$[Rh_2(COD)_2(Dppm)(\mu_2\text{-}Cl)]BF_4$: Precursor for a Selective Hydrogenation Catalyst and Its Recycling by Silica Entrapment

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The synthesis of $[Rh_2(COD)_2(dppm)(\mu_2\text{-}Cl)]BF_4$ (**1**) (COD = 1,5-cyclooctadiene, dppm = bis(diphenylphosphino)methane) from simple precursors is reported. This is a rare example of a dirhodium complex with an open $[Rh_2(\mu_2\text{-}dppm)(\mu_2\text{-}Cl)]$ core. The complex has been used to affect the hydrogenation of styrene and benzo[*b*]thiophene with total selectivity and competitive rates of reaction. The recycling of the catalyst has been achieved by the entrapment of **1** in silica by a sol−gel method to produce a recyclable solid catalyst.

Introduction

The synthesis of dinuclear metal complexes has attracted much attention. Bimetallic rhodium complexes have been of particular interest due to their potential to act as homogeneous catalysts. Homobimetallic complexes can bind to unsaturated substrates in modes not possible for their monometallic analogues, and this can lead to new substrate reactivity and cooperative effects. Stanley and co-workers[1] have demonstrated the remarkable homobimetallic cooperative activity of rhodium catalysts in the hydroformylation reaction.

Bimetallic complexes have been frequently constructed using a binucleating ligand as a framework. Diphosphinomethanes have been employed to prepare a wide range of complexes,[2] including heterobimetallic complexes.[3] When reacting bis(diphenylphosphino)methane (dppm)[4] with rhodium(I), there is a strong tendency to form complexes in which two metal ions are surrounded by two bridging ligands *trans* to each other forming an "A-frame".[5,6] Rhodium complexes with two dppm ligands arranged in a $[Rh_2(dppm)_2]$ core have been rigorously investigated.[2,6] Of note is the ability of A-frame complexes to coordinate small molecules such as carbon monoxide, sulfur dioxide, and acetylenes in a bridging fashion.[2,7] This phenomenon has relevance to catalytic processes occurring either on transition-metal clusters or on metal surfaces, and a number of A-frame complexes are capable of catalyzing homogeneous hydrogenation and the water gas shift reactions.[7c,8]

Despite concentrated effort for over 30 years, surprisingly few homodinuclear complexes of rhodium containing only one dppm as a bridging group have been synthesized and structurally characterized.[8,9] The absence of literature examples of these species can be attributed to the lack of a convenient synthetic precursor containing one dppm and a homobimetallic structure. We now report the preparation and X-ray structural characterization of a new heterobridged homodinuclear complex of rhodium containing one dppm and one chloride as bridging groups (Figure 1). In this study we demonstrate the potential of this complex by comparing its ability to provide selective hydrogenation catalysts with well-established di- and triphosphine catalysts such as $[RhCl(PPh_3)_3]$ and show how $[Rh_2(COD)_2(dppm)(\mu_2\text{-}Cl)]BF_4$ (**1**) can be recycled by entrapping it in a silica matrix.

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(4) Abbreviations used: acac, acetyl acetonate; COD, 1,5-cyclooctadiene; dppm, bis(diphenylphosphino)methane; TMS, tetramethylsilane; TOF, turnover frequency; ICP-OES, inductively coupled plasma optical emission spectrometry; BET, Brunner−Emmett−Teller; TEM, transmission electron microscopy.

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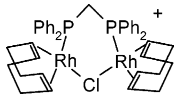

Figure 1. Structure of the cationic core of $[Rh_2(COD)_2(dppm)(\mu_2\text{-}Cl)]BF_4$ (**1**).

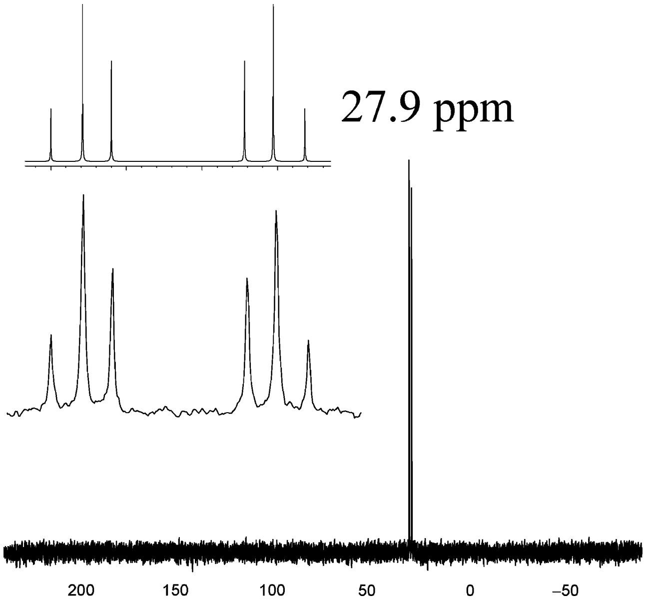

Figure 2. Observed and simulated $^{31}P\{^1H\}$ NMR spectra ($CDCl_3$, H_3PO_4) of $[Rh_2(COD)_2(dppm)(\mu_2\text{-}Cl)]BF_4$ (**1**).

Results and Discussions

Synthesis of $[Rh_2(COD)_2(dppm)(\mu_2\text{-}Cl)]BF_4$ (1). The stepwise addition of dppm in toluene and $AgBF_4$ in acetone to a solution of $[Rh(COD)Cl]_2$ in dichloromethane (CH_2Cl_2) leads to the formation of the binuclear complex $[Rh_2(COD)_2(\mu_2\text{-}dppm)(\mu_2\text{-}Cl)]BF_4$ (**1**) as an orange crystalline powder and orange crystals. Complex **1** is air-stable as a solid, and its solutions in dichloromethane and chloroform are stable for 1 day and 6 days, respectively.

The observed and simulated[10] ^{31}P NMR spectra of **1** are shown in Figure 2. The $^{31}P\{^1H\}$ NMR spectrum of **1** (in $CDCl_3$, relative to H_3PO_4) exhibits a pattern typical of an AA′XX′ spin system centered at δ 27.9: $^1J_{Rh-P} = 150.35$, $^2J_{Rh-P} = 2.74$, $^1J_{Rh-Rh} = -0.07$, $^1J_{P-C-P} = 48.61$ Hz. $^1J_{Rh-P}$ and $^1J_{Rh-Rh}$ values are consistent with Rh(I) ions in a square-planar environment.[9g,11] $^1J_{Rh-Rh}$ is essentially zero, and $^1J_{Rh-P}$ is comparable to A-frame complexes without intramolecular metal−metal bonds.[12] The values of the chemical shift and the coupling constants fall in the range quoted for other related dinuclear rhodium complexes with dppm as a bridging ligand to the two metal centers.[9a,c,d,f,g,i]

