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The advantages of covalently attaching organometallic catalysts to a carbon black support: Recyclable Rh(I) complexes that deliver enhanced conversion and product selectivity

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Pure carbon black (CB) was covalently attached to a bidentate nitrogen coordination motif with a carbon-carbon bond by spontaneous reaction with an *in situ* generated ligand precursor. The functionalized support was treated with $[Rh(CO)_2Cl]_2$ to form a heterogeneous carbon-based support covalently linked to a well defined Rh(I) coordination complex . The hybrid material was characterized using X-ray photoelectron spectroscopy (XPS), thermogravimetric analysis (TGA), Infrared (IR) spectroscopy and inductively coupled plasma mass spectrometry (ICP-MS). The CB-supported Rh(I) catalyst was active in both hydroamination and dihydroalkoxylation reactions achieving turnover numbers approaching 1000 and was readily recycled. The selectivity of an intramolecular dihydroalkoxylation reaction was significantly improved by covalently anchoring the catalyst to the CB surface.

Introduction

The immobilization of structurally well-defined transition metal (TM)-based catalysts onto solid supports has the potential to combine the rapid substrate turnover and exquisite selectivity that can be delivered by contemporary homogeneous catalysis with the inherent practicality and industrial viability of heterogeneous catalysis.[1] As such, several classes of solid support have been extensively investigated as scaffolds for covalently anchored transition metal-based catalysts, including silica and aluminosilicates,[2] metal-organic frameworks and coordination polymers,[3] organic polymers and resins,[4] and carbon-based materials.[5] Whilst carbon allotropes are excellent candidates for catalyst scaffolds –due to their large surface area, thermal and chemical stability, tolerance of extreme pH, well-developed surface chemistry and commercial availability– their integration into hybrid catalyst systems is arguably underdeveloped in comparison with other suitable supports. Over the last decade several groups have demonstrated the catalytic activity and recyclability of TM complexes covalently attached to graphene oxide,[6] carbon nanotubes[7] and activated carbon.[8]
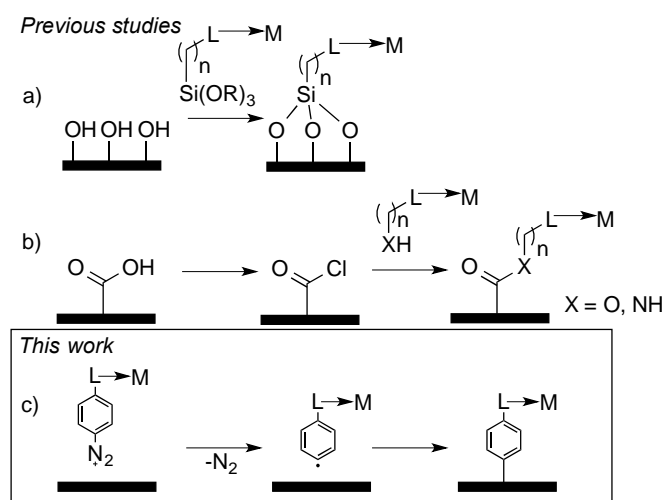

Scheme 1. Covalent anchoring of metal complexes on carbon surface via the formation of: a) silicon-oxygen bonds, b) carbon-oxygen/nitrogen bonds, c) carbon-carbon bonds

In addition, TM-complexes have recently been attached non-covalently, using a pyrene tether, to carbon nanotubes[9] and reduced graphene oxide[10] and the resultant materials were

shown to have catalytic properties over multiple reaction cycles.

To date the majority of the studies devoted to covalently attaching functional molecules onto carbon supports make use of surface oxygen functionalities (primarily alcohols and carboxylic acids) generated following partial oxidation of the carbon surface as anchor points (Scheme 1a, b). We reasoned that a complementary strategy, exploiting the spontaneous reaction of diazonium salts directly with carbon surfaces (Scheme 1c) would promote the development of hybrid catalysts that could tolerate harsh reaction conditions due to the robust nature of the C-C bond (for example the basic conditions required for key organic transformations such as the Heck, Suzuki and Sonogashira cross coupling reactions).[11] The use of diazonium salts for surface functionalization is well established,[12] but has not been previously exploited for the direct attachment of TM catalysts. As such, we reasoned that this strategy could expand the toolbox of carbon materials available as inert heterogeneous catalyst supports.[13]

Recently we reported on the covalent immobilization of Rh(I) complexes onto glassy carbon electrodes and demonstrated that these hybrid materials could catalyse intramolecular hydroamination reactions with turnover numbers[14] (TONs) approaching 100,000.[15] Although the enhanced activity of the surface-tethered catalyst was extremely encouraging, complete substrate conversion was not observed (*ca*. 50% conversion in 72 hours). The modest conversion was attributed to the low surface area of the glassy carbon electrode. To overcome the low conversion, we became interested in using a chemically analogous carbon material with a larger surface area. For this reason we began to explore the possibility of using high purity carbon black (Vulcan XC-72R, CB) as an inexpensive catalyst support. Vulcan is a virtually pure form of carbon widely used in underground power cables and as a support for electrocatalysis[16] and fuel cells.[17] Although CB is a particularly inert form of carbon, the Cabot Coorperation[18] and Belanger[19] have previously demonstrated that it can be covalently modified via spontaneous reaction with adsorbed aryl diazonium salts (spontaneous adsorption)[20] in a manner closely analogous to the electrografting[21] method we employed in our previous study.[15]
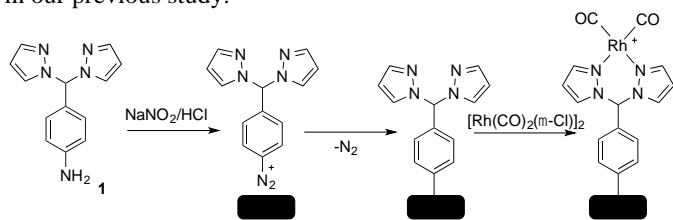
Scheme 2. Immobilization of the Rh(I) bpm complex on the surface of glassy carbon/carbon black.

