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Introduction

Surface immobilized organometallic catalysts, viz. hybrid catalysts, are a young class of materials with potential for application in industrially important chemical transformations that combine the advantages of homogeneous and heterogeneous catalysts. A major challenge of homogeneous catalysis is the ready separation of the catalyst from the product and hence the recyclability of the catalyst.1 While these challenges are addressed by heterogeneous catalysts,² fine tuning the reactivity is difficult. Hybrid catalysts aim to combine the advantages of homogeneous and heterogeneous catalysts being comprised of typically soluble homogeneous catalysts immobilized on insoluble supports.3,4 This immobilization renders the catalyst insoluble, making removal and recycling straightforward while reactivity is maintained. Of particular

Carbon supported hybrid catalysts for controlled product selectivity in the hydrosilylation of alkynes†

Max Roemer, ⁽¹⁾*^{ab} Vinicius R. Gonçales, ⁽¹⁾^c Sinead T. Keaveney, ⁽¹⁾^b Indrek Pernik, ⁽¹⁾^a Jiaxin Lian,^c James Downes, ⁽¹⁾^d J. Justin Gooding ⁽¹⁾^c and Barbara A. Messerle ⁽¹⁾*^{bc}

A series of Rh- and Ir-hybrid catalysts with varying tether lengths has been prepared by immobilization of Rh¹, Rh^{III} and Ir^{III} complexes on carbon black *via* radical grafting. The performance of the different catalysts was assessed for the hydrosilylation of phenylacetylene with Et₃SiH. The efficiency of the catalysts was dependent on the length of the tethers to the surface. The Rh^{III}- and Ir^{III} hybrids afforded the $\beta(Z)$ -vinylsilanes, as observed for the analogous homogeneous Rh^{III} catalysts. No distinct product selectivity was observed when using the homogeneous Rh^I precursors as catalysts. However, on using the Rh^{III} hybrid catalysts derived from the Rh^I precursors to promote hydrosilylation, the major products were the α -vinylsilanes and the origin of the difference in reactivity was found to be a chemical modification of the catalysts during immobilization. Substrate scope is demonstrated for a number of alkynes, and feasible mechanisms supported by DFT calculations are proposed.

interest are carbon supports such as graphene, glassy carbon and carbon black (CB), as they are relatively inert supports that are suitable for catalyst immobilization.⁵⁻⁹

Rh- and Ir based hybrid catalysts on carbon supports have been applied in the promotion of hydroamination,⁷ hydrogen borrowing9 and hydrosilylation reactions.6,10 Hydrosilylation of alkynes is an excellent way to gain access to organosilicon compounds, which are important synthons in organic chemistry and industrially highly relevant due to stability and ease of modification, low cost and toxicity.11 However, gaining control over the distribution of formed isomers can be challenging, particularly towards the α -isomer. Typically, this has been achieved in homogeneous catalysis by tailoring the interplay between metal, ligand and substrate, altering the accessibility of intermediates in the catalytic cycle.¹¹⁻¹⁸ Further recent examples include a silica supported Rh catalyst¹⁹ and Pt-clusters.²⁰ Supporting catalysts on surfaces potentially adds another dimension to controlling the catalysis outcomes.

Packing and headgroup orientation are well known to be influenced by the alkyl chain length in monolayer systems of inorganic compounds linked to surfaces, affecting their physical properties.^{21,22} This in turn could influence the outcomes of catalysis when using surface immobilized catalysts, both in efficiency and/or selectivity. We were interested in establishing the dependence of catalyst structure on the performance of organometallic catalysts that comprise Rh- and Ir-complexes tethered covalently to CB *via* linkers. We were particularly interested in understanding



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^a School of Chemistry, The University of Sydney, Sydney, NSW 2006, Australia. E-mail: max.roemer@sydney.edu.au

^b Department of Molecular Sciences, Macquarie University, Sydney, NSW 2109, Australia. E-mail: barbara.messerle@mq.edu.au

^c School of Chemistry and the Australian Centre for NanoMedicine, The University of New South Wales, Sydney, NSW 2052, Australia

^d Department of Physics and Astronomy, Macquarie University, Sydney, NSW 2109, Australia

[†] Electronic supplementary information (ESI) available: Experimental details, spectral and catalysis data (PDF), crystallographic data in cif-format for **3a**, **6a** and **6b**. CCDC: 1961819–1961821. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0cy02136a

relative efficiency, depending on the linker length, and stereoselectivity in the promotion of the hydrosilylation of phenylacetylene and diphenylacetylene, both important model reactions (Fig. 1).

Here, we present a series of Rh- and Ir-hybrid catalysts attached to carbon via alkyl linkers where the length of the linker was varied to modulate the packing of the layer, the flexibility of the headgroup and the catalyst-surface distance, with the aim of optimizing the catalytic efficiency. We investigated the efficiency and selectivity of the catalysts for the hydrosilvlation of a series of alkynes. Intriguingly, the catalysts derived from the Rh^I precursors afforded a quite different selectivity following surface immobilization by the well-established diazonium route to both that of the homogeneous Rh^I precursors, and to that of the Rh^{III}- and Ir^{III} catalysts. This dichotomy led us to investigate the active species in more detail. In order to understand the relationship between hybrid catalyst structure and catalytic reactivity, we employed X-ray absorption spectroscopy (XAS) and conducted a number of control experiments, and propose feasible reaction mechanisms for the transformations, supported by DFT calculations.