The ^1H NMR spectrum of **1** (in $CDCl_3$, relative to TMS) shows signals attributable to the phenyl groups (δ 7.68−7.43), COD (═CH, δ 4.77, 3.05; CH_2, δ 2.13−1.58),[13] and methylene (δ 3.54) hydrogens. The methylene protons of the dppm ligand resonate as a "triplet" centered at δ 3.54 ($J_{P-H} = 9.41$ Hz). We suggest that this is due to a rapid conformational change in the CP_2Rh_2 ring leading to fluxional equivalence of the PCH_2P protons. Cooling the sample to −60 °C led to some broadening of this signal, consistent with an exchange process, but unfortunately we were unable to reach a point of coalescence. In the absence of such motion, the methylene hydrogen resonances often consist of two superimposed multiplets at δ 2.00−2.50.[9f] Resonances for the methylene protons of the dppm ligand similar to that observed for **1** have been found for the following complexes: $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AgY)]$ (Y = CH_3CO_2, $(C_2H_5)_2NCS_2$),[9c] $[\{Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)\}_2\{\mu\text{-}Ag_2(CO_2)_2CH_2\}]$,[9c] $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}AuPPh_3)]X$ (X = BF_4, PF_6),[9f] $[Rh_2(\eta\text{-}C_5H_5)_2(\mu\text{-}CO)(\mu\text{-}dppm)(\mu\text{-}CuX)]$ (X = Cl, I),[9d] and $[Rh_2(quin)_2(CO)_2(\mu\text{-}dppm)]$ (quin = 2-quinaldinate, $C_9H_6N\text{-}COO^-$).[9g]

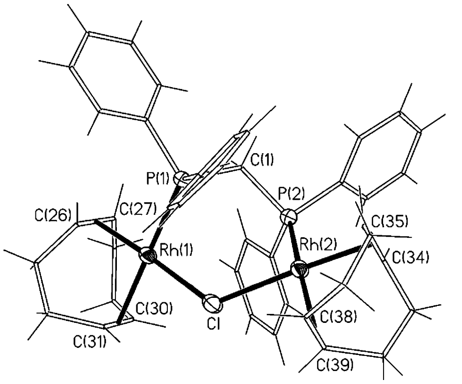

Figure 3. View of the structure of $[Rh_2(COD)_2(\mu_2\text{-}dppm)(\mu_2\text{-}Cl)]^+$. The ellipsoids of Rh, Cl, and P are at 30% probability. Selected distances (Å) and angles (deg), Cyo = centroids of the double bonds of cyclooctadienes: Rh(1)−Cyo(1), 2.010(9); Rh(1)−Cyo(2), 2.130(9); Rh(1)−P(1), 2.297(3); Rh(1)−Cl, 2.411(3); Rh(2)−Cyo(3), 2.003(8); Rh(2)−Cyo(4), 2.121(8); Rh(2)−P(2), 2.301(3); Rh(2)−Cl, 2.427(3); Cyo(1)−Rh(1)−Cyo(2), 86.6(4); Cyo(1)−Rh(1)−P(1), 93.5(3); Cyo(1)−Rh(1)−Cl, 176.1(3); Cyo(2)−Rh(1)−P(1), 178.7(2); Cyo(2)−Rh(1)−Cl, 89.6(3); P(1)−Rh(1)−Cl, 90.3(1); Cyo(3)−Rh(2)−Cyo(4), 86.7(4); Cyo(3)−Rh(2)−P(2), 94.4(3); Cyo(3)−Rh(2)−Cl, 175.8(3); Cyo(4)−Rh(2)−P(2), 169.3(2); Cyo(4)−Rh(2)−Cl, 89.2(3); P(2)−Rh(2)−Cl, 89.9(1); Rh(1)−Cl−Rh2, 123.1(1); Rh(1)−P(1)−C(1), 110.4(4); P(1)−C(1)−P(2), 116.7(5); C(1)−P(2)−Rh(2), 117.5(3). The structure has been deposited in the Cambridge database, CCDC 234930.

The X-ray structure of the cation $[Rh_2(COD)_2(\mu_2\text{-}dppm)(\mu_2\text{-}Cl)]^+$ is shown in Figure 3. The two rhodium atoms are approximately square-planar coordinated, if the centroids of the ethenylidene groups of cyclooctadienes are considered as ligands. The ligands around Rh(1) make an almost perfect plane, and the metal atom deviates only 0.020 Å from it; the ligands around Rh(2) are instead slightly more misaligned, and Rh(2) deviates 0.098 Å from their mean plane. The two coordination planes make a dihedral angle of 43.9°.

This angle is a consequence of the heavy puckering of the six-membered ring Rh(1), Cl, Rh(2), P(2), C(1), P(1) mainly resulting from the gap between the Rh(1)···Rh(2) (4.253 Å) distance and the bite of the diphosphine (P(1)···P(2) (3.134 Å).

To check whether the crystal used for the structure determination corresponded to the main reaction product, the X-ray diffraction pattern of a milled sample of the residual solid was compared with the pattern calculated from the structure data of **1**; the two patterns were almost coincident.

$[Rh_2(COD)_2(\mu_2\text{-}dppm)(\mu_2\text{-}Cl)]BF_4$ (1) as a Precursor for Homogeneous Hydrogenation. Hydrogenation of Styrene. While testing the activity of **1** as a styrene hydroformylation catalyst, the discovery of ethylbenzene in the product mixture prompted us to investigate the activity toward the hydrogenation of styrene. The hydrogenation of styrene can yield a mixture

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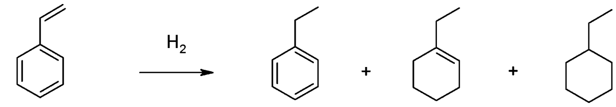

Figure 4. Common products of the hydrogenation of styrene.

of products including ethyl benzene, 1-ethyl-cyclohexene, and ethyl cyclohexane (Figure 4).

The catalytic activity of **1** has been compared with that of different catalyst precursors. Catalytic studies carried out on the hydrogenation of styrene using **1** at 28 bar H_2, 100 °C (Table 1) demonstrated that **1** acts as a precursor to a chemoselective alkene hydrogenation catalyst. It should be noted that all turnover frequencies (TOFs) are quoted per rhodium atom. The catalysts tested were tolerant to CH_2Cl_2 and performed equally well in acetone. CH_2Cl_2 was chosen for the experiments due to difficulties in dissolving many of the precursors in acetone. Of the precursors tested, only $[RhCl(PPh_3)_3]$,[14] $[Rh(COD)(PPh_3)_2]BPh_4$,[15] and **1** gave complete selectivity and total conversion in 2 h. Addition of dppm to $[Rh(acac)(CO)_2]$ failed to increase the activity of this selective but sluggish catalyst. Increasing the reaction time had no effect on the selectivity of the catalyst derived from **1**. The selectivities observed for the various catalytic runs (1−11 Table 1) are plotted in Chart 1. It is interesting to note that, starting from $[Rh(COD)Cl]_2$ as the source of rhodium, selectivity was relatively poor (72%). The addition of 1 or 2 equiv of dppm did not improve this considerably; however the addition of PPh_3 did have an affect on selectivity, as we would expect from the formation of a stable homogeneous catalyst with 2 equiv of phosphine per metal. Consistent with this hypothesis is the total (100%) selectivity observed on addition of 4 equiv of PPh_3. We conclude that the catalytic system responsible for the selective catalyst on the addition of **1** as a source of rhodium was not formed by the separate addition of $[Rh(COD)Cl]_2$ and dppm. Using a heterogeneous catalyst (5% Rh on carbon) hydrogenation of the arene function was considerable, as expected for a Rh(0) catalyst.[16]

No comparison of turnover frequencies could be made for these batch catalytic runs, as the reactions went to completion; therefore a series of gas uptake experiments were conducted for the three best catalytic systems: **1**, $[RhCl(PPh_3)_3]$, and $[Rh(COD)(PPh_3)_2]BPh_4$. The apparatus used (supplied by HEL reactors) consisted of a heated, stirred autoclave attached to a hydrogen cylinder through a solenoid control valve. This enabled the rate of gas uptake to be measured at constant reaction pressure. For catalyst concentrations of 8×10^{-4} mol·dm^{-3} (the concentration used in the batch autoclave runs) initial rates were too fast to be measured reliably and the concentration of the catalyst had to be reduced to a quarter to achieve measurable rates. The initial rates are reported in Table 2.