Here we report on the immobilization of a *bis*(pyrazol-1-yl)methane (bpm) ligand on to glassy carbon (GC) electrodes and CB via spontaneous absorption of its corresponding aryl diazonium salt. The immobilized ligand was subsequently bound to Rh(I) and the resultant carbon–TM-complex material

was utilized as a recyclable catalyst for hydroamination and dihydroalkoxylation reactions with excellent activity even after multiple cycles.

Results and discussion

Immobilization of a Rh(I) bpm complex onto glassy carbon electrodes without electrochemical assistance:

In order to determine the viablity of the spontaneous ligand immobilization protocol, glassy carbon (GC) electrodes were used as test scaffolds. We have previously established that electrografting can be used to form a monolayer of catalyst on the surface of an electrode.[15] Polished GC electrodes were treated with an acidic solution of sodium nitrite and **1**, rinsed thoroughly and then exposed to a solution of [Rh(CO)$_2$(Cl)]$_2$ (Scheme 2). Following copious rinsing, the extent of the surface attachment of ligands and subsequent TM ion uptake was investigated using X-ray photoelectron spectroscopy (XPS). The survey XP spectra of the polished GC electrode, the electrode with immobilized bpm ligand (GC-bpm) and the electrode with bound Rh(I) complex (GC-[Rh(bpm)(CO)$_2$]) are
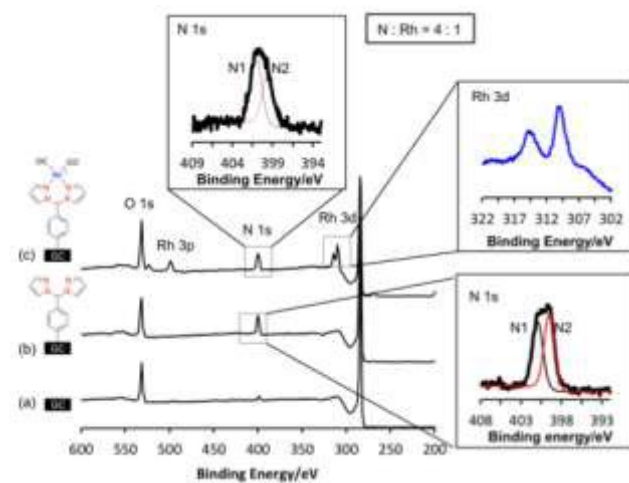
shown in Figure 1.

Figure 1. XP survey spectra of; (a) the unmodified glassy carbon (GC) electrode, (b) the GC electrode after treatment with **1** (GC-bpm), (c) the GC electrode after treatment with **1** and [Rh(CO)$_2$Cl]$_2$ (GC-[Rh(bpm)(CO)$_2$]).

A large increase in the nitrogen to carbon ratio is clearly visible when comparing GC with GC-bpm (Figure 1a vs. 1b). The N 1s peak located at *ca*. 400 eV was deconvoluted and fitted with two N 1s peaks. The peak with a lower binding energy was assigned to the pyridine-like nitrogen atom (N1), whereas the peak with a higher binding energy was assigned to pyrrole-like nitrogen atom (N2). The relative ratio of N1 to N2 was calculated to be close to 1:1 suggesting that the observed peak is due to the attached bpm ligand. Furthermore, the XPS signals corresponding to the immobilized bpm ligand are similar to those for the same ligand attached via electrochemical reduction of the corresponding diazonium salt.[15] The appearance of Rh 3p and 3d peaks in the XP

spectrum of GC-[Rh(bpm)(CO)$_2$] (Figure 1c) confirm the presence of rhodium on the surface of the electrode. In addition, the observed atomic ratio of N:Rh on the surface of the electrode is close to the expected ratio of 4:1 assuming every Rh(I) ion is bound to a bpm ligand. Furthermore, the binding energy for Rh $3d_{5/2}$ peak is ca. 310 eV and this value is very similar to that reported for the electrochemically immobilized complex.[15] In line with previous studies[22] the nature of the counter-ions for the positively charged immobilized complexes could not be established unambiguously by XPS.[23]

Immobilization of the Rh(I) bpm complex onto carbon black:

The success of the spontaneous immobilization of the Rh(I) complex on glassy carbon electrodes without electrochemical assistance encouraged us to proceed with the immobilization of the complex onto CB. The synthesis of carbon black modified with a bpm ligand (CB-bpm) and then subsequent complexation with Rh(I) (CB-[Rh(bpm)(CO)$_2$]) was carried out in a similar manner to that described for the GC electrodes (see Scheme 2 and experimental section). The quantitative evaluation of the products was accomplished through both XPS and thermogravimetric analysis (TGA). CB-[Rh(bpm)(CO)$_2$]) was further characterized using Raman and IR spectroscopy and Inductively Coupled Plasma Mass Spectrometry (ICP-MS).
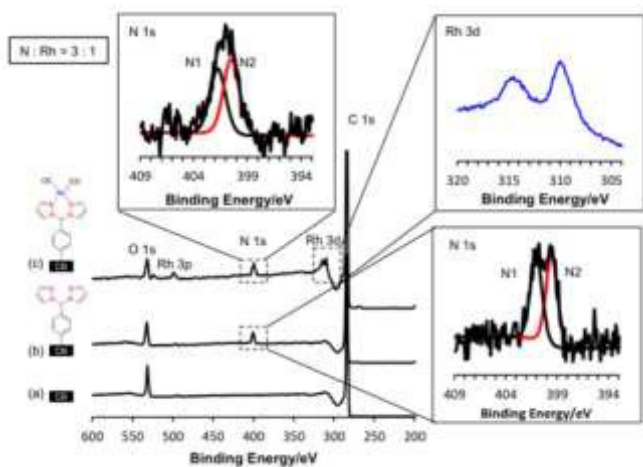

Figure 2. XP survey spectra of (a) unmodified carbon black (CB), (b) CB after treatment with **1** (CB-bpm), (c) CB after treatment with **1** and [Rh(CO)$_2$Cl]$_2$ (CB-[Rh(bpm)(CO)$_2$]).

The XP survey spectra of unmodified carbon black (CB), CB-bpm and CB-[Rh(bpm)(CO)$_2$] are in good agreement with the data recorded for the analogous GC-electrodes described above (Figure 2). The largely increased ratio of N relative to C following attachment of the ligand (Figure 2 b) strongly suggests that the ligand is present on the surface of the CB. In addition, following Rh(I) coordination, both the N 1s and Rh 3d diagnostic peaks have the same signature binding energies observed previously for the GC electrodes. However, in this case the atomic ratio of N:Rh obtained for CB-[Rh(bpm)(CO)$_2$] is ca. 3:1, possibly due to the presence of non-specifically

bound Rh(I) on the surface of the Vulcan XC-72R (Figure 2c). As with immobilization onto GC electrodes the chloride ion was observed by XPS (see table S1 for example) but not in a ratio that matched the % Rh on the surface suggesting that residual negative ions associated with the CB surface also act as counterions to the catalyst.

The results of TGA, run under an atmosphere of argon, are shown in Figure 3. The thermogram of unmodified CB is largely featureless (Figure 3, black trace) and the overall weight loss measured after analysis is only ca. 0.5%. In contrast, TGA of CB-bpm (Figure 3, blue trace) indicates a more pronounced overall weight loss of ca. 2.5%[24] largely due to three distinct processes starting at ca. 140, 250 and 400 °C. The relatively high temperatures at which two of the major decompositions occur (accounting for > 1.5% of the mass loss) suggests that covalent attachment was predominantly successful and most of the ligands are not simply physically adsorbed on the surface of the CB. These data are also consistent with previously reported TGA of functionalized CB.[25]
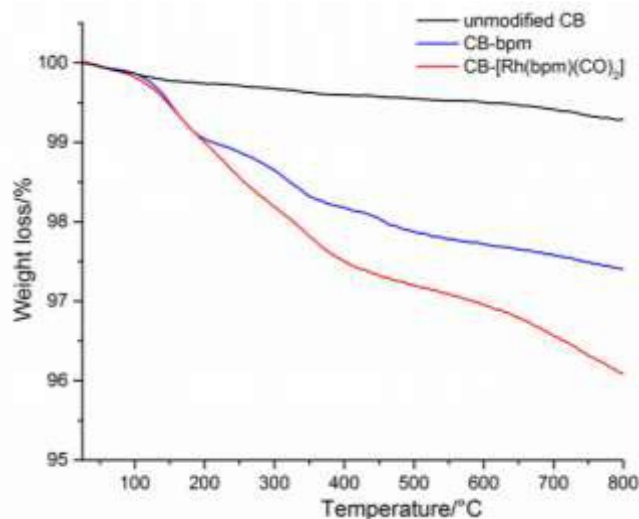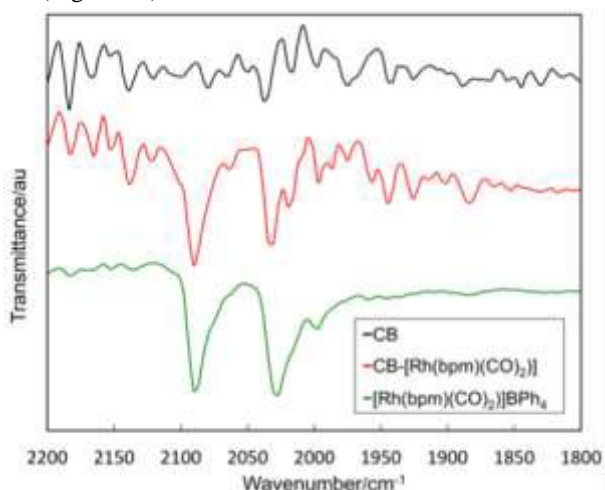

Figure 3. TGA curves for unmodified carbon black (CB, black trace), bpm-modified carbon black (CB-bpm, blue trace) and carbon black modified with Rh complex (CB-[Rh(bpm)(CO)$_2$], red trace) recorded under an atmosphere of argon.