Results and discussion

Syntheses of ligands and metal complexes

We prepared the catalysts by coordination of metal precursors with pyrazole–triazole (PyT) ligands. Ligands with different length alkyl chain linkers were obtained in several steps from compound **1** (Scheme 1). Tin mediated Friedel–Crafts acylation of **2** gives access to the *p*-bromo-alkylbenzenes **3a/b** which are challenging to obtain by other methods. This approach is analogous to that used in the preparation of **1**'-alkyl-substituted iodoferrocenes.^{23,24} Surprisingly, many halobenzenes with long functionalized alkyl chains have not yet been prepared. The synthesis of **3a**



Fig. 1 Control over regio- and stereoselectivity in hydrosilylation reactions of terminal alkynes using Rh and Ir based hybrid catalysts.



Scheme 1 Syntheses of ligands 6a/b and their molecular structures obtained from X-ray single crystal diffraction (H-atoms are omitted for clarity).

using an Ir-catalyzed ring opening reaction has been reported just recently,²⁵ while no procedure for the synthesis of **3b** has been reported thus far. Ligands **6a/b**, prepared in three steps from **3a/b**, were used to synthesise the new Rh- and Ir-catalysts, following established procedures (Scheme S1, ESI†).²⁶

The ligands were reacted with $[Rh(CO)_2Cl]_2$, $[RhCp^*Cl_2]_2$ or $[IrCp^*Cl_2]_2$, followed by chloride abstraction with NaBAr^F₄. **Rh^IC**₀ and Ir^{III}Cp^{*}C₀ were prepared in an analogous fashion.⁷ We furthermore prepared two control compounds, **Rh^IC**₀**Ph** and **Rh^{III}Cp^{*}C**₀**Ph**, which do not bear the terminal NH₂group.^{26,27}

Surface immobilization and characterization

We immobilized the complexes on CB by *in situ* radical generation from the anilines^{6,7} and formation of covalent C–C bonds to the CB support (Fig. 2). The immobilization *via* binding of a phenyl radical to the carbon support, generated from a terminal aniline by treatment with HCl/NaNO₂, resulted for the Rh^I precursors simultaneously in surface attachment and *in situ* generation of a modified catalyst head-group by the generation of a Rh^{III} species with a different ligand environment. Our results also show that the Rh^{III} and Ir^{III} catalyst head-groups remain unchanged following immobilization.

We initially varied the quantity of $\mathbf{Rh^{I}C_{11}}$ and $\mathbf{Rh^{I}C_{0}}$ precursors with the goal to optimize the surface coverages/ metal loadings on the hybrid catalysts, $\mathbf{Rh^{III}C_{0}CB}$ and $\mathbf{Rh^{III}C_{11}CB}$. In each case, the ratio of complex to CB was varied from 0.07 to 1.4 µmol mg⁻¹. The samples were analysed by energy dispersive X-ray spectroscopy (EDX) and X-ray photoelectron spectroscopy (XPS). Both characterization methods show an increase in metal concentration on the surface in accordance with increasing amounts of complex added to the grafting mixture (Fig. 3 and S19–S22, ESI†). The Rh loadings for $\mathbf{Rh^{III}C_0CB}$ were slightly higher compared to



Fig. 2 a) Surface immobilization of Ir^{III} and Rh^{III} complexes groups affording hybrid catalysts with pyrazole-triazole (PyT)/Cp*/Cl head groups, abbreviated Ir^{III}Cp* and Rh^{III}Cp*. The inset illustrates the diazonium grafting. b) Surface immobilization of Rh^I complexes groups affording hybrid catalysts with a modified head group bearing two PyT groups and two co-ligands. The control compounds in panel a and b bear the same Rh catalyst function, but no aniline which would generate a radical under the grafting conditions.

those of $Rh^{III}C_{11}CB$ (Fig. 3), which is likely due to the relative size and structure of the molecules. Smaller molecules may



Fig. 3 Rh loadings for Rh^{III}C₁₁CB and Rh^{III}C₀CB determined by EDX and XPS for varying amounts of catalyst applied for immobilization. The error bars represent the standard deviation of a minimum of five different areas analyzed on a single surface. The lines serve as guides for the eye only. SEM image and EDX maps (C, Rh, Cl) of Rh^{III}C₁₁CB.

bind more efficiently as they can access more available sites while larger flexible alkyl chains may also result in bent structures. Furthermore, SEM/EDX shows a homogeneous distribution of Rh on the surface for each sample. The optimization approach indicates that using ~0.7 µmol of catalyst per mg of CB gives a layer that is near to the maximum surface coverage, *i.e.* 0.96 at% Rh for Rh^{III}C₁₁CB and 1.22 at% Rh for Rh^{III}C₀CB (XPS).

We considered this to be the optimal loading and applied the same procedure for immobilization of all other catalysts, which were characterized in an analogous fashion (ESI,† Table S3). The **Rh^{III}Cp*C**₁₁- and Ir^{III}Cp*C_n-hybrid catalysts showed consistently lower loadings than the Rh^{III}C_nCB catalysts, *i.e.* 0.6 at% (XPS) for **Rh^{III}Cp*C**₁₁CB and 0.2–0.3 at% (XPS) for Ir^{III}Cp*C_nCB (n = 0, 6, 11), which is in agreement with a previous example of Ir^{III}Cp*C₀CB.⁷ The XPS survey scans show the expected signals of complexes and CB. The Rh:N ratios were near to 1:5, which agrees with the molecular structures of the precursors. The BAr^F₄ anion bears 24 F and thus a Rh:F ratio of 1:24 was expected, however, the detected ratio was typically 1:3 or less.