The rates measured are more than 100 times faster than those estimated for $[Rh(acac)(CO)_2]$ (acac = acetylacetonate) and $[Rh(acac)(CO)_2]$ + dppm (Table 1). The three catalysts behaved similarly under hydrogenation conditions. The solutions exhibited considerably higher rates of gas uptake for the conditions quoted compared with milder conditions. Projecting from the initial rate data, we can surmise that the batch autoclave runs reported in Table 1, entries 1, 2, and 3, were complete after less than 10 min and ethyl benzene was not prone to any further hydrogenation for catalysts **1**, $[RhCl(PPh_3)_3]$, and $[Rh(COD)(PPh_3)_2]BPh_4$.

Further experiments were conducted to probe the stability and flexibility of the new catalyst. Under identical reaction conditions (see Table 1 footnote) a catalytic run was carried out using a very small quantity of $[Rh_2(COD)_2(\mu_2\text{-dppm})(\mu_2\text{-Cl})]BF_4$ (**1**) (8.6×10^{-7} mol). After 6 h at 100 °C over 8.3×10^{-3} mol of styrene were converted selectively to ethyl benzene, this corresponding to 9651 turnovers of a bimetallic catalyst (4836 per rhodium). In addition the hydrogenation activity of **1** was tested at room temperature and 28 bar (other reaction conditions as quoted in Table 1); after 24 h full conversion was observed.

The selectivity of the catalyst derived from **1** strongly points to a catalytic cycle involving a Rh(I) molecular catalyst. Indeed it has been suggested[16] that the hydrogenation of the arene functionality (absent for reactions catalyzed by **1**) is diagnostic of the formation of Rh(0). We suggest a dirhodium ($dppmRh_2$) molecular catalyst and evoke a cooperative effect in order to explain the high activity and selectivity observed. The similarity to $[RhCl(PPh_3)_3]$ and $[Rh(COD)(PPh_3)_2]BPh_4$ would suggest a $Rh^{I/III}$ cycle involving H_2 oxidative addition, 1,2-migratory insertion, and reductive elimination steps. Further work is being conducted to understand the mechanism.

Hydrogenation of 1-Hexene. The hydrogenation ability of **1** was compared with that of $[Rh(acac)(CO)_2]$, $[Rh(acac)(CO)_2]$ + dppm (1:1), and $[RhCl(PPh_3)_3]$ (Table 3). All four catalysts were totally selective for the hydrogenation of 1-hexene to *n*-hexane.

Hydrogenation of benzo[*b*]thiophene. Attempts to increase sustainability will lead to the need to use more diverse natural materials as chemical feedstocks.[17] Chemists will require an abundance of catalysts capable of transforming difficult molecules into useful chemicals. As many of the molecules found naturally are highly unsaturated and/or highly oxidized, hydrogenation will be increasingly important.[18] To probe the tolerance of our new catalytic system to difficult substrates, we investigated the hydrogenation of benzo[*b*]thiophene. A major contaminant of crude oil and coal, benzo[*b*]thiophene is an abundant substrate for model studies.[19] The hydrodesulfurization (HDS) of crude feedstocks is required in order to prevent environmental pollution and to improve the efficiency of catalytic reactions. Sulfur-containing molecules such as benzo[*b*]thiophene are toxic environmental pollutants in their own right, classified as polynuclear aromatic hydrocarbons, and furthermore chemical oxidation at sulfur can lead to the formation of oxides that cause acid rain. The presence of sulfur in substrates for catalysis (either chemical or automotive) often leads to irreversible poisoning of catalytic centers.[20] Heterogeneous catalysts are particularly vulnerable to irreversible sulfur poisoning, as sulfur attached to the metal surface at defect sites cannot be easily hydrogenated (to H_2S) and thus removed (unlike nitrogen and carbon).[20] Molecular catalysts have the potential to offer invaluable information on how to avoid sulfur poisoning, as the reactivity at the catalytic centers can be systematically altered and the effects on recycling assessed.

The activity of **1** as a catalyst for the hydrogenation of benzo[*b*]thiophene was screened against a number of established homogeneous hydrogenation catalysts. The results are summarized in Tables 4−8. Rates observed at 100 °C (Table 4) were consistent with values reported in the literature (initial rates 0.3−6.2 turnovers h^{-1}) for a range of catalysts including [RhCl-

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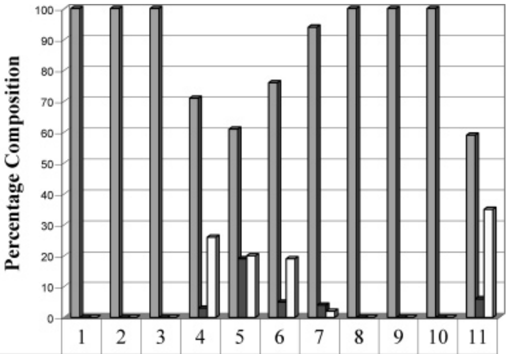
Table 1. Homogeneous Hydrogenation[a] of Styrene

test no.	catalyst	[Rh]/10^{-4} mol dm^{-3}	conversion/%	selectivity/%	TOF/10^2 h^{-1}
1	$[Rh_2(COD)_2(dppm)(Cl)]BF_4$	8.0	100	100	≥5.0
2	$RhCl(PPh_3)_3$	6.6	100	100	≥6.0
3	$[Rh(COD)(PPh_3)_2]BPh_4$	8.6	100	100	≥4.6
4	$[Rh(COD)Cl]_2$	11.1	100	71	>3.6
5	$[Rh(COD)Cl]_2$ + 1dppm	11.1	100	61	>3.6
6	$[Rh(COD)Cl]_2$ + 2dppm	16.2	100	76	>2.4
7	$[Rh(COD)Cl]_2$ + 2PPh$_3$	13.6	100	94	>2.9
8	$[Rh(COD)Cl]_2$ + 4PPh$_3$	20.4	100	100	≥1.9
9	$[Rh(acac)(CO)_2]$	6.9	34	100	2.0
10	$[Rh(acac)(CO)_2]$ + 1dppm	6.9	31	100	1.8
11	Rh on carbon (5%)	6.8	100	59	≥5.8

[a] All reactions in CH_2Cl_2, $T = 100$ °C, $P_{(100\ °C)} = 28$ bar, [styrene] = 0.793 mol dm^{-3}; the reaction was run for 2 h at stir rate 1200 rpm; selectivities are quoted as % ethyl benzene.

