

Soluble Gold and Palladium Complexes Heterogenized on MCM-41 Are Effective and Versatile Catalysts

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Chiral Schiff base–gold and –palladium complexes were immobilized on ordered mesoporous silica supports (MCM-41), and their catalytic hydrogenation ability is studied and compared with that of their homogeneous counterparts. The high accessibility introduced by the structure of the supports allows the preparation of highly efficient immobilized catalysts with TOFs of up to 6000 h⁻¹ for the hydrogenation of diethyl itaconate. The easily recoverable immobilized catalysts duplicate the activity of their homogeneous analogues, and no

deactivation of the catalysts is observed after repeated recycling. Gold(III) homogeneous or heterogenized complexes also catalyze the homocoupling of arylboronic acids or alkynes to afford symmetrical biaryls, whereas the respective gold(I) and palladium(II) complexes catalyze the corresponding cross-coupling reaction.

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Introduction

The use of gold compounds in homogeneously and heterogeneously catalysed organic reactions has been undervalued for many years due to the preconceived idea that gold is chemically inert. However, recent reports have changed this assessment, and gold compounds have been shown to display high catalytic activity.^[1] Indeed, Au^{III} can act as a Lewis acid catalyst for a large variety of reactions.^[2,3] Solid gold catalysts can be recycled, and when prepared in the form of gold nanoparticles they are highly active and selective for reactions such as CO oxidation,^[4] chemoselective reduction of nitro-substituted aromatic compounds by H₂,^[5] selective oxidation of alcohols^[6] and some C–C bond-forming reactions.^[7] Moreover, the use of Au complexes in homogeneous catalysis has undergone a renaissance, and spectacular achievements have been reported recently.^[8]

Remarkable developments in homogeneous catalysis have taken place over the past two decades,^[9] and there have been many approaches to “heterogenizing” homogeneous catalysts by attaching well-defined molecular species to polymeric supports.^[10] Despite the development of some very effective supported systems,^[11] a general strategy for mimicking solution behaviour is yet to be developed. Reac-

tions on supports are generally slower and less predictable than their solution counterparts and commonly require excesses of reagents, higher temperatures and longer reaction times.^[12]

We have shown recently that Au^{III}–phenolic Schiff-base complexes catalyze the homocoupling of arylboronic acids but are unable to catalyze the Suzuki cross-coupling.^[13] However, Au^I, which has the same d¹⁰ electronic configuration as Pd⁰, is an active catalyst for the Suzuki and Sonogashira cross-coupling reactions.^[14] We have also reported that stable unsymmetrical N-heterocyclic carbene (NHC)–gold(I) complexes (both soluble and heterogenized) are effective catalysts for Suzuki cross-coupling and hydrogenation reactions.^[15] Herein we report the detailed synthesis and characterisation of Au^I, Au^{III} and Pd^{II} complexes with Schiff-base ligands derived from 1,1'-binaphthyl-2,2'-diamine and a comparison of the different behaviours shown by these Au^I, Au^{III} and Pd^{II} complexes with respect to catalyzing the hydrogenation of olefins and Suzuki and Sonogashira C–C coupling reactions. Au^I and Pd^{II} catalyze Suzuki and Sonogashira C–C cross-coupling, while Au^{III} complexes with the same ligands can only catalyze the homocoupling of arylboronic acids or alkynes. Moreover, by properly choosing the support it is possible to achieve an important increase in activity with respect to the homogeneous counterpart due to a cooperative effect of the support, which may stabilize the charged reaction transition state.