Additionally, Cl signals were present in the XPS and EDX for all samples. The presence of Cl signals was not expected for the Rh^{III}C_nCB hybrid catalysts as the Rh^I precursors do not contain Cl. The detected Rh:Cl ratios were ~2:1 (EDX) and ~1.3:1 (XPS) for the different Rh^{III}C_nCB catalysts. On treating a control sample of blank CB with HCl under the applied grafting conditions, no significant Cl content was detected (ESI,† S25) indicating that any Cl⁻ is bound to the

immobilized molecules. This suggests that catalyst structure may have been altered, and hence further characterization was warranted.

To probe the local electronic structure of the metals, we recorded extended X-ray absorption fine structure spectra (EXAFS) at the Rh K edge for the Rh based materials and at the Ir L₃ edge for the Ir based materials (Fig. 4). Comparison of the X-ray absorption near edge (XANES) regions of the spectra for the compounds $Rh^{I}C_{n}$ (n = 0, 6, 11; before immobilization), and $Rh^{III}C_nCB$ (n = 0, 6, 11, afterimmobilization on CB), indicates a change in oxidation state after immobilization (Fig. 4a). The energy of the Rh K edge for the $Rh^{I}C_{n}$ (n = 0, 6, 11) series is at 23.242 keV, in agreement with other reported Rh^I examples.²⁸ However, for $Rh^{III}C_nCB$ (*n* = 0, 6, 11), the edge is shifted to a higher energy (23.250 keV). This effect is consistent across the whole series of different chain lengths and points towards an increase in oxidation state. Strikingly, when comparing $Rh^{I}C_{n}$ and Rh^{III} - $C_n CB$ (*n* = 0, 6, 11), not only the edge shifts about +0.008 keV after immobilization, but nearly all features of the spectra change. This change is also reflected in the radial distribution (Fig. 4a, inset). In contrast, the EXAFS of Rh^{III} and Ir^{III} examples did not show any significant edge shifts when comparing data from before and after immobilization (Fig. 4b and c, insets). The Rh K edge was for both Rh^{III}Cp*C₁₁ and Rh^{III}Cp*C₁₁CB at 23.244 keV while the Ir L₃ edge was for $Ir^{III}Cp^*C_n$ and $Ir^{III}Cp^*C_nCB$ (n = 0, 6, 11) at 11.218 keV, with no observed changes in radial distribution.

We also conducted analyses of the involved scattering paths by comparison of models generated from FEFF calculations²⁹ using known X-ray structures of derivatives of the catalysts, *i.e.* the simple pyrazole–triazole based catalysts, that do not feature the alkyl chain tether or surface anchoring groups. Results strongly suggest that for the surface immobilized species Rh^{III}C_nCB the CO ligands are absent, as a major scattering path at 2.5 Å observed for Rh^IC_n is absent after immobilization. This path was assigned with the aid of FEFF calculations to the CO ligands, suggesting that CO is no longer present in Rh^{III}C_n-CB (Fig. S23, ESI†).

Fourier transformed EXAFS data (k^2 weighted) and corresponding fitted curves obtained using the known X-ray structures of the PyT head-groups and fitting parameters for all homogeneous- and hybrid catalysts and are reported in the SI (Fig. S24-S27, Tables S25-S28†). In particular, the levels of correlation between the curves for the M^{III}Cp*C_nCB derivatives are high with only little difference between the curves obtained for the complexes before and after immobilization. On the other hand the fits for $Rh^{I}C_{n}$ and $Rh^{III}C_nCB$ (*n* = 0, 6, 11) exhibited a considerable amount of misfit to the calculated data from X-ray crystallography of $Rh^{I}(CO)_{2}PyT$. This was unsurprising for $Rh^{III}C_{n}CB$ as the oxidation state changed from Rh(I) to Rh(III) after immobilization and the coordination sphere around the metal centre changed too. However, for the homogeneous Rh^{I} complexes (*i.e.* $Rh^{I}C_{n}$) this was not expected as the structure of these complexes was confirmed using NMR spectroscopy, mass spectrometry and elemental analysis. We postulate that the observed misfit originates mainly in a nonphysical interatomic distance signal at approximately 1 Å, which does not correspond to a bond length (Fig. 4a, inset; red traces). Overall, EXAFS supports our structural proposals for the herein described catalysts.

Control experiments

To test the integrity of the hybrid complexes formed on using the Rh^I precursor catalysts, we conducted a series of control experiments. Specifically, we treated the Rh^I precursors as if we were immobilising them, but in the absence of CB. We treated Rh^IC₁₁ and Rh^IC₀ with HCl/NaNO₂ in MeNO₂, in the absence of CB and analysed the resulting materials using NMR- and IR spectroscopy and mass spectrometry. We were only able to unambiguously identify BAr^F₄ counterions in the two product samples for the ¹H NMR- and ESI⁻ mass spectra. Signals other than those of BAr^F₄ in the ¹H NMR spectra appeared broad, thus inconclusive as to the exact nature of these protons. IR spectroscopy confirmed that the CO ligands are absent after treatment of the Rh^I precursors with HCl/ NaNO₂ as the CO stretching bands at 2108 and 2048 cm⁻¹ for



Fig. 4 EXAFS spectra recorded at the Rh K edge and Ir L3 edge of the catalysts and hybrid catalysts; (a) $Rh^{II}C_n$ and $Rh^{III}C_nCB$, (b) $Rh^{III}Cp*C_{11}$ and $Rh^{III}Cp*C_{11}CB$ and (c) $Ir^{III}Cp*C_n$ and $Ir^{III}Cp*C_nCB$. The insets show the k^2 weighted radial distributions.