Chart 1. Selectivity Data for the Hydrogenation[a] of Styrene for Catalysts 1−11[b]



	1	2	3	4	5	6	7	8	9	10	11
▨ ethyl benzene	100	100	100	71	61	76	94	100	100	100	59
■ 1-ethyl-cyclohexene	0	0	0	3	19	5	4	0	0	0	6
□ ethyl cyclohexane	0	0	0	26	20	19	2	0	0	0	35

Catalytic Run

[a] Conversions are given in Table 1. [b]1: $[Rh_2(COD)_2(dppm)(Cl)]BF_4$, 2: $RhCl(PPh_3)_3$, 3: $[Rh(COD)(PPh_3)_2]BPh_4$, 4: $[Rh(COD)Cl]_2$, 5: $[Rh(COD)Cl]_2$ + 1dppm, 6: $[Rh(COD)Cl]_2$ + 2dppm, 7: $[Rh(COD)Cl]_2$ + 2PPh$_3$, 8: $[Rh(COD)Cl]_2$ + 4PPh$_3$, 9: $[Rh(acac)(CO)_2]$, 10: $[Rh(acac)(CO)_2]$ + 1dppm, 11: Rh on carbon (5%).

Table 2. Initial Rate of Hydrogenation[a] of Styrene by Gas Uptake

catalyst	[Rh]/ 10^{-4} mol dm^{-3}	rate/ mol dm^{-3} h^{-1}	TOF/ 10^2 h^{-1}
$[Rh_2(COD)_2(dppm)(Cl)]BF_4$	1.96	5.24	270
$RhCl(PPh_3)_3$	1.97	6.32	320
$[Rh(COD)(PPh_3)_2]BPh_4$	1.90	5.07	270

[a] All reactions in CH_2Cl_2, $T = 100$ °C, $P_{(100\ °C)} = 27$ bar, [styrene] = 0.793 mol dm^{-3}, the reaction was stirred at 1000 rpm.

Table 3. Homogeneous Hydrogenation[a] of 1-Hexene

catalyst	[Rh]/ 10^{-4} mol dm^{-3}	conversion/ %	TOF/ 10^2 h^{-1}
$[Rh(acac)(CO)_2]$	7.3	32	1.6
$[Rh(acac)(CO)_2]$ + dppm	7.3	14	0.7
$[RhCl(PPh_3)_3]$	6.9	100	≥5.3
$[Rh_2(COD)_2(dppm)(Cl)]BF_4$	7.6	100	≥4.8

[a] All reactions in CH_2Cl_2, $T = 100$ °C, $P_{(100\ °C)} = 28$ bar, [1-hexene] = 0.727 mol dm^{-3}; the reaction was run for 2 h at stir rate 1200 rpm. The reaction using $[Rh_2(COD)_2(dppm)(Cl)]BF_4$ was also performed in acetone; results were identical.

$(PPh_3)_3]$,[21,22] $[Cp^*Rh(MeCN)_3](BF_4)_2]$,[23] $[Rh(COD)(PPh_3)_2]PF_6$,[21] $[RuHCl(CO)(PPh_3)_3]$,[21] $[OsHCl(CO)(PPh_3)_3]$,[21] $[Ir(COD)(PPh_3)_2]PF_6$,[21] $[RuCl_2(PPh_3)_3]$,[21,24] and (TRIPHOS)-Rh{(η^3-S(C_6H_4)-CH=CH$_2$] (TRIPHOS = MeC(CH$_2$PPh$_2$)$_3$).[25] In every case the only hydrogenation product observed was 2,3-dihydrobenzo[*b*]thiophene (Figure 5). The rate of reaction, reported as the turnover frequency (turnovers h^{-1}), is at the upper end of the literature range, and it should be noted that this approaches rates reported by Sánchez-Delgado at 170 °C and 115 bar pH$_2$.[21]

The most active catalyst measured was $[Rh_2(COD)_2(dppm)(Cl)]BF_4$ (**1**). The extent of hydrogenation catalyzed by **1** as a function of time was calculated by doing separate batch autoclave runs for 12, 15, 24, and 71 h at [Rh]:[substrate] ratio 1:20 (Table 5). Clearly there is a loss of activity as a function of time, and this may be due to changes in the composition of the solution (increased 2,3-dihydrobenzo[*b*]thiophene, decreased benzo[*b*]thiophene) or catalyst deactivation.

Similar results were obtained at 125 °C (34 bar). At this temperature the effect of altering the [Rh]:[substrate] ratio was investigated (Table 6). For a 2 h catalytic run changes in rate are entirely consistent with first-order variance with respect to substrate concentration. From this we would expect a decrease in rate as a function of time, and we deduce substrate concentration is rate limiting (non-zero order). We conclude that turnover frequencies calculated from batch runs at longer reaction times are misleading, as the rate of reaction slows during the run due to the reduction in the concentration of benzo[*b*]thiophene. At longer reaction times (136 h) the selectivity of the catalytic system is lost, and this may be an indicator of catalyst decomposition. The product mixture after long reaction times is complex, containing a mixture of unreacted benzo[*b*]thiophene (BT), 2,3-dihydrobenzo[*b*]thiophene (DHBT), 2-methylbenzo[*b*]thiophene (2-M-BT), 3-methylbenzo[*b*]thiophene (3-M-BT), 5-methylbenzo[*b*]thiophene (5-M-BT), 2,7-dimethylbenzo[*b*]thiophene (2,7-dM-BT), 2-ethylbenzo[*b*]thiophene (2-Et-BT), and 3,4-dihydro-2*H*-1-benzo[*b*]thiopyran (3,4-dH-BTP) (Figure 6). These side products are the result of C−C bond forming reactions, and the origin of the additional carbon atoms is likely to be the CH_2Cl_2 solvent. Such side reactions are more prevalent at 150 °C for most catalytic systems, and work at this temperature enabled us to quantify the side products.

Results for catalytic runs at 150 °C (45 bar) employing a range of catalysts are displayed in Tables 7 and 8. At 150 °C the new catalyst precursor **1** forms a much more active and selective hydrogenation catalyst than $[RhCl(PPh_3)_3]$, $[Rh(COD)(PPh_3)_2]BPh_4$, $[RuHCl(CO)(PPh_3)_3]$, or $[RuCl_2(PPh_3)_3]$. Total

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Table 4. Homogeneous Hydrogenation[a] of Benzo[*b*]thiophene

catalyst	[Rh]/ 10^{-4} mol dm^{-3}	[substrate]/ 10^{-2} mol dm^{-3}	[substrate]/ [catalyst]	convn/ %	rate/ 10^{-4} mol dm^{-3} h^{-1}	TOF/ h^{-1}
1[b]	13.4	7.27	54	19	69.1	5.2
$RhCl(PPh_3)_3$	3.8	2.01	53	10	10.1	2.7
$[Rh(COD)(PPh_3)_2]BPh_4$	9.6	5.34	56	17	45.4	4.7
$RuHCl(CO)(PPh_3)_3$	4.9	2.80	57	5	7.0	1.4
$RuCl_2(PPh_3)_3$	4.6	2.67	58	5	6.7	1.5

[a] All reactions in CH_2Cl_2, $T = 100$ °C, $P_{(100\ °C)} = 28$ bar; the reaction was run for 2 h at stir rate 1200 rpm. [b] **1** = $[Rh_2(COD)_2(dppm)(Cl)]BF_4$.