The thermogram of CB-[Rh(bpm)(CO)$_2$] indicates an overall weight loss of ca. 3.8% with the first process beginning at ~120 °C and a second distinct smaller weight loss event occurring at ~ 600 °C (Figure 3). In the case of CB-[Rh(bpm)(CO)$_2$] the onset of the weight loss is slightly lower and less well defined than that observed for CB-bpm. It is possible that residual physisorbed Rh(I) precursor is subliming in the early stages of the TGA. It was not possible to definitively confirm the covalent attachment of CB-[Rh(bpm)(CO)$_2$] using TGA.

In addition, as the major mass loss event for CB-[Rh(bpm)(CO)$_2$] takes place over a large temperature range we suspect that the Rh(I) is catalyzing the oxidation of the carbon surface at these elevated temperatures. The hypothesized Rh(I)

catalyzed oxidation of the carbon support was also observed when the samples were subjected to TGA under an atmosphere of air (Figure S1).

Figure 4. IR spectra for unmodified carbon black (CB, black trace), carbon black modified with Rh complex (CB-[Rh(bpm)(CO)$_2$], red trace) and homogenous catalyst ([Rh(bpm)(CO)$_2$]BPh$_4$, green trace).

The presence of Rh-bound CO groups on the surface of CB-[Rh(bpm)(CO)$_2$] was confirmed using Infrared (IR) spectroscopy (Figure 4). The appearance of two absorption peaks at *ca* 2090 cm^{-1} and 2030 cm^{-1} in the IR spectrum of CB-[Rh(bpm)(CO)$_2$] (Figure 4, red trace) strongly suggests the presence of CO groups on the surface. In addition, the IR spectrum of CB-[Rh(bpm)(CO)$_2$] closely matches the same region of an IR spectrum of authentic [Rh(bpm)(CO)$_2$]BPh$_4$ (Figure 4, green trace). Raman spectroscopy of the unmodified CB and CB-[Rh(bpm)(CO)$_2$] revealed that the disorder (D) band increased slightly relative to the graphite (G) band following functionalization suggesting that the catalyst was covalently linked to the CB surface (Figure S2).[26]

Finally, inductively coupled plasma mass spectrometry (ICP-MS) confirmed the presence of Rh(I) in the sample quantitatively as 1.0 % of the total mass (see Tables S5 and S6 for more details) which correlates reasonably well with the mass loss observed by TGA (theoretical contribution from Rh = 0.9 wt%).

Catalytic activity of CB-[Rh(bpm)(CO)$_2$]:

Following characterization, CB-[Rh(bpm)(CO)$_2$] was investigated as a catalyst for hydroamination and dihydroalkoxylation reactions.

A) HYDROAMINATION:
The TM-catalyzed hydroamination reaction has proven to be an extremely effective method for the one step synthesis of amines, imines and enamines.[27] In this study we chose to investigate the cycloisomerisation of two alkynylamines (pent-4-yn-1-amine and 5-phenylpent-4-yn-1-amine (**2a/2b**) to evaluate the utility of CB-[Rh(bpm)(CO)$_2$] as a catalyst and the results of these experiments are summarized in Table 1.

Table 1. Hydroamination of 2 using heterogeneous and homogeneous [Rh(bpm)(CO)$_2$]-based catalysts.

Entry	Catalyst (Rh mol%)	Subst.	Conv. (%)	TON
1	CB-[Rh(bpm)(CO)$_2$] (0.1)	**2a**	11	110
2	CB-[Rh(bpm)(CO)$_2$] (4.6)	**2a**	83	18
3	CB	**2a**	0	0
4	CB + [Rh(CO)$_2$Cl]$_2$ (4.6)	**2a**	29[#]	6
5	[Rh(bpm)(CO)$_2$]BPh$_4$ (1.5)[28]	**2a**	90	60
6	CB-[Rh(bpm)(CO)$_2$] (0.1)	**2b**	10	100
7	CB-[Rh(bpm)(CO)$_2$] (4.6)	**2b**	>98	26
8	CB	**2b**	0	0
9	[Rh(bpm)(CO)$_2$]BPh$_4$ (4.6)[28]	**2b**	87[*]	19

[*]^{1}H NMR spectrum recorded after 4.5 h, [#]13% in the second reaction cycle.

At low Rh loading (0.1 mol%), heating **2a** in dioxane for 12 h at 95 °C in the presence of CB-[Rh(bpm)(CO)$_2$] only results in 11% conversion to **3a** (Table 1 entry 1). Increasing the catalyst loading to 4.6 mol% leads 83% conversion of **2a** to **3a**, albeit with a decrease in calculated TON from 110 to 18 (Table 1 entry 2). Not surprisingly, pristine CB displayed no catalytic activity (Table 1, entry 3). Furthermore, a second control material (CB + [Rh(CO)$_2$Cl]$_2$) proved to be a poor catalyst for hydroamination (29% conversion) and was almost completely inactive (13% conversion) in the second reaction cycle (Table 1, entry 4). Broadly speaking, CB-[Rh(bpm)(CO)$_2$] performs comparably to its homogeneous analog [Rh(bpm)(CO)$_2$]BPh$_4$ (Table 1, entry 5). In line with previous studies,[28] both the homogeneous and heterogeneous catalysts promote only *endo*-cyclization forming **3a** selectively as confirmed by ^{1}H-NMR spectroscopy. CB-[Rh(bpm)(CO)$_2$] was shown to competently transform 5-phenylpent-4-yn-1-amine (**2b**) into 5-benzyl-3,4-dihydro-2H-pyrrole (**3b**) with an activity similar to that observed in the reaction of **2a** (Table 1, entries 6-9).