Fig. 5 Infrared spectra in the ranges of 2200–900 cm⁻¹ of $Rh^{I}C_{11}$ and $Rh^{I}C_{0}Ph$, and after treatment of the compounds with HCl/NaNO₂ in nitromethane.

 RhC_{11} and 2110 and 2049 cm⁻¹ for RhC_0 , are absent, while most other significant features of the IR spectra are retained (Fig. 5 and S28–S29, ESI[†]). This confirms removal of the CO ligands during the immobilization procedure, but otherwise there were no major structural changes to the PyT-ligand.

As a further control we investigated the behaviour of the control compound Rh^IC₀Ph, which does not bear an NH₂group, under grafting conditions. As the grafting relies on formation of the phenyl radical via the reaction of an NH2substituent and elimination of N2, this control should not generate a phenyl radical under the applied grafting conditions. We again observed the disappearance of the CO stretching vibrations at 2108 and 2049 cm⁻¹ (Fig. 5 and S30[†]). For $\mathbf{Rh}^{\mathbf{I}}\mathbf{C_{0}}\mathbf{Ph}$, we were able to obtain a complex ¹H NMR spectrum (Fig. S31, ESI[†]), which suggests the material obtained following the grafting procedure, even in the absence of the key NH₂-group, is a mixture of compounds. We analysed different batches of this control reaction at different time points, which showed a rising complexity of the ¹H NMR spectra as the time points became longer. Analysis by ESI⁺ mass spectrometry (Fig. S32–S40, ESI⁺) showed a number of different ions are present with the highest intensity singly charged mass fragments being 623.1 (after 1.5 h reaction time) and 634.1 (after 16 h reaction time). These ions were assigned by high resolution measurements (ESI^{+}) to $[RhCl_2(PyT)_2]^{+}$ and $[RhCl(NO_2)]^{+}$ $(PyT)_2$ ⁺, respectively. A doubly charged species with a mass of 276.5 was detected for both samples and assigned to $[Rh(PyT)_2]^{2+}$.

Intriguingly, this analysis has confirmed that the original Rh^I complexes are converted during the immobilization treatment to Rh^{III} species bearing two PyT ligands and combinations of Cl, NO₂, NO₃, OH as two additional coligands. Each of these species were detected and assigned by mass spectrometry, with the experimental and calculated MS

patterns shown in Fig. S34–S36 (ESI†). These different species likely form through ligand exchanges in the reactive mixture of aqueous HCl/NaNO₂, thus resulting in different compositions depending on the reaction time. The Rh bound Cl is also manifested in the detected Cl by EDX and XPS in the hybrid catalyst samples after surface immobilization.

We propose the transformation of the Rh^I complexes on attachment to the CB surfaces occurs via the reaction as shown in Scheme 2 for Rh^IC₀Ph. In the first step, the Rh^I center is oxidized to Rh^{III}, on release of CO, by the oxidative mixture of HCl/NaNO2. The coordinatively unsaturated Rh^{III} intermediate that is formed is stabilized by reaction with remaining Rh^I starting material under loss of CO and one equivalent of Rh, to yield the new catalytically active species. The metal complex that forms the hybrid catalyst head-group can have a number of configurations in the case of the different stereoisomers as illustrated in Scheme 2. The various possible three-dimensional structures of the new Rh^{III} products with two PvT-ligands, without surface anchoring group, and with two Cl co-ligands were modelled (Scheme 2). DFT calculations show that the isomer with PyT-ligands in anti-configuration and Cl co-ligands in para configuration has the lowest relative energy (0 kcal mol⁻¹) amongst the other possible isomers (1.2 to 3.1 kcal mol^{-1}). If the two coligands X_1 and X_2 (Scheme 2) are not identical, the number of possible isomers increases significantly. Thus, the generated mixture is complex, which results in the observed complexity in the NMR spectra of the materials generated. Furthermore, this explains why the only significant change in the IR spectra is the absence of the CO stretching vibrations, as those ligands ae removed, whereas the PyT-ligands remain unchanged.

Based on the results above that provide the unexpected structures of the Rh^{III}C_nCB hybrid species, the complexes generated from the parent $Rh^{I}C_{n}$ precursors bearing the aniline should have two anchoring groups, given the reaction generating the phenyl radical goes to completion for both binding ligands. The in situ generated species bearing two PyT ligands may bind more efficiently to the surfaces compared to the counterparts with only a single PyT ligand, due to the two available anchoring groups. In addition, bidentate binding to the carbon surface may also occur. Indeed, this effect appears to be visible for the whole series in the current work as the hybrid catalysts based on the Rh^I complexes consistently show higher metal loading on the surface compared to the monodentate Rh^{III} and Ir^{III} hybrid catalysts. In addition, this effect is reflected in the isolated yields of the hybrid catalysts: samples based on the Rh^I precursors gave consistently about 20% higher yields compared to the Rh^{III} and Ir^{III} hybrid catalysts. With these new insights in mind, we revise also the earlier reported structures of mono- and heterobimetallic layers based on the **Rh^IC**₀ precursor.⁷

The thermostability of the hybrid catalysts $Rh^{III}C_nCB$ was tested by thermogravimetric analysis (TGA) (Fig. S41, ESI†). The TGA curves indicate that all hybrid catalysts are stable



Scheme 2 Treatment of the control compound $Rh^{I}C_{0}Ph$ with HCl/NaNO₂ to yield different bis-pyrazole-triazole Rh complexes and calculated structures of the five isomers of $Rh^{III}Cl_{2}$ and their relative energies reported in kcal mol^{-1} .