Table 5. Hydrogenation[a] of Benzo[*b*]thiophene Using $[Rh_2(COD)_2(dppm)(Cl)]BF_4$ for Different Reaction Times

[Rh]/10^{-4} mol dm^{-3}	[substrate]/ 10^{-2} mol dm^{-3}	time/ h	conversion/ %	rate/ 10^{-4} mol dm^{-3} h^{-1}	TOF/ h^{-1}
8.0	1.69	12	27	3.8	0.5
11.2	2.38	15	33	5.2	0.5
9.0	1.81	24	40	3.0	0.3
11.4	2.22	71	47	1.5	0.1

[a] All reactions in CH_2Cl_2, $T = 100$ °C, $P_{(100\ °C)} = 28$ bar, stir rate 1200 rpm.

selectivity could be maintained for 12 h using a substrate-to-catalyst ratio of 51:1; under similar conditions (55:1) all other catalysts tested gave considerable amounts of side products (Table 8). The highest rate of hydrogenation measured for the 2 h run was 0.0127 mol dm^{-3} h^{-1} using **1**, corresponding with a TOF of 7.2 h^{-1}.

The increased instances of C−C coupling reactions at higher temperatures are consistent with a high kinetic barrier for this reaction, and increased selectivity with increased substrate concentration is consistent with a rate of hydrogenation that is substrate-concentration dependent. The high selectivity exhibited by **1** compared to the other catalysts tested may be due to the presence of a bimetallic active core that restricts the modes of binding of benzo[*b*]thiophene. Baralt et al.[23] and Sánchez-Delgado et al.[26] have noted that benzo[*b*]thiophene can bind to rhodium via S-bonded, η^2, η,[4] η^5, or η^6 modes, and these additional modes may provide lower energy reaction pathways for side reactions by mechanisms such as ring slippage.

To test the recycling of catalysts derived from **1**, we prepared a silica-entrapped catalyst.

Entrapment of 1 in a Silica Matrix. Previously we reported the facile recycling of a totally selective solid hydrogenation catalyst made by the sol−gel entrapment of $[RhCl(PPh_3)_3]$ by conventional sol−gel and ionic-liquid-mediated routes.[27] To entrap[28] a molecular catalyst, the metal complex is added to the sol−gel recipe for the solid oxide material, and on formation of the oxide, the catalyst becomes imprisoned (entrapped) within the solid matrix. Provided a material of the correct physical nature (porosity, surface area) is produced, the result is a catalyst with molecular reactivity that can be recycled many times in catalytic experiments. Blum and Avnir[29,30] have reported the advantages of this method for producing catalysts that have a high resistance to poisoning and the use of entrapment to enable the combination of incompatible catalysts within the same reaction vessel and facilitate cascade processes.

We were able to entrap **1** in silica by a conventional sol−gel method similar to that reported previously.[27] The resultant material had a BET of 139.5 ± 0.25 m^2/g and a metal loading of 0.06 wt % (by inductively coupled plasma optical emission spectrometry, ICP-OES). The ^{31}P solid-state NMR spectrum of the material produced is shown in Figure 7. Comparison with Figure 2 shows a great correlation between the resonances, suggesting that $[Rh_2(COD)_2(dppm)(\mu_2\text{-}Cl)]BF_4$ is entrapped intact.

Catalytic Testing of $[Rh_2(COD)_2(dppm)(\mu_2\text{-}Cl)]BF_4$ (1) Entrapped in Silica. Silica-entrapped **1** was tested as a reusable catalyst for the hydrogenation of styrene (Chart 2) and benzo[*b*]thiophene (Chart 3) at 100 °C. Due to the dramatic differences in rate for the two reactions, each styrene experiment was conducted for 30 min and each benzo[*b*]thiophene experiment for 21 h.

To catalyze the hydrogenation of styrene, 0.0152 g of a 0.06% weight percentage rhodium catalyst prepared by the sol−gel entrapment of $[Rh_2(COD)_2(dppm)(\mu_2\text{-}Cl)]BF_4$ (**1**) in silica was used. For comparison with the homogeneous catalysts the amount of metal added corresponds to 8.9×10^{-8} mol of rhodium and a concentration of 8.1×10^{-6} mol dm^{-3} in each run. After each run the product solution was removed and analyzed for organic product composition and rhodium concentration (in order to screen for catalyst leaching). In all cases the catalyst was 100% selective, yielding only ethyl benzene. Running the reaction for 2 h gave 100% conversion to ethyl benzene with no ring hydrogenation. Over the 10 runs the catalyst completed more than 6.7×10^5 turnovers, corresponding to the hydrogenation of 6.9 cm^3 of styrene. In all but one solution the leaching rate was beyond the limit of detection (<0.003%). The solution of run 3 contained Rh consistent with leaching of 0.003% (Rh concentration 2.4×10^{-10} mol dm^{-3}). The conversion of styrene (Chart 2) varies from 72% in the first two runs to 67% in the final run, a 7% reduction in overall activity; most of this reduction occurs between the second and third run. The erosion of rate cannot be explained purely by metal leaching, which is less than 0.03% (2.7×10^{-11} mol Rh) over the 10 runs. BET analysis of the catalyst after treatment under reaction conditions for 6 h reveals that there has been a considerable change in the surface area of the matrix. The effective surface area was reduced from 139.5 m^2/g in the freshly prepared catalyst to 72.3 m^2/g after use. This helps to explain the reduction in activity between runs 2 and 3 (Chart 2). We suggest that the reduction in surface area is associated with a closing of the structure, causing a small loss of rhodium (0.003%) and making the remaining active catalytic centers less available to the substrate. We are currently investigating entrapment methods that yield more robust materials.[27] Transmission electron microscopy (TEM) was used to analyze the homogeneity of the used catalyst (Figure 8). Rhodium could be detected by EDX metal analysis, but no Rh(0) nano- or microparticles were observed. This result in addition to the complete selectivity observed suggests that the entrapped metal remains in a molecular form.

Taking 72% conversion in 30 min as a measure of the activity of the catalyst, the rate was 1.14 mol dm^{-3} h^{-1} and the TOF

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Table 6. Effects of Altering [Rh]:[Substrate] Ratio on Rates of Hydrogenation[a] of Benzo[*b*]thiophene Catalyzed by $[Rh_2(COD)_2(dppm)(Cl)]BF_4$ at 125 °C

[Rh]/10^{-4} mol dm^{-3}	[substrate]/10^{-2} mol dm^{-3}	[substrate]/[catalyst]	time/h	conversion/%	rate/10^{-4} mol dm^{-3} h^{-1}	TOF/h^{-1}
8.8	0.85	10	2	20	8.5	1.0
11.6	2.32	20	2	23	26.4	2.3
9.4	5.20	55	2	18	46.8	5.0
8.4	0.79	10	12	42	2.8	0.3
11.4	2.37	21	12	49	9.7	0.9

[a] All reactions in CH_2Cl_2, $T = 125$ °C, $P_{(125\ °C)} = 34$ bar, stir rate 1200 rpm.