In order to test the recyclability of the carbon bound catalyst, CB-[Rh(bpm)(CO)$_2$] was recovered by centrifugation followed by filtration and then rinsed with several portions of 1,4-dioxane before being reused for catalysis. The results of four consecutive hydroamination experiments catalyzed by CB-[Rh(bpm)(CO)$_2$] using **2b** as a substrate are summarized in Table 2.

Table 2. Recycling experiments using CB-[Rh(bpm)(CO)$_2$] as a catalyst for the hydroamination of **2b** (5-phenylpent-4-yn-1-amine)

Run	Conversion after 12h (%)	Rh content (%)[29]	
		Recovered catalyst	Reaction solvent+washings
1	>98	91	8.8
2	80	88.8	2.0
3	77	86.3	2.3
4	72	84	2.4

Overall, the catalyst performed competently in the recycling experiment when **2b** was used as a substrate for hydroamination with a drop in conversion from >98% to 72 by the fourth consecutive run (Table 2, column 1). After the first hydroamination reaction *ca.* 9% of the available Rh leached into the solution as evidenced by ICP-MS of both the digested catalyst and the reaction solvent/subsequent catalyst washings (Table 2, run 1). The third and fourth recycling runs are characterized by a gradual decrease in catalyst efficiency and this is in agreement with the low level (ca. 2%) of Rh leaching observed for following these experiments (Table 2, entries 3 and 4).

B) DIHYDROALKOXYLATION:

Table 3. Dihydroalkoxylation of **4** using heterogeneous and homogeneous [Rh(bpm)(CO)$_2$]-based catalysts.
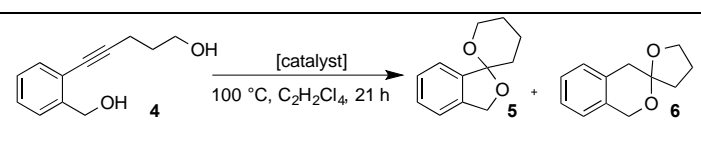
	Catalyst (Rh mol%)	Conversion (%)	Ratio **6:5**	TON
1	CB-[Rh(bpm)(CO)$_2$] (0.1)	76*	2.0:1.0	760
2	CB-[Rh(bpm)(CO)$_2$] (4.6)	> 98	2.3:1.0	21
3	CB (0)	0	N/A	0
4	CB + [Rh(CO)$_2$Cl]$_2$ (4.6)	52[†]	2.5:1	10
5	[Rh(bpm)(CO)$_2$]BPh$_4$ (1)[30]	> 98	1.4:1.0	98

* Reaction run for 60 h, [†] 24% in second cycle.

The intramolecular dihydroalkoxylation of alkyne diols is an efficient and atom economical method for preparing pharmaceutically relevant spiroketals.[31] For this reason we have previously used 5-(2-(hydroxymethyl)phenyl)pent-4-yn-1-ol (**4**) as a 'screening' compound to quantify the efficacy of novel catalysts in our laboratory.[32] The results of the dihydroalkoxylation experiments are summarized in Table 3. Stirring a solution of **4** and dispersed CB-[Rh(bpm)(CO)$_2$] (calculated Rh loading of 0.1 mol%) in tetrachloroethane (TCE) at 100 °C for 60 h resulted in the formation of **5** and **6** with a combined total conversion of 76 % and a calculated TON of 760 (Table 3, entry 1). Quantitative conversion of diol **4** to the cyclized products **5** and **6** was achieved in 21 h by increasing the catalyst loading (0.1% to 4.6%, Table 3, entry 2).

To eliminate the unlikely possibility of CB catalyzing the dihydroalkoxylation of **4**, a control experiment was run using CB without any catalyst (Table 3, entry 3). As expected no conversion of the substrate was observed. In addition, unfunctionalised CB was simply mixed with [Rh(CO)$_2$Cl]$_2$, filtered and the resultant solid was employed as a catalyst in the dihydroxyalkoxylation reaction (Table 3, entry 4). This control material was significantly less effective in catalysing the dihydroalkoxylation reaction when compared with CB-[Rh(bpm)(CO)$_2$], but did result in 52% product formation. Interestingly a relatively high product selectivity was observed

in this case (**6:5**, 2:0.8) but as the conversion was low this ratio is less conclusive with respect to product selectivity. However, in a subsequent reaction cycle the activity of the control material (CB + [Rh(CO)$_2$Cl]$_2$) dropped markedly to only 24%, whereas CB-[Rh(bpm)(CO)$_2$] was shown to be active over multiple reaction cycles (*vida infra*). Finally, CB-[Rh(bpm)(CO)$_2$] displays similar activity to one of our benchmark homogenous Rh(I) catalysts, [Rh(bpm)(CO)$_2$]BPh$_4$ (Table 3, entry 5) but the TON was lower due to higher catalyst loading on the carbon support. Interestingly, CB-[Rh(bpm)(CO)$_2$] appears to preferentially promote the synthesis of **6** over **5** compared with [Rh(bpm)(CO)$_2$]BPh$_4$ (Table 3, column 4). This might be due to spatial restrictions around the organometallic complex caused by immobilization onto the CB surface.