Results and Discussion

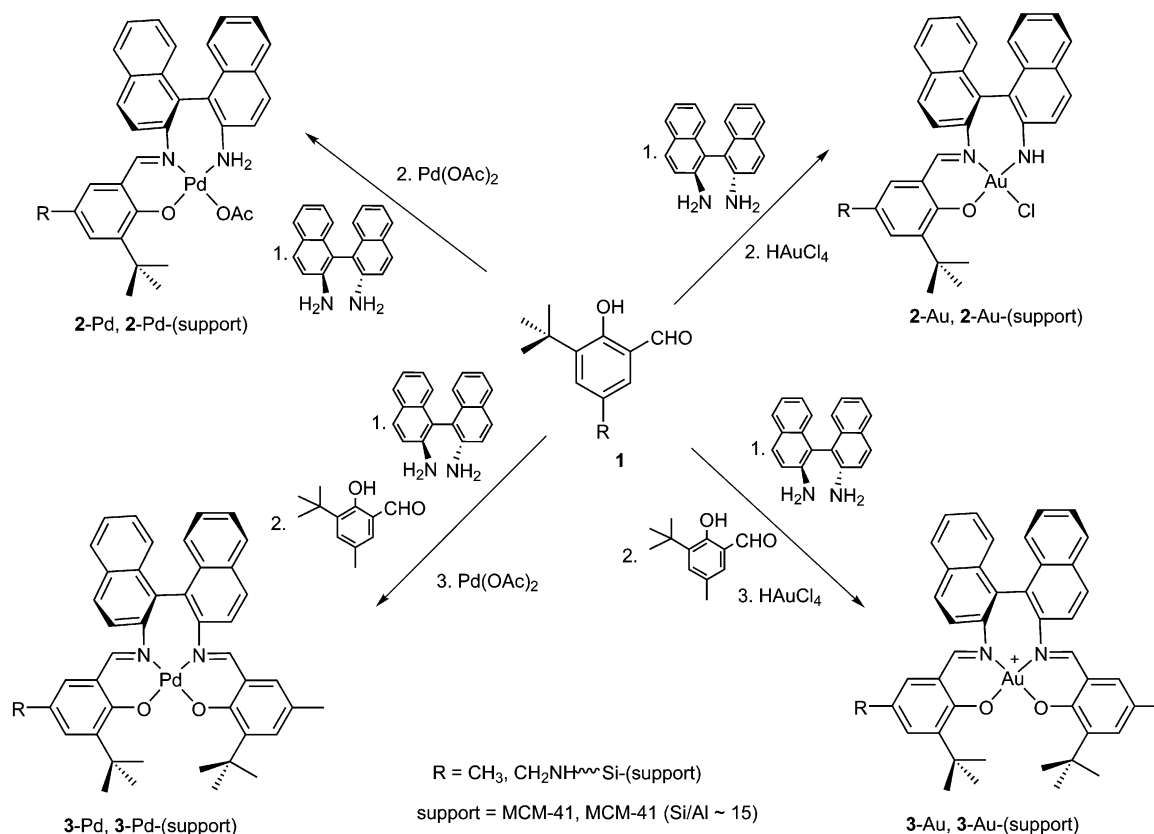
Synthesis of Ligands and Complexes

All soluble ligands and their respective palladium and gold complexes (reference systems) relevant for this work

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Supporting information for this article is available on the WWW under <http://www.eurjic.org> or from the author.



Scheme 1. Synthesis of ligands and complexes.

were obtained in high yields by a method similar to that described previously (Scheme 1).^[16]

Preparation of Immobilized Ligands and Complexes

In the last few years we have developed a modular system for combining functionalised ligands with different supports and linkers in order to have a systematic access to a variety of immobilized chiral catalysts.^[17] We have applied this methodology here (Scheme 1) to immobilize Schiff-base ligands on a mesoporous silica support such as MCM-41 [BET surface area = 1030 m² g⁻¹; micropore surface (t-plot) = 0 m² g⁻¹; external (or mesoporous) surface area = 1030 m² g⁻¹]. MCM-41 is a short-range amorphous material containing a large number of silanol groups available for grafting. However, MCM-41 also presents a long-range ordering with hexagonal symmetry with regular monodirectional channels of 3.5 nm in diameter. An amorphous silica support (BET surface area = 750 m² g⁻¹) was also used as a support but the results were poor.

All solids were functionalised in the same manner according to the procedure shown in Scheme 1.^[18] Supported precursors were obtained by refluxing a mixture of the precursor and the respective support in toluene for 16 h. These anchored aldehydes were treated with an equimolar amount of (*S*)-1,1'-binaphthyl-2,2'-diamine to afford the supported chiral Schiff-base ligands **2/3**-(support) as fine powdered solids. These materials were characterised by microanalysis

and FT IR and ¹³C NMR spectroscopy. The COH carbon signal appears at $\delta \approx 157$ –158 ppm in the ¹³C NMR spectra and the imine carbon atoms signals appear at $\delta \approx 162$ –167 ppm.

Synthesis and Characterisation of Heterogenized Complexes

The heterogenized ligands were treated with palladium(II) acetate or tetrachloroauric acid to give the corresponding anchored Pd and Au complexes, which were used subsequently for catalytic reactions. The catalytic activity of the anchored complexes was also compared to their homogeneous analogs (**2/3**-Pd and **2/3**-Au), which were synthesized from **2/3** as shown in Scheme 1. The catalysts prepared in this way have a metal loading of 0.1–0.30 mmol of metal per gram of support, as determined by atomic absorption analysis. The solids were characterised by FT IR, DFTR and ¹³C NMR spectroscopy.