Table 7. Hydrogenation[a] of Benzo[*b*]thiophene at 150 °C

catalyst	[Rh]/10^{-4} mol dm^{-3}	[substrate]/10^{-2} mol dm^{-3}	[substrate]/[catalyst]	time/h	convn (select.)/%	rate/10^{-4} mol $dm^{-3}h^{-1}$	TOF/h^{-1}
1[b]	8.2	0.78	10	2	22 (100)	8.6	1.0
1	7.8	2.09	27	2	26 (100)	27.2	3.5
1[c]	17.6	9.38	53	2	27 (100)	126.6	7.2
1	11.4	5.76	51	12	40 (100)	19.2	1.7
1	8.2	2.18	27	12	25 (80)	3.6	0.4
1	6.0	2.29	38	14	22 (42)	1.5	0.3
1	8.4	0.77	9	15.5	30 (80)	1.2	0.1
$RhCl(PPh_3)_3$	4.2	2.29	55	2	8 (27)	2.4	0.6
$[Rh(COD)(PPh_3)_2]^+$	9.7	5.34	55	2	13 (39)	13.5	1.4
$RuHCl(CO)(PPh_3)_3$	5.5	3.03	55	2	7 (14)	1.5	0.3
$RuCl_2(PPh_3)_3$	5.0	2.77	55	2	7 (25)	2.4	0.5

[a] All reactions in CH_2Cl_2, $T = 150$ °C, $P_{(150\ °C)} = 45$ bar, stir rate 1200 rpm. Selectivity is quoted as percentage 2,3-dihydrobenzo[*b*]thiophene; rate is quoted for hydrogenation only. [b] **1** = $[Rh_2(COD)_2(dppm)(Cl)]BF_4$. [c] The conversion for a reaction run in toluene was far poorer (7% compared with 27% in CH_2Cl_2).

Table 8. Percentage Composition of the Product Solutions Yielded from the Hydrogenation[a] of Benzo[*b*]thiophene at 150 °C[b]

catalyst	DBT	2-M-BT[c]	3-M-BT	5-M-BT	2,7-dM-BT	2-Et-BT	3,4-dH-BTP
1[d]	100	0	0	0	0	0	0
$RhCl(PPh_3)_3$	27	43	3	18	6	2	1
$[Rh(COD)(PPh_3)_2]BPh_4$	39	36	9	16	0	0	0
$RuHCl(CO)(PPh_3)_3$	14	41	3	35	0	5	2
$RuCl_2(PPh_3)_3$	25	33	2	33	0	5	2

[a] All reactions in CH_2Cl_2, $T = 150$ °C, $P_{(150\ °C)} = 45$ bar; the reaction was run for 2 h at stir rate 1200 rpm. [b] Further reaction conditions are quoted in Table 7, entries 3, 8, 9, 10, and 11. [c] Abbreviations are explained in Figure 6. [d] **1** = $[Rh_2(COD)_2(dppm)(Cl)]BF_4$.

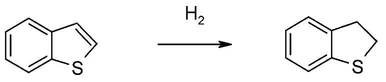

Figure 5. Hydrogenation of benzo[*b*]thiophene to 2,3-dihydrobenzo[*b*]thiophene.

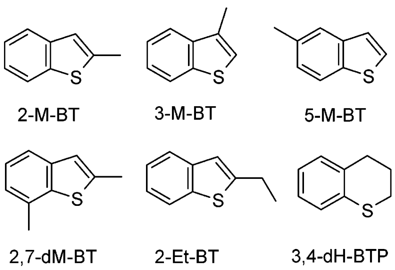

Figure 6. Side products from the hydrogenation of benzo[*b*]thiophene in CH_2Cl_2.

1.4×10^5 h^{-1}. This TOF is 5 times higher than that achieved homogeneously (Table 2). In all runs the TOF is between 1.3 and 1.4×10^5 h^{-1}. This result illustrates the role of the matrix in reinforcing molecular reactivity and contrasts with many other methods of heterogenizing homogeneous catalysts that lead to a reduction in activity.[31] High activity was also observed[27] for the hydrogenation of styrene catalyzed by $[RhCl(PPh_3)_3]$ entrapped by an ionic-liquid-mediated method (TOF 6.84×10^4 h^{-1}).

A 0.1024 g sample of the 0.06% weight percentage rhodium catalyst was used repeatedly for the hydrogenation of benzo[*b*]thiophene (Chart 3). For comparison with the homogeneous catalysts this would correspond to a concentration of 5.97×10^{-5} mol dm^{-3}. In all cases the only product detected was 2,3-dihydrobenzo[*b*]thiophene. This is consistent with the homogeneous catalyst testing at 100 °C. There is a 5% variation in the weight of benzo[*b*]thiophene added to the catalyst throughout the 10 runs, and therefore a small variance in conversion, such as that shown in the first five catalytic runs (first 105 h), can be expected. After the fifth run there is a noticeable drop in performance, and the overall trend over the 10 runs is downward. No rhodium leaching could be detected by ICP-OES analysis of the product solutions. Assuming 20% conversion to be the true activity of the catalyst before decomposition, this represents a rate of 5.06×10^{-4} mol dm^{-3} h^{-1} and a TOF

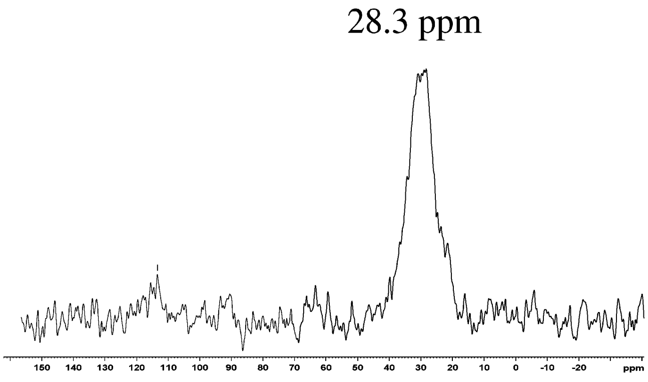

Figure 7. Solid-state ^{31}P spectrum of $[Rh_2(COD)_2(dppm)(\mu_2\text{-}Cl)]BF_4$ (**1**) entrapped in silica.

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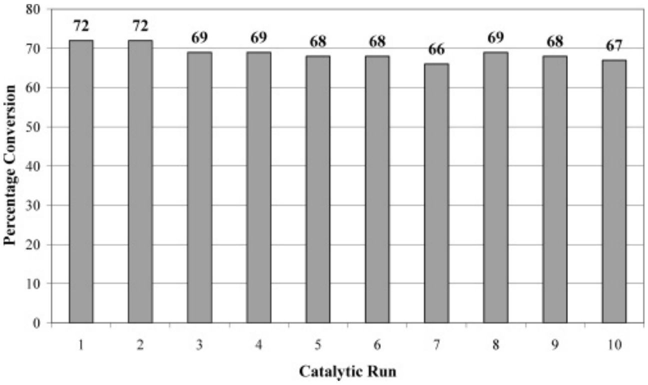
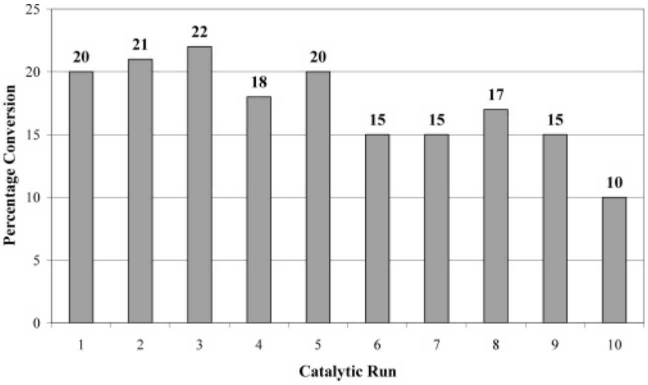
Chart 2. Percentage Conversion for the Hydrogenation[a] of Styrene Catalyzed by Recycled Entrapped 1



[a] All runs in CH_2Cl_2, 28 bar H_2, 100 °C, [styrene] = 0.793 mol dm^{-3}, each run was 30 min, stir rate 1200 rpm.