The catalytically active material was also tested over multiple reaction cycles. CB-[Rh(bpm)(CO)$_2$] was recovered by centrifugation followed by filtration and then rinsed with several portions of TCE before being reused for catalysis. The results of four consecutive dihydroalkoxylation experiments catalyzed by CB-[Rh(bpm)(CO)$_2$] are summarized in Table 4.

Additional screening of this reaction was performed using 4-(2-(hydroxymethyl)phenyl)but-3-yn-1-ol (S1) with similar results as to those described above (see ESI for details).

Table 4. Recycling experiments using CB-[Rh(bpm)(CO)$_2$] as a catalyst for the dihydroalkoxylation of 2 (5-(2-(hydroxymethyl)phenyl)pent-4-yn-1-ol)

Run	Conversion after 21h (%)	Product ratio **6:5**	Rh content (%)[29]	
			Recovered catalyst	Reaction solvent + washings
1	> 98	2.3 : 1.0	91	9.1
2	85	3.6 : 1.0	88	2.0
3	76	4.4 : 1.0	86	2.3
4	70	4.7 : 1.0	83	2.1

The activity of the recovered catalyst CB-[Rh(bpm)(CO)$_2$] in the dihydroalkoxylation reaction notably decreased in the second run of the catalyst recycling experiment (> 98% to 85% conversion) followed by a less pronounced drop in performance in subsequent runs (Table 4, column 2). In line with the observed loss of activity, ICP-MS analysis of digested catalyst samples recovered after every run showed that the Rh content of CB-[Rh(bpm)(CO)$_2$] drops by approximately 9% after the first cycle, but only by ~2% after runs 3 and 4 (Table 4, column 4). The mass balance of the Rh(I) was accounted for following ICP-MS analysis of the reaction solvent and catalyst washings (Table 4, column 5), confirming that lost Rh(I) was due to leaching into solution.

Overall, the Rh leaching pattern correlates well with the reduced conversion of **4** to **5** and **6** observed after completion of each catalytic run. The relatively large loss of rhodium in the first run could be explained by desorption of non-specifically bound (physisorbed) Rh from the support surface and this is in

agreement with the higher than expected Rh/N ratio observed by XPS (Figure 2) of the fresh catalyst. The less pronounced Rh leaching observed after the completion of the second and following runs is significantly lower than that in the first run, and this could be due to slow abstraction of Rh from the surface bound bpm ligand.

Interestingly, the ratio of the dihydroalkoxylation products (**6**:**5**) increases significantly after the first run (Table 4, column 3). It is conceivable that during the first run, nonspecifically bound Rh(I) was also catalyzing the reaction with reduced selectivity, resulting in the observed 2.3:1 product ratio. In the second, and following, runs all the physisorbed Rh(I) has most likely been washed away and the observed higher selectivity is due only to the previously mentioned spatial restrictions around the organometallic complex caused by immobilization onto the CB surface.

In order to investigate this increased selectivity further an additional control experiment was performed. CB powder was added to a homogeneous solution of $[Rh(bpm)(CO)_2]BPh_4$ (CB + $[Rh(bpm)(CO)_2]BPh_4$, 4.6 mol% catalyst loading) and the mixture was employed as a catalyst in the same dihydroalkoxylation reaction. During the first cycle almost complete (92%) consumption of substrate **4** was observed with the expected products (**6** and **5**) formed in a 1.4:1 ratio. As predicted, the product ratio is the same as that observed when using the homogenous catalyst $[Rh(bpm)(CO)_2]BPh_4$ without any carbon support present in the mixture (Table 3 entry 4). Not surprisingly, CB + $[Rh(bpm)(CO)_2]BPh_4$ was not active following recycling presumably because the catalyst was washed away at the end of the first run.[33] In summary, we believe that the covalent attachment of the catalyst onto CB results in enhanced selectivity for the dihydroalkoxylation reaction of **4** changing the product ratio from 1.4:1 to 4.7:1.

Stability of the immobilized catalyst under catalytic conditions:
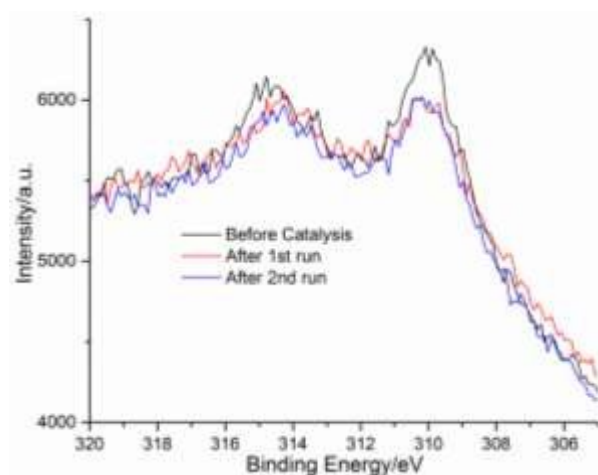
Figure 5. Rh 3d high resolution XP spectra of the catalyst CB-[Rh(bpm)(CO)₂] before dihydroalkoxylation (black trace) and after the first (red trace) and second (blue trace) runs.

Samples of CB-[Rh(bpm)(CO)₂] were recovered following completion of the first and the second catalytic runs of the dihydroalkoxylation reaction and analyzed using XPS (Figure 5). Crucially, the Rh $3d_{3/2}$ and $3d_{5/2}$ are clearly observed after two reaction cycles, which indicates, firstly, that the material still contains Rh, and secondly, that the metal ion has not been oxidized during the recycling experiments. Furthermore, after the second run of the dihydroalkoxylation reaction the measured N/Rh ratio is *ca.* 4:1 in line with the anticipated value assuming all surface Rh(I) is now bound to a covalently anchored bpm ligand.