>300 °C with no significant weight loss occurring up to that temperature. Weight loss starts at around 350 °C, with one weakly pronounced process for all samples. This is followed by another process at around 500 °C for the Rh samples, which show more overall weight loss than the Ir samples.

Application in catalysis - hydrosilylation of alkynes

Having established the formation of hybrid catalysts with high metal loadings and their composition, the surfacebound catalysts, and their homogeneous analogues, were tested for the promotion of the hydrosilylation of

Table 1 Summary of the hydrosilylation reaction of phenylacetylene with triethylsilane promoted by the Rh- and Ir catalysts								
$\begin{array}{c c} Et_{3}SiH \\ \hline Catalyst \end{array} Ph \overbrace{(E)}^{SiEt_{3}} Ph \overbrace{(Z)}^{SiEt_{3}} Ph \overbrace{\alpha}^{F} Ph \overbrace{\alpha}^{SiEt_{3}} \end{array}$								
Catalyst	Metal ^a [mol%]	Loading EDX [at%]	Loading XPS [at%]	Conversion [%]	Ratio $\beta(E)/\beta(Z)/\alpha$			
Hvbrid								
Rh ^{III} C ₁₁ CB	1.0	0.49	0.96	96	11/4/85			
Rh ^{III} C ₆ CB	1.0	0.52	0.97	95	11/4/85			
Rh ^{III} C ₀ CB	1.0	0.82	1.22	56	10/8/82			
Homogeneous								
Rh ^I C ₁₁	1.0	_	_	98	39/22/39			
Rh ^I C ₆	1.0	_	_	94	42/22/36			
Rh ^I C ₀	1.0	—	—	100	41/22/37			
Controls								
Rh ^I C ₀ Ph	1.0	_	_	98	42/21/37			
$\mathbf{Rh}^{\mathbf{III}}\mathbf{Cl}_{2}^{b}$	1.0	_	_	99	10/4/86			
$\mathbf{Rh^{III}C_{11}Cl_2}^b$	1.0	—	—	100	9/2/89			
Hybrid								
Rh ^{III} Cp*C ₁₁ CB	0.5	0.25	0.63	91	1/96/3			
Ir ^{III} Cp [*] C ₁₁ CB	0.5	0.13	0.24	98	2/95/3			
Ir ^{III} Cp*C ₆ CB	0.5	0.11	0.28	60	2/95/3			
Ir ^{III} Cp*C ₀ CB	0.5	0.08	0.22	85	2/95/3			
Homogeneous								
Rh ^{III} Cp*C ₁₁	1.0	_	_	Traces	Complex			
$Ir^{III}Cp^*C_n$	1.0	_	_	Traces	Complex			
Control								
Rh ^{III} Cp*C ₀ Ph	1.0	_	_	93	2/96/2			

Reaction conditions: 1 mL THF under Ar, 0.1 mmol scale and 1.8 eq. of Et_3SiH , 1 h, 60 °C. ^{*a*} Calculated mol% metal applied in the reaction, based on the loading obtained from EDX. ^{*b*} These homogeneous control compounds were obtained by treating Rh^IC_0Ph and Rh^IC_{11} with grafting conditions under absence of CB.

phenylacetylene (Table 1). The full set of the hybrid catalysts are efficient catalysts, which can operate under mild conditions. The catalysts $Rh^{III}C_nCB$ (n = 0, 6, 11) all afford the α -isomer as the major product (>80%), followed by minor amounts of the $\beta(E)$ - and $\beta(Z)$ -isomers. In contrast, the precursor $Rh^{I}C_{n}$ (*n* = 0, 6, 11) used as homogeneous catalysts in solution do not promote distinct product selectivity, while the control compound $\mathbf{Rh}^{\mathbf{I}}\mathbf{C}_{\mathbf{0}}\mathbf{Ph}$ without the NH₂-group, gave the same result as the derivatives bearing an NH₂-group. As the Rh^I precursors are modified during immobilization, we also tested the materials obtained from treatment of Rh^IC₁₁ and Rh^IC₀Ph with NaNO₂/HCl for catalytic activity. Rh^{III}Cl₂ (derived from Rh^IC₀Ph) and Rh^{III}C₁₁Cl₂ (derived from $\mathbf{Rh}^{\mathbf{I}}\mathbf{C}_{11}$), both reproduce nicely the observed α -selectivity of the Rh^{III}C_nCB hybrid catalysts. Thus, the observed effect is due to the chemical modification of the head-group. As discussed above, all systems with the in situ modified catalytically active group bear mixed species co-ligands (Cl, NO₂, NO₃, OH) which originate in the grafting process. We have used the systems as prepared and note that co-ligand variation would need to be taken be into account to assess performance in dependence of the coligands.