Chart 3. Percentage Conversion for the Hydrogenation[a] of Benzo[*b*]thiophene Catalyzed by Recycled Entrapped 1



[a] All runs in CH_2Cl_2, 28 bar H_2, 100 °C, [benzo[*b*]thiophene] = 0.05 mol dm^{-3}, each run was 21 h, stir rate 1200 rpm.

of 8.5 h^{-1}, consistent with the best result obtained in homogeneous solution (7.2 at 150 °C, see Table 7). The successful operation of catalyst **1** for 100 h is consistent with observations under homogeneous conditions in which substrate-limited activity was maintained for 71 h. We attribute the loss of activity after this to decomposition or rearrangement of the catalyst. This is not accompanied by a loss of selectivity.

Conclusion

We have reported a straightforward route for the preparation of the rare [(μ-dppm)Rh_2] functionality and have demonstrated that $[Rh_2(COD)_2(dppm)(\mu_2\text{-}Cl)]BF_4$ (**1**) acts as a precursor for a chemo- and regioselective hydrogenation catalyst. Rates of reaction are similar to or greater than those obtained with catalyst precursors containing ≥ 2 phosphines per metal atom. The entrapment of **1** within a silica matrix by the sol−gel method yields a catalyst with identical selectivity and enhanced activity in the hydrogenation of styrene and benzo[*b*]thiophene that can be recycled at least 10 times.

Experimental Section

General Procedures. All preparations were carried out in standard Schlenk tubes under a dinitrogen atmosphere. Elemental analyses were performed by ASEP, The Queen's University of Belfast. Solid samples of the synthesized complexes were stored at room temperature. CH_2Cl_2 and diethyl ether were purified and dried by standard procedures. Toluene and acetone were thoroughly degassed prior to use and saturated with inert or reactant gas. $[Rh(COD)Cl]_2$,[32] $[RhCl(PPh_3)_3]$,[14] and $[Rh(COD)_2(PPh_3)_2]BPh_4$[15] were prepared by established routes. $[Rh(acac)(CO)_2]$, $[RuHCl(CO)(PPh_3)_3]$, $[RuCl_2(PPh_3)_3]$, and benzo[*b*]thiophene were purchased from Aldrich. All other reagents were used as commercially available. ^1H and ^{31}P NMR spectra were obtained on a Bruker Advance DPX 300 spectrometer. Chemical shifts of the ^1H NMR spectrum are reported on $CDCl_3$ solutions relative to Me_4Si. Chemical shifts of the ^{31}P NMR spectra are reported on $CDCl_3$ solutions relative to 85% H_3PO_4. The GC-MS were performed by ASEP, The Queen's University of Belfast; the GC column used was a Restek rtx5 60 m within a Perkin-Elmer Turbo-Mass GC mass spectrometer. Solid-state NMR experiments were performed on a Bruker Avance 400 NMR spectrometer operating at 100.61 MHz for ^{31}P. High-power decoupling experiments were carried out using a standard HPDEC pulse sequence. The samples were spun at magic angle at a rate of 14.031 kHz. A ^1P $\pi/2$ pulse time of 3.5 μs and a recycle delay of 10 s between scans were used for all the samples. Surface area was calculated by the BET method on a Micromeritics ASAP 2010.

The catalytic tests were conducted using a Parr Series 5500 high-pressure stainless steel 50 cm^3 compact laboratory reactor stirred by a magnetically driven four-blade impeller. Reaction time was started once the reactor had heated to the reaction temperature.

$[Rh_2(COD)_2(dppm)(\mu_2\text{-}Cl)]BF_4$ (1). A solution of dppm (0.207 g, 0.538 mmol) in toluene (3 cm^3) was added to a solution of $[Rh(COD)Cl]_2$ (0.255 g, 0.516 mmol) in CH_2Cl_2 (4 cm^3). After stirring for 5 min, a solution of $AgBF_4$ (0.192 g, 0.958 mmol) in acetone (9 cm^3) was added. A white solid (AgCl) instantly precipitated from the brown solution. The resulting mixture was stirred for 30 min. The solid was then filtered and washed with CH_2Cl_2 (30 cm^3), until the CH_2Cl_2 (then added to the filtrate) remained colorless. The volume of the filtrate was then reduced under reduced pressure, and the product precipitated by cooling to −18 °C or adding diethyl ether. **1** was obtained as an orange crystalline powder or orange crystals. The product was filtered, washed with diethyl ether (2 × 7 cm^3), and dried in vacuo ($P = 4 \times 10^{-2}$ Torr) at room temperature. The total yield of the product was 0.413 g (86%); ^1H NMR (in $CDCl_3$, relative to TMS) δ 7.68−7.43 (20H, m, *H phenyl*), 4.77, 3.05 (8H, m, =C*H COD*), 2.13−1.58 (16H, m, CH_2 COD), 3.54 ppm (2H, t, PCH_2P); $^{31}P\{^1H\}$ NMR (in $CDCl_3$, relative to H_3PO_4) δ 27.9 ppm (AA′XX′ system, $^1J_{Rh-P} = 150.35$, $^2J_{Rh-P} = 2.74$, $^1J_{Rh-Rh} = -0.07$, $^1J_{P-C-P} = 48.61$ Hz). Anal. Calcd for $C_{41}H_{46}BClF_4P_2Rh_2$: C, 53.02; H, 4.99; Cl, 3.82; F, 8.18. Found: C, 53.37; H, 4.94; Cl + F, 12.15. FAB-MS (*m*/*z*): 841 [M^+] (calcd 841). Samples of the powder and crystals were used for X-ray diffraction studies.

Crystal data for **1**, $C_{41}H_{46}BClF_4P_2Rh_2$: $M_r = 928.80$, monoclinic, space group $P2_1/n$ (no. 14), $a = 10.220(3)$ Å, $b = 14.987(4)$ Å, $c = 25.454(9)$ Å, $\beta = 96.67(1)°$, $V = 3872(2)$ Å^3, $T = 293(2)$ K, $Z = 4$, μ(Mo Kα) = 1.053 mm^{-1}, 4844 independent reflections measured, $d_{calc} = 1.593$ g cm^{-3}, $R_1 = 0.0600$, $wR_2 = 0.1160$ (for $I > 2\sigma(I)$), and 447 refined parameters. Orientational disorder was present in the anion. The structure has been deposited in the Cambridge database, CCDC 234930.