Thus, the Rh leaching observed after the first catalytic run is most likely due to non-specifically (physisorbed) bound Rh, which is relatively easily washed off during the first reaction. The relatively minor Rh leaching after the second and subsequent runs is most likely due to abstraction of Rh from the bpm ligands.

Experimental

Raw materials: All manipulations of metal complexes and air sensitive reagents were carried out using standard Schlenk techniques or in a Braun nitrogen-filled glove box. Carbon Black (Vulcan XC-72R) was kindly donated by the Cabot Corporation. Rhodium(III) chloride hydrate was obtained from Precious Metals Online. All other reagents were purchased from Aldrich Chemicals and used directly as received. Tetrahydrofuran and 1,4-dioxane were distilled from sodium benzophenone ketyl under nitrogen. Methanol was distilled from dimethoxymagnesium under a nitrogen atmosphere. For the purpose of air sensitive manipulations and preparation of metal complexes, solvents were dispensed from a PuraSolv solvent purification system and stored under N_2. Deuterated solvents were dried prior to use over calcium sulfate (acetone-d_6) or calcium hydride (DCM-d_2), or used as received from the manufacturer (Cambridge Isotope Laboratories: TCE-d_2, acetone-d_6, CDCl₃). 2-(5-hydroxypent-1-ynyl)benzyl alcohol,[34] 5-Phenyl-4-pentyn-1-amine,[35] [Rh(CO)₂(μ-Cl)]₂[36] and 4-[*bis*(pyrazol-1-yl)methyl]aniline (bpm-NH₂)[15] were prepared using literature procedures. Glassy carbon electrodes (1 cm²) were purchased from Goodfellow, Cambridge Ltd.

Immobilization of bpm on glassy carbon electrode without electrochemical assistance: A solution of aryl diazonium salt of bpm-NH₂ was prepared using the method described for the modification of GC plates using electrochemical assistance.[15] The glassy carbon electrodes were polished successively with 1.0, 0.3, and 0.05 μm alumina (Al₂O₃) slurries and MilliQ water on microcloth pads. The carbon plates were thoroughly rinsed with MilliQ water after polishing and then soaked for 30 min in dichloromethane. Before modification, the electrodes were dried under a stream of nitrogen. The GC plate surface modifications with the bpm ligand were achieved by soaking GC plates in the solution of the in situ generated aryl diazonium salt of bpm-NH₂ for 16 h at room temperature to afford GC-bpm. The modified GC plates were rinsed with copious

amounts of MilliQ water, acetonitrile, and ethanol, and then dried under a stream of nitrogen.

Complexation of GC-bpm with [Rh(CO)₂(μ-Cl)]₂: The modified electrodes bearing the immobilized ligands (GC-bpm) were placed in a THF solution of [Rh(CO)₂(μ-Cl)]₂ (0.5 mM, 2 mL) under an atmosphere of argon for 2 h. After decantation of the solvent, the electrodes were consecutively rinsed three times with THF (5 mL) and methanol (5 mL) and then dried under a stream of nitrogen.[15]

Preparation of bpm-functionalized carbon black CB-bpm: Vulcan XC-72R (1.0 g) was dispersed in 100 mL of MilliQ water, and the resulting suspension was sonicated for 30 min. The suspension was transferred into a vial equipped with a thermostatic jacket (the temperature of the coolant was 2 °C). The suspension was allowed to cool for 30 min with constant stirring and then bpm-NH₂ (0.10 g, 0.42 mmol) and sodium nitrite (0.05 g, 0.76 mmol) were added to the suspension. The mixture was left to stir for 15 minutes before HCl (37%, 10.0 mL) was added and then the resultant solution was left to stir overnight. The modified carbon was separated from the mother liquor by centrifugation (4000 rpm) and consecutively washed with MilliQ water followed by sonication for 5 min, and then centrifuged again. The same cycle was performed using methanol, dimethylformamide, acetonitrile, methanol, and finally MilliQ water as the 'washing' liquid. Finally the washed powder was dried under vacuum at 40 °C overnight.

Preparation of immobilized catalyst CB-[Rh(bpm)(CO)₂]: Bpm-functionalized carbon black CB-bpm (0.5 g) was dispersed in THF (10 mL) under nitrogen. To this suspension, a solution of [Rh(CO)₂(μ-Cl)]₂ (0.020 g) in THF (15 mL) was added. The resulting mixture was stirred for 2 hours, and then the solvent was removed by filtration using a Teflon membrane affording the immobilized Rh catalyst CB-[Rh(bpm)(CO)₂]. The black solid was washed with THF (3×50 mL) and methanol (50 mL) and then dried under vacuum overnight.

Characterization of modified carbon powders: Surface analysis of modified surfaces was performed by XPS using an EscaLab 250 Xi (Thermo Scientific) spectrometer with a monochromated Al K$_\alpha$ source. The measurements were recorded at a pressure of below 10^{-8} mbar in the analysis chamber and a take-off angle normal to the sample surface. The pass energy and the step size for the survey scan was 100 and 1.0 eV, respectively, and 20 and 0.1 eV, respectively, when monitoring narrow scans. The analysis was focused on the center of the modified area to avoid contamination from the edges of the electrodes. Spectral analysis was performed using the Avantage 4.73 software, the background spectra were considered as Shirley type and curve fitting was carried out using a mixture of Gaussian-Lorentzian functions.