Infrared and Electronic Spectra

Peaks due to the support dominate the spectra. These include the O–H vibration in the range 3700–3300 cm⁻¹. Some of the characteristic bands of the complexes could, however, be distinguished. Major zeolite framework bands appear around 1140, 1040, 960, 785 and 740 cm⁻¹, and the FT IR spectra are characteristic of the binding of imine nitrogen atoms. The bands around 1600 cm⁻¹ can be assigned to C=C and azomethine C=N vibrations, which are

shifted to lower wavenumbers (relative to the free ligands) due to N-coordination of the imine.^[19] The IR spectra of the palladium complexes also show strong bands at 1290 and around 1500 cm⁻¹ due to the symmetric and asymmetric $\nu(\text{COO})$ vibrations, respectively, in agreement with those expected for monocoordinated acetate ligands.^[20] New bands in the 500–600 cm⁻¹ region are ascribed to $\nu(\text{M}-\text{O})$, and $\nu(\text{Au}-\text{Cl})$ appears at about 350 cm⁻¹.

The chiral Schiff-base-Pd^{II} or -Au^{III} complexes immobilized on supports were characterised by diffuse-reflectance UV spectroscopy. The complexes show bands due to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in the aromatic ring and azomethine-group and charge-transfer transitions.^[21] The bands in the 400–450 nm region correspond to the d–d transitions expected for planar complexes^[22] and MLCT bands. The diffuse-reflectance spectra of the complexes are almost identical before and after heterogenization, thereby indicating that there is no significant distortion in the geometry and electronic environment of these complexes upon heterogenization.

NMR Spectra

In all cases the spectra show the simultaneous occurrence of two sets of signals attributable to the substituted benzalimine entity and to the aliphatic part of the ligand. The ¹³C NMR spectra show signals assigned to the C=N carbon atom, which are shifted to high field, and to the C1 atom at $\delta \approx 162$ ppm, which are shifted downfield, thereby confirming that metallation has occurred.

Catalytic Hydrogenation

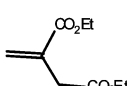
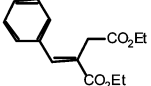
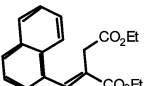
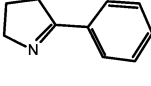
With these structurally well-defined Pd^{II} and Au^{III} complexes available, we explored their ability to catalyse the hydrogenation of alkenes (diethyl itaconate, diethyl 2-benzylidenesuccinate, diethyl 2-naphthylidenesuccinate) and imines (5-phenyl-3,4-dihydro-2H-pyrrole) under standard conditions (EtOH as the solvent, 4 atm of hydrogen pressure,

40 °C). The possibility of recovering the catalysts, the influence of the nature of the support, and the comparison of the activity and stability of supported catalysts with their homogeneous counterparts were all studied. Table 1 summarises the catalytic results obtained with homogeneous Schiff-base complexes immobilized on different supports. The results show that the homogeneous Pd and Au systems lead to quantitative conversion of olefins under these hydrogenation conditions and that the order of reactivity can be explained on the basis of the steric factors.

As Table 1 shows, the heterogenized catalysts generally have higher activities than their homogeneous counterparts (Figure 1) as, depending on the substrate studied, the TOFs are higher than those observed for the homogeneous catalysts. These results indicate that either the support or the metal complexes have a considerable effect on the catalytic process that results from the stability of the active metallic species formed. The fact that the heterogenized catalysts have higher reaction rates is one of the expected advantages of using heterogenized catalysts and is in good agreement with our previous results.^[18] The higher reaction rates observed for heterogenized samples in different systems can be explained by the site isolation effect in these systems, which means that the complex is not subject to self-degradation as it is present in a molecularly dispersed form. After prolonged storage (3–6 months) at room temperature, our heterogenized catalysts show the same activity and selectivity as the freshly prepared catalysts in the standard hydrogenation reaction. We used our less conventional imine hydrogenation catalysts based on Pd- and Au-Schiff bases to carry out the hydrogenation reaction as they are economically attractive compared to those based on Rh, Ru or Ir. The reaction conditions chosen were also milder ($P \leq 10$ bar) than those reported previously.

The results presented in Table 1 show that the Pd and Au complexes described here are very active in the homogeneous phase, with TOFs of about 5000 h⁻¹. We checked that the catalytic activity observed is due to the complex and not to any metal formed by decomposition of the complex

Table 1. Turnover rates (TOF)^[a] for the catalytic hydrogenation of diethyl itaconate, diethyl 2-benzylidenesuccinate, diethyl 2-naphthylidenesuccinate and 5-phenyl-3,4-dihydro-2H-pyrrole with Pd^{II} and Au^{III} catalysts,^[b] with the *ee* values (%) given in parentheses.