Silica Entrapment of 1. Tetraethoxysilane (TEOS) (2.42 g, 0.0107 mol) was added to ethanol (1.73 g, 0.03604 mol) and stirred for 20 min in a plastic container. Four drops of water (distilled) were added and stirred in for a further 10 min. **1** (0.096 g, 0.000103 mol) was dissolved in the minimum quantity of dichloromethane (0.5 cm^3). This catalyst solution was added to the mixture and stirred for 60 s. Four drops of benzylamine were added, and the mixture was vigorous stirred until the gel point was reached. The magnetic flea was removed, and the sample was left to age for 1 week, after which time the sample was ground into a powder with a mortar

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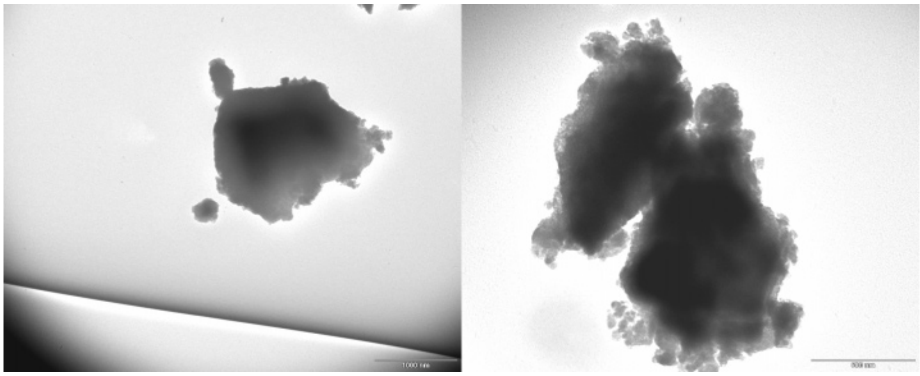

Figure 8. TEM images of silica-entrapped **1** after catalysis.

and pestle. Soxhlet extraction was carried out with CH_2Cl_2 to remove any catalyst that was not entrapped, and the resultant pale yellow powder was dried in a desiccator over silica gel. The product contained 0.06% weight percentage rhodium by ICP-OES, ^{31}P NMR δ 28.3 ppm.

ICP-OES Analysis of the Entrapped Catalyst. A mixture of concentrated HCl (11.5 M, 2.5 cm^3) and concentrated HNO_3 (16 M, 2.5 cm^3) was heated and added to the sample to be digested (0.01 g). The solution was stirred until homogeneous, and then distilled water was added to make the volume up to 100 cm^3. Once cooled, a 10 cm^3 aliquot was submitted for analysis on a ThermoElemental IRIS Duo.

ICP-OES Analysis of Product Solutions. All volatile organics were removed under vacuum, and the resultant residue was dissolved by digesting in a preheated mixture of concentrated HCl (11.5 M, 0.25 cm^3) and HNO_3 (16 M, 0.25 cm^3). Once homogeneous, distilled water was added to make the volume up to 10 cm^3. Once cooled, the solution was submitted for analysis on a ThermoElemental IRIS Duo.

Homogeneous Catalytic Experiments. Batch Catalytic Runs. Hydrogenation of Styrene and 1-Hexane. The catalyst and modifier (if required, see Tables 1 and 3 for rhodium concentration) were dissolved in CH_2Cl_2 (10 cm^3) and injected into the autoclave. Styrene (1 cm^3, 0.0087 mol) or 1-hexane (1 cm^3, 0.0080 mol) was injected, and the autoclave was pressurized to 20 bar with H_2. The stirrer was started (stir rate 1200 rpm), and the autoclave was heated to 100 °C (internal temperature). The pressure at 100 °C was 28 bar.

After the reaction time the autoclave was cooled rapidly and degassed and the resultant solution analyzed by GC and GC-MS.

Hydrogenation of Benzo[*b*]thiophene. The benzo[*b*]thiophene and catalyst were dissolved in CH_2Cl_2 (10 cm^3) and injected into the autoclave (for rhodium and benzo[*b*]thiophene concentrations see Tables 4−7). The autoclave was pressurized to 20 bar with H_2. The stirrer was started (stir rate 1200 rpm), the autoclave was heated to 100, 125, or 150 °C, and the resultant pressure was 28, 34, or 45 bar, respectively.

After the reaction time the autoclave was cooled rapidly and degassed and the resultant solution analyzed by GC and GC-MS.

Gas Uptake Experiments. The hydrogen uptake experiments were carried out in a 50 cm^3 stainless steel Hazards Evaluation Laboratories (HEL) reactor system, equipped with on-line control and analysis of reaction temperature, pressure, and gas uptake. The gas uptake and reactor pressure control utilized a Brooks mass flow controller, and the temperature control employed the use of an external oil heating jacket (Julabo F32). The temperature was monitored in the reaction solution.

A solution of **1** (0.0010 g 2.2×10^{-6} mol), $[RhCl(PPh_3)_3]$ (0.0020 g, 2.2×10^{-6} mol), or $[Rh(COD)(PPh_3)_2]BPh_4$ (0.0022 g, 2.1×10^{-6} mol) in styrene (1 cm^3, 0.0087 mol) and CH_2Cl_2 (10 cm^3) was charged to the reactor under N_2. The reactor vessel was then purged with H_2 (BOC, 99.995% purity) for 2 min at a flow rate of 50 cm^3 min^{-1}, after which the magnetically driven gas entrainment impeller was set to 1000 rpm and the vessel pressurized to 10 bar of H_2. The temperature was then gradually increased until a constant temperature of 100 °C was attained. The reactor was then immediately pressurized to 27 bar of H_2, which corresponded to reaction $t = 0$. The mass flow controller constantly replaced consumed H_2, maintaining the reactor pressure. Rate data were calculated from the rate of uptake of H_2 to the solution.

Silica-Entrapped Catalyst Recycle. Hydrogenation of Styrene. A 0.0152 g sample of the 0.06% Rh in silica catalyst was weighed into the autoclave. The autoclave and catalyst were evacuated and flushed with nitrogen and CH_2Cl_2 (10 cm^3), and styrene (1 cm^3, 0.0087mol) was injected. The autoclave was pressurized to 20 bar with H_2 and the stirrer started (stir rate 1200 rpm). The apparatus was heated to 100 °C (internal temperature) for 30 min, rapidly cooled, and degassed, and the liquid products were removed and analyzed for rhodium content by ICP-OES and organic content by GC and GC-MS.

The autoclave containing the solid catalyst was sealed, evacuated, and flushed with nitrogen. Further aliquots of CH_2Cl_2 (10 cm^3) and styrene (1 cm^3, 0.0087 mol) were injected. The autoclave was pressurized, stirred, heated, cooled, degassed, and analyzed as before. This procedure was repeated until 10 catalytic runs had been completed.

Hydrogenation of Benzo[*b*]thiophene. A 0.1024 g sample of the 0.06% Rh on silica catalyst was weighed out into the autoclave. A solution of benzo[*b*]thiophene (0.0713 g, 5.31×10^{-4}mol) in CH_2Cl_2 (10 cm^3) was injected. The autoclave was pressurized to 20 bar with H_2 and the stirrer started (1200 rpm). The autoclave was heated to 100 °C for 21 h and then cooled and degassed. Then the liquids were removed and analyzed for Rh content and product composition.

The autoclave containing the solid catalyst was resealed and evacuated, then flushed with nitrogen. The procedure was repeated nine further times using 0.0683, 0.0720, 0.0708, 0.0718, 0.0698, 0.0711, 0.0719, 0.0720, and 0.0709 g of benzo[*b*]thiophene, respectively.

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