mL) was added. The reactions vials were stirred and heated in an oil bath at 50 °C for 0.25-24 hours. At set time intervals until completion of the reaction, the reaction vial was removed from the oil bath and immediately cooled in an ice bath to room temperature.

For the reaction vial containing the glassy carbon hybrid catalyst, the reaction mixture was removed from the vial and solvent evaporated. The product was dissolved in CDCl3 for NMR analysis. The reaction vial containing the hybrid catalysts on carbon black and graphene was centrifuged and the supernatant was collected into a round bottom flask. The solvent was evaporated and the CDCl3 was added to dissolve the products for NMR analysis. In all cases, the product conversions were calculated by integration of the chosen product peak in the 1H NMR spectrum against the integration of the chosen starting material (diphenylacetylene) peak.

During the recycling experiments, the glassy carbon electrode catalyst was removed from the reaction mixture, washed with methanol thoroughly (6mL) and the electrode was dried under a gentle flow of nitrogen for 1 minute and reused subsequently. The carbon-rhodium catalysts on carbon black and graphene was washed with methanol (3 x 2 mL) and centrifuged to remove the solvent used in between each cycle. The carbon-rhodium catalyst was then dried under vacuum and reused in the next cycle. All supernatant and washings were collected and analyzed by ICP-MS.

Acknowledgements

Financial support from the University of New South Wales and the Australian Research Council are gratefully acknowledged. This research was supported under the Australian Research Council’s Discovery Projects funding scheme (project numbers DP130101838 and DP150103065). We are grateful to Prof. John Stride for providing the graphene and Cabot Corporation for the donation of the carbon black (Vulcan XC-72R). We thank Dr. Karen Privat of the Mark Wainwright Analytical Centre (UNSW) for collecting the SEM images and Mr. Fei Han for collecting the TEM images. CMW thanks the Australian Government for the award of an International Research Postgraduate Scholarship (IPRS).

Notes and references

31. The nature of the counter-ions for the positively charged immobilized complexes could not be established unambiguously by XPS, which was consistent with previous reports; D. R. Laws, J. Sheats, A. L. Rheingold and W. E. Geiger, Langmuir, 2010, 26, 15010-15021.
32. We also observed in all hybrid cases, a very minor peak within the N1s peak at about 399-400 eV indicative of the azo bond (N=N) formation due to some incomplete diazonium reaction and this is consistent with previous reports; A. L. Gui, E. Luais, J. R. Peterson, J. J. Gooding, ACS Appl. Mater. Interfaces, 2013, 5, 4827-4835.
35. In all cases, the E isomer (5) of the alkene product was formed in >99:1 ratio to the Z isomer (6).
47. S. W. Kwok, J. R. Fotsing, R. J. Fraser, V. O. Rodionov and V. V. Fokin, Org. Lett., 2010, 12, 4217-4219.