Each of the $M^{III}Cp^*C_nCB$ (M = Rh, n = 11; M = Ir, n = 0, 6, 11) hybrid catalysts promoted the formation of the $\beta(Z)$ isomer with high selectivity, which is analogous to the reported outcome on using a homogeneous Cp*Rh^{III} catalyst.³⁰ The **Rh^{III}Cp***C₁₁ and Ir^{III}Cp*C_n examples in solution also afford the $\beta(Z)$ isomer. However, a significant amount of starting material was present in all cases, and side-product formation was also observed. Thus, the homogeneous catalysts are inferior to the hybrid catalysts. In contrast, application of the control compound Rh^{III}Cp*C₀Ph, without NH2-group, resulted in a clean reaction with near quantitative conversion, reproducing the observed reactivity of the hybrid analogues. This suggests that the divergent reactivity of the M^{III} catalysts, when not immobilized, originates from the presence of the NH₂-group. We furthermore tested the whole set of hybrid catalysts in the hydrosilylation of diphenylacetylene (Table S31, S72, ESI†). The catalysts based on the Rh^I precursors afford the $\beta(E)$ isomer, while the M^{III}Cp* (M = Rh, Ir) hybrid catalysts do not show catalytic competency for this transformation.

Linker length

Of all the Rh^{III}C_nCB series, the Rh^{III}C₁₁CB and Rh^{III}C₆CB are the most efficient in promoting the hydrosilylation reactions, followed by Rh^{III}C₀CB which is the least efficient catalyst (Fig. 6). Similarly, concerning the phenylacetylene substrate, Ir^{III}Cp*C₁₁CB performs best among the Ir^{III}-series, followed by Ir^{III}Cp*C₀CB and Ir^{III}Cp*C₆CB. These results demonstrate how the length of the tether can influence the performance of the catalyst. The catalysts with longer linkers tend to be more effective. This effect is more pronounced at early time points, *i.e.* at 20 min for the substrate phenylacetylene (Fig. 6a) and at 15 min for diphenylacetylene (Fig. 6b).

The origin of the longer linker hybrid catalysts being the better catalysts compared to the shorter linker analogues may be due to the higher flexibility of the linker and consequently greater potential mobility of the head-group, allowing the substrates to bind more readily to the catalyst. Furthermore, the longer linker examples could potentially align with head-groups pointing towards the surface instead of away from the surface, which could also affect the catalytic activity through sterics and/ or electronics resulting from the consequent interactions of the headgroup with the carbon surface. However, a densely packed layer, which we obtained by optimisation of the surface grafting conditions, would likely reduce such effects as the layer is more rigid. Additionally, the packing of the catalyst layer on the surface may depend on the chain lengths of the catalysts and it is possible that the layers obtained from the longer chain derivatives differ in structure from the layers obtained from the shorter chain derivatives.

Recyclability

We tested the recyclability of $\mathbf{Rh^{III}C_{11}CB}$ for a number of consecutive runs for hydrosilylation of phenylacetylene by removing the catalyst by centrifugation from the reaction mixture, washing it and re-using it. The reactivity is maintained over the course of seven repeated catalytic experiments (Fig. 7). XPS analysis of a recycled sample of $\mathbf{Rh^{III}C_{11}CB}$ showed a Rh content of 0.86 at% after five runs, compared to 0.96 at% for the freshly prepared hybrid catalyst (Fig. S44, ESI[†]).



Fig. 6 Performance of the Rh^{III}C_nCB hybrid catalysts in terms of overall conversion to the products in the hydrosilylation reaction of phenylacetylene and diphenylacetylene with triethylsilane at selected time points. The reaction temperatures were 60 °C (a) and 75 °C (b).



Fig. 7 Recyclability of Rh^{III}C₁₁CB for seven consecutive runs for the hydrosilylation of phenylacetylene. The product ratio of isomers for the first run was at $\beta(E)/\beta(Z)/\alpha = 10/2/88$ and remained constant for the subsequent runs (2–7) at 10/1/89.

We furthermore tested catalytic activity of the soluble fraction of a reaction solution by a hot filtration test,³¹ with the aliquot after filtration showing no catalytic activity, suggesting the catalyst is of heterogeneous nature (ESI,† S69).

Scope

In the next step we examined the scope of the catalysed hydrosilation reaction for a number of terminal alkyne substrates using two of the hybrid catalysts, $Rh^{III}C_{11}CB$ and $Rh^{III}Cp^*C_{11}CB$. To test the compatibility of the transformation with various substrates we chose electron

rich, electron deficient, *ortho-* and *para-substituted* aromatic systems as well as a cyclohexene and two alkyl derivatives. As the reactions proceeded slower for some substrates compared to phenylacetylene, we tested the whole set of substrates at a slightly higher temperature. We were delighted to see that both hybrid catalysts reproduce the observed product selectivity for the parent phenylacetylene for the vast majority of tested alkynes (Table 2). Conversions are excellent with most examples showing conversions of 90% or greater for both catalysts. Exceptions are the alkynes 7 and 9 with substituents in the *ortho*-position, which give somewhat lower conversion for both $Rh^{III}Cp*C_{11}CB$ and $Rh^{III}C_{11}CB$. We