Catalyst								
	TOF	<i>ee</i> %	TOF	<i>ee</i> %	TOF	<i>ee</i> %	TOF	<i>ee</i> %
2-Pd	3368	6 (S)	2316	12 (S)	30	15 (S)	47	< 5
2-Pd-(MCM-41)	4340	4 (S)	2560	2 (S)	70	16 (S)	79	< 5
	5148 ^[c]	4 (S)						
2-Au	4920	< 5 (S)	2040	15 (S)	55	18 (S)	83	< 10
2-Au-(MCM-41)	5148	3 (S)	2460	13 (S)	88	18 (S)	162	< 10
	5880 ^[c]	5 (S)						
3-Pd	3204	5 (R)	1152	14 (R)	61	12 (R)	200	< 5
3-Pd-(MCM-41)	3408	3 (R)	1960	14 (R)	76	12 (R)	287	< 5
	(4272) ^[c]	10 (R)						
3-Au	3396	< 5 (R)	1410	10 (R)	119	16 (R)	235	< 10
3-Au-(MCM-41)	5916	< 5 (R)	2880	13 (R)	160	15 (R)	344	< 10
	632 ^[c]	9 (R)						

[a] TOF: h⁻¹. [b] Conditions: 4 atm., 40 °C, S/C ratio 1000:1. [c] MCM-41 (Si/Al $\approx$ 15) as support.

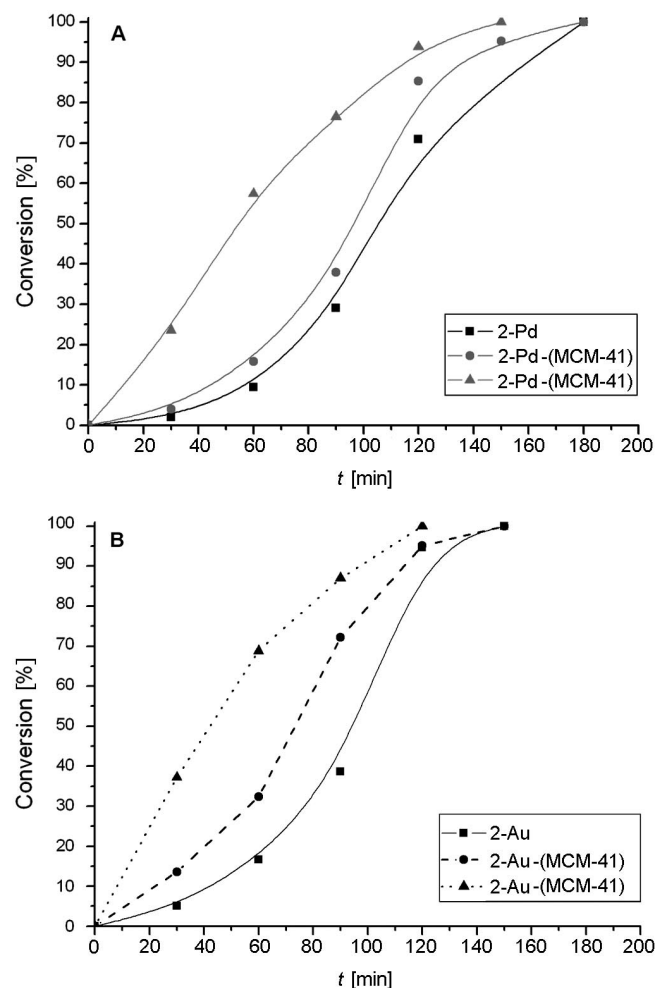


Figure 1. Comparison of the catalytic activities of homogeneous and heterogenized catalysts in the hydrogenation of 5-phenyl-3,4-dihydro-2H-pyrrole.

in the reaction media by applying the methodology described in the literature.^[23] The presence of bulk metal was eliminated as follows: the reaction mixtures were passed through a micropore filter, the reactor was washed with ethanol, and the washings were filtered. The filter did not show traces of bulk metal (microscope, 100 $\times$ magnification). Another problem that can affect the results may arise from the unperceived presence of colloidal metal in "homogeneous" catalysts. Such colloidal particles can be catalytically active and may be responsible for all of the observed catalytic activity even though they may not subsequently precipitate. It is not sufficient, therefore, to verify merely that the solutions are clear, nor to show that any bulk metal that does precipitate is catalytically inactive.