Thermogravimetric analysis was conducted using a Mettler Toledo TGA/DSC 1 STAR^e instrument. The temperature scan was kept between 35 – 800 °C for the samples analyzed in

argon. The scan rate was 10 °C/min and the gas flow rate was 30 mL/minute.

The Rh content in the immobilized catalyst was determined using inductively coupled plasma mass spectrometry (ICP-MS) using a PerkinElmer NexIon 300D instrument. The catalyst sample was digested in a mixture of refluxing H_2SO_4 and HNO_3 following a literature procedure.[37]

Raman spectroscopy was performed on an inVia Renishaw Raman microscope using green (514 nm) laser excitation, Scans were taken on an extended range (0–4,000 cm^{-1}), the exposure time was 60 s and the power was set at 25 mW. Samples were briefly sonicated in acetone and drops applied to a glass slide for observation. The sample was viewed using a green laser apparatus under a maximum magnification of x 50.

The FTIR analyses were carried out on Cary 630 FTIR spectrophotometer equipped with a diffuse reflectance sampling interface and a diamond attenuated total reflectance (ATR) accessory (Agilent Technologies, USA). FTIR spectra were recorded in the wavenumber range between 4000 and 0 cm^{-1}, averaging 32 scans per sample using a nominal resolution of 8 cm^{-1}. The Cary 630 MicroLab PC software was used for data collection and Agilent Resolution Pro software was used to process and analyze the data. Samples of CB and CB-[Rh(bpm)(CO)₂]) were ground up with KBr (1:10 by weight) and the mixture was placed directly onto the crystal surface. A background spectrum was recorded with the press in the down position.

Mother liquors and subsequent washings recovered after the first and following runs of the catalyzed hydroamination and dihydroalkoxylation reactions were transferred individually to 25.0 mL conical flasks. The solvent was evaporated by heating at 150 °C, and the residues were calcined at 280 °C for 20 min. The contents of the flask were cooled to ambient temperature before the addition of sulfuric acid (98 %, 2.0 mL). The resulting dark brown mixture was heated at 280 °C for 20 min. After cooling to room temperature the residues were treated with *aqua regia* (3.0 mL). The resulting orange solution was transferred to a 25.0 mL volumetric flask and MilliQ water was added until the graduation mark. The solution was then analyzed by ICP-MS.

General procedures for catalyzed hydroamination and hydroalkoxylation reactions: The catalyzed double cyclization of 2-(5-hydroxypent-1-ynyl)benzyl alcohol (**1**) was carried out in thick glass tubes (Ace Glass pressure tubes) under an atmosphere of nitrogen. In a typical experiment, a tube was charged with a solution of 2-(5-hydroxypent-1-ynyl)benzyl alcohol (*ca*. 20.0 mg) in 2.0 mL of 1,1,2,2-tetrachloroethane, the immobilized catalyst (0.05 g, 4.6 mol %), and a stirring bar and sealed with a screw on cap. The loadings of the immobilized catalyst were calculated based on the results of ICP-MS assuming that all Rh present in the catalyst corresponds to the expected immobilized Rh complex. The resulting black suspension was sonicated for 2 mins and then heated in an oil bath at 100 °C for 21 h and then cooled to the ambient temperature. The catalyst was separated by

centrifugation (4000 rpm) and the mother liquor obtained was concentrated under reduced pressure. The resultant solid residue was redissolved in CDCl₃ and analyzed using ¹H NMR spectroscopy. A fresh 5 mL portion of 1,1,2,2-tetrachloroethane was added to the catalyst, and the resultant suspension was sonicated for 5 min prior to centrifugation. This cycle was repeated twice prior the addition of fresh portions of the substrate (2-(5-hydroxypent-1-ynyl)benzyl alcohol) and solvent (1,1,2,2-tetrachloroethane).

The catalyzed cyclization of 5-phenyl-4-pentyn-1-amine was performed using the procedures described above with 1,4-dioxane used in place of 1,1,2,2-tetrachloroethane. The reaction was conducted at 95 °C over 12 h.

Conclusions

Here we have shown that it is possible to covalently anchor a well-defined rhodium complex to the surface of both glassy carbon electrodes and high purity carbon black via spontaneous adsorption of the corresponding diazonium salt followed by coordination of a Rh(I) ion. The resultant surface bound complexes were characterized using a combination of XPS, TGA, ICP-MS and Raman and IR spectroscopy.

The Rh(I) complex immobilized onto carbon black was demonstrated to be active as a catalyst for both hydroamination and dihydroalkoxylation with excellent substrate conversion observed over four reaction cycles. Unexpectedly, when CB-[Rh(bpm)(CO)₂] is used as a catalyst for the dihydroalkoxylation of 5-(2-(hydroxymethyl)phenyl)pent-4-yn-1-ol (**4**) enhanced product selectivity is observed after the first reaction cycle (**6** formed preferentially over **5**).

This the first time Vulcan XC-72R has been utilized as a scaffold for structurally well defined TM-catalysts and we aim to further optimize this method as CB is a cheap and readily available heterogeneous carbon support material. In future we plan to demonstrate that this versatile immobilization technique can be used to introduce ligands that can coordinate Rh(I) more strongly and form complexes designed to direct a range of challenging organic transformations.

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Notes and references

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