Terminal alkyne	Hybrid catalyst	Products $\beta(E)/\beta(Z)/\alpha$	Conversion [%]	Product ratio $\beta(E)/\beta(Z)/\alpha$
	Rh ^{III} C ₁₁ CB	7a/7b/7c	85 (1 h)	5/0/95
		7a/7b/7c	100 (4 h)	4/0/96
	Rh ^{III} Cp*C ₁₁ CB	7a/7b/7c	37 (1 h)	0/93/7
	-	7a/7b/7c	51 (4 h)	0/95/5
F2C.	Rh ^{III} C ₁₁ CB	8a/8b/8c	90 (1 h)	5/0/95
, T T		8a/8b/8c	100 (4 h)	4/0/96
	Rh ^{III} Cp*C ₁₁ CB	8a/8b/8c	73 (1 h)	0/93/7
ĊF ₃		8a/8b/8c	93 (4 h)	0/95/5
~ //	Rh ^{III} C ₁₁ CB	9a/9b/9c	35 (1 h)	12/2/86
		9a/9b/9c	67 (4 h)	4/0/86
CF ₃	Rh ^{III} Cp*C ₁₁ CB	9a/9b/9c	70 (1 h)	1/97/2
Ū		9a/9b/9c	98 (4 h)	0/98/2
	Rh ^{III} C ₁₁ CB	10a/10b/10c	99 (1 h)	4/2/94
		10a/10b/10c	100 (4 h)	7/6/87
	Rh ^{III} Cp*C ₁₁ CB	10a/10b/10c	56 (1 h)	6/91/3
		10a/10b/10c	91 (4 h)	3/95/2
~//	Rh ^{III} C ₁₁ CB	11a/11b/11c	19 (1 h)	14/0/86
		11a/11b/11c	95 (4 h)	10/4/86
	Rh ^{III} Cp*C ₁₁ CB	11a/11b/11c	97 (1 h)	18/80/2
~ ~//	Rh ^{III} C ₁₁ CB	12a/12b/12c	40 (1 h)	12/4/84
		12a/12b/12c	100 (4 h)	7/3/90
	Rh ^{III} Cp*C ₁₁ CB	12a/12b/12c	81 (1 h)	7/91/2
		12a/12b/12c	99 (4 h)	4/93/3
	Rh ^{III} C ₁₁ CB	13a/13b/13c	51 (1 h)	10/2/88
		13a/13b/13c	89 (4 h)	10/1/89
	Rh ^{III} Cp*C ₁₁ CB	13a/13b/13c	73 (1 h)	0/97/3
		13a/13b/13c	97 (4 h)	0/96/4
~ //	Rh ^{III} C ₁₁ CB	14a/14b/14c	40 (1 h)	28/5/67
ſ Ĭ		14a/14b/14c	96 (4 h)	27/5/68
	Rh ^{III} Cp*C ₁₁ CB	14a/14b/14c	82 (1 h)	25/75/0
		14a/14b/14c	97 (4 h)	6/94/0
CI	Rh ^{III} C ₁₁ CB	15a/15b/15c	69 (1 h)	15/9/76
1		15a/15b/15c	100 (4 h)	16/3/81
	Rh ^{III} Cp*C ₁₁ CB	15a/15b/15c	100 (1 h)	0/100/0
~ //	Rh ^{III} C ₁₁ CB	16a/16b/16c	100 (1 h)	17/6/77
$\sim \sim$	Rh ^{III} Cp*C ₁₁ CB	16a/16b/16c	100 (1 h)	0/100/0

Reaction conditions: 1.8 eq. of Et_3SiH , 75 °C in THF under Ar in a sealed Schlenk tube. Catalyst loading: 1.0 mol%. Conversions were determined after 1 h or 4 h reaction by integration of the vinylic proton resonances of the combined isomeric product mixture *vs.* remaining alkyne in the ¹H NMR spectrum before purification.

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isolated most products as isomeric mixtures, and characterized the mixtures using 1H- and 13C NMR spectroscopy and mass spectrometry, or compared the obtained ¹H NMR spectra to the literature. Isolated yields for most examples are good to excellent (ESI,† S73-S80). Application of the Rh^{III}C₁₁CB catalyst resulted in a selectivity of 68–99% for formation of the α -isomer with 10 out of 11 examples, giving a product selectivity of greater than 82%. The cyclohexene derivative 14 shows a noteworthy decrease in selectivity towards the β -isomer (68%), producing significantly more $\beta(E)$ -isomer (27%) compared to the other compounds studied. The methoxy and phenoxy substituted compounds 11 and 12, as well as compound 13, gave the $\beta(E)$ -isomer in ~10%. On using the **Rh^{III}Cp*C**₁₁**CB** catalyst, the $\beta(Z)$ -isomer formed with a selectivity of 75–100%. Most alkynes showed a selectivity of >90%, with the hexyne derivatives 15 and 16 showing quantitative conversion to the $\beta(Z)$ -isomer. Noteworthy, the reaction involving the hexynes showed better conversions compared to the aromatic systems, which is presumably due to steric hindrance as the **Rh^{III}Cp*C₁₁CB** bears a bulky Cp* ligand which makes it less accessible for the substrates with substituents in close proximity.

Mechanism

The hybrid catalysts lead to two different outcomes on catalysis – on using the **Rh^{III}Cp*C₁₁CB** (and Ir^{III}Cp*C_nCB) catalyst the product selectivity is directed to $\beta(Z)$ while on using Rh^{III}C_nCB

the selectivity is directed to α . Furthermore, the nonimmobilized Rh^I derivatives show no distinct selectivity with all isomers ($\beta(E)$, $\beta(Z)$, α) being produced. The selectivity of the different catalysts is determined by the structure of the catalyst head-group – that is, whether it is Rh^I(CO)₂PyT, Rh^{III}ClCp*PyT or Rh^{III}(X₁)(X₂)(PyT)₂. As the homogeneous Rh^{III} control compounds without amine and alkyl tethers reproduce the selectivity as the hybrid catalysts, the homogeneous control complexes **Rh^{III}C₀Ph** and **Rh^{III}Cl₂** (Scheme 2 and Fig. 2) may serve as tentative models for the hybrid catalysts. Furthermore, the **Rh^{IC}₀Ph** control compound also promotes the formation of the product mixture as observed for the non-immobilized Rh^IC_n thus is may serve as well as model for the reactions using the series of homogeneous catalysts Rh^IC_n (Table 1).

To probe feasible reaction mechanisms, we performed DFT calculations on the model systems, using CPCM (THF) M06L/def2TZVP//wB97XD/6-31G(d)+SDD level of theory. Results show that a Chalk–Harrod type mechanism,^{11,32–34} involving oxidative addition of the silane to Rh followed by insertion of the alkyne into the Si–Rh bond, possible *cis–trans* isomerisation, product formation and regeneration of the catalysts, is feasible for the Rh^I species in solution with all required intermediates readily located in the calculations for Rh^IC₀Ph (Scheme S4, S82, ESI†).

In contrast, for the $\mathbf{Rh^{III}Cp*C_0Ph}$ and $\mathbf{Rh^{III}Cl_2}$ model systems attempts to locate a H–Rh–Si intermediate were unsuccessful, suggesting that a step-wise Chalk–Harrod type mechanism is unlikely. However, intermediates where Rh has coordinated to the silane *via* a bridging hydrogen were



Scheme 3 Proposed mechanisms and calculated structures of involved intermediates and transition states; a) for the Rh^{III}Cp*C₀Ph catalyst leading to $\beta(Z)$ -product formation. b) For the Rh^{III}Cl₂ catalyst leading to α -product formation. Energies are reported in kcal mol⁻¹.

located (13.5 kcal mol⁻¹ for $Rh^{III}Cp^*C_0Ph$ and -7.0 kcal mol⁻¹ for $Rh^{III}Cl_2$, similar to that reported in other work^{35,36}). The formation of these Rh–H–Si intermediates suggests that oxidative addition and alkyne insertion occurs in a concerted fashion for the Rh^{III} catalysts, as reported for $Ru^{II}.^{12,13,36}$

As such, for the mechanism involving $\mathbf{Rh}^{\mathrm{III}}\mathbf{Cp}^*\mathbf{C_0Ph}$ (Scheme 3a) we postulate that the less sterically congested anti-Markovnikov type transition state is favoured, leading to selective generation of \mathbf{C}^{Si} -(*E*). The formed \mathbf{C}^{Si} -(*E*) intermediate (65.6 kcal mol⁻¹) is significantly higher in energy than \mathbf{C}^{Si} -(*Z*) (43.8 kcal mol⁻¹), thus isomerization of \mathbf{C}^{Si} -(*E*) to \mathbf{C}^{Si} -(*Z*) is highly likely. This is consistent with the reported isomerization of \mathbf{C}^{Si} -(*E*) to \mathbf{C}^{Si} -(*Z*) promoted by the bulky Cp* ligand.³⁷ Alternatively, considering the high energy of \mathbf{C}^{Si} -(*E*), direct formation of \mathbf{C}^{Si} -(*Z*) through concerted oxidation addition–silyl insertion may occur, as suggested previously for Ir(m).³⁸ The \mathbf{C}^{Si} -(*Z*)-intermediate subsequently undergoes reductive elimination to selectively generate the $\beta(Z)$ isomer.

Lastly, the α selective Rh^{III}Cl₂ catalyst will be considered (Scheme 3b). Modelling a potential reaction mechanism showed a reaction involving a low energy Rh-H-Si intermediate (-7.0 kcal mol⁻¹) is feasible with only one PyTligand coordinated to the Rh. Surprisingly, it was difficult to locate any of the key intermediates generated after alkyne insertion, with the only intermediate located being a C^{Si} - α type species where interaction between Cl and an alkenyl C results in lengthening of the alkene C-C bond (1.44 Å). A low energy reductive elimination transition state (18.8 kcal mol⁻¹) from C^{Si} - α was located, confirming that α -product formation using Rh^{III}Cl₂ is feasible. As the intermediates and reductive elimination transition states that would lead to $\beta(E)$ or $\beta(Z)$ product formation were not able to be located, it is likely that the α-product is directly generated through a Markovnikov type concerted oxidative addition-insertion pathway, as previously reported for Ru^{II.12,13,36} Furthermore, involvement of metallacyclopropene intermediates³⁶ for the system under investigation here would require involvement of +V oxidation states (or higher) for Rh, thus making this pathway less likely.

Conclusions

In summary, we have prepared a series of carbon black based Rh- and Ir-hybrid catalysts with varying surface linker lengths. The hybrid catalysts were characterized by XPS, EDX and synchrotron based EXAFS spectroscopy. The catalysts efficiently catalyse the hydrosilylation of terminal alkynes under mild conditions. The hybrid catalysts with longer chain surface linkers achieved a more rapid transformation of the alkynes compared to those with shorter chain surface linkers. The surface immobilization of the described Rh^I catalysts induces a chemical modification of the active catalyst, which renders the complexes α -selective. In contrast, the Rh^I precursor catalysts show no selectivity when applied in solution. The Rh^{III-} and Ir^{III} catalysts afford the $\beta(Z)$ -

isomers with high levels of selectivity. Proposed mechanisms are supported by DFT calculations. The hybrid catalysts are robust, selective and recyclable, thus providing a green approach towards important industrially relevant building blocks.

Author contributions

M. R. synthesized the compounds and hybrid catalysts, characterized the surfaces by XAS, EDX, TGA and applied the hybrid catalysts in the catalytic transformations. V. R. G, J. L. and J. J. G. characterized the surfaces by XPS. S. T. K. performed the DFT calculations and characterized the surfaces by XAS. B. A. M. and M. R. conceived the experiments. All authors discussed the data, and contributed to writing the manuscript.

Conflicts of interest

The authors declare no conflicts of interest.

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