It appears from the experiments described above that Au- and Pd-Schiff-base complexes are stable under these reaction conditions and are very active hydrogenation catalysts. The activity of these catalysts increases when they are supported on mesoporous MCM-41. We carried out the heterogeneous asymmetric hydrogenation of olefins until completion, filtered and washed the heterogenized catalyst, then added fresh substrate and solvent without further ad-

dition of catalyst several times and found that both yield and activity were retained. A portion of the supported catalyst was analysed after each experiment to determine the concentration of metal still present on the support. The filtrate was used in a new reaction and was not found to catalyze the hydrogenation reaction.

We have shown in a previous paper^[18] that the rate of hydrogenation can be increased by introducing some acidity on the support due to stabilisation of the transition state by the H⁺ in the reaction medium. In light of these findings we prepared an MCM-41 containing tetrahedrally coordinated framework Al. An increase in the reaction rate with respect to catalysts on non-acidic supports was observed when hydrogenation was performed with Pd- and Au-Schiff-base complexes grafted onto this acidic MCM-41 (Si/Al $\approx$ 15; Table 1).

We were unable to achieve high enantioselectivity with these catalysts. Indeed, despite their very high activity, the Pd and Au catalysts gave enantioselectivities of only 10–15%. We believe that the low enantioselectivity of the complexes for hydrogenation of prochiral substrates could be due to the planarity of the metal complex. The intermediate species also has a square-planar structure, which means that the approximation of the substrate to only one face of the catalytic centre is not sufficiently favoured in this case.

We studied the mechanism of the reaction in detail by a combination of kinetic experiments and theoretical calculations^[24] and propose a reaction pathway based on heterolytic hydrogen cleavage on the basis of these experimental results. The mechanism of the reaction involves the heterolytic cleavage of H₂, which is the controlling step of the reaction, as demonstrated by the presence of an induction period in the kinetic curve, as the first step. The correct choice of solvent plays a critical role in lowering the activation barrier of this step. After the induction period, which corresponds to the formation of the active catalytic species, the new controlling step of the reaction is the insertion of the olefin. Supporting the Au^{III} complexes on a polar support increases the catalytic activity rather than decreasing it. This increase is even larger when the surface of the carrier contains Brønsted acid sites.

Catalytic C–C Coupling Reactions

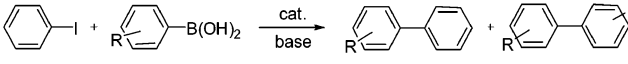
Carbon–carbon coupling reactions are ubiquitous in organic synthesis, with Heck,^[25] Suzuki^[26] and Sonogashira couplings^[27] occupying a special place among such reactions due to their mild reaction conditions. The coupling products are mostly used as intermediates for polymers, natural products and bioactive compounds. The most commonly used catalytic systems for C–C coupling reactions include [PdCl₂(PPh₃)₂], PdCl₂/PPh₃ and [Pd(PPh₃)₄], together with CuI as a co-catalyst (Sonogashira reaction), and large amounts of amines as the solvents or co-solvents.^[28] Most of the ligands used are air- and moisture-sensitive, require multistep syntheses and are difficult to separate from the final product, all of which makes supported cata-

lysts an attractive option. We therefore decided to investigate the use of our Pd^{II}, Au^I and Au^{III} complexes, supported or not on silica-based mesoporous solids, for the C–C coupling reactions.

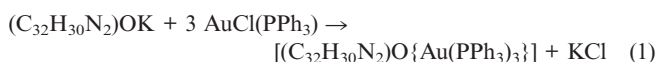
Suzuki Coupling

Suzuki coupling has become increasingly popular due to its compatibility with a variety of functional groups, the stability of the organoboron precursors and the ease of workup of the reaction mixture. Furthermore, a wide variety of arylboronic acids are now available commercially. Herein we present a very easy and widely applicable approach using Pd^{II} and Au^I complexes, supported or not on silica-based mesoporous solids, as catalysts for the Suzuki reaction (Table 2). The Au^I complex was synthesised according to Equation (1). Thus, a solution of [AuCl(PPh₃)] (1 mmol) in thf was added to a solution of the phenolate ligand **2** (1 mmol) in thf (20 mL) at 40 °C and the resultant mixture stirred for 2 h. It was then cooled to room temperature, filtered and concentrated under vacuum. The residue was extracted with dichloromethane and precipitated with pentane, and the precipitate was washed several times, filtered and dried to afford a yellow-brown, air-stable solid in high yields.

Table 2. Pd^{II}- and Au^I-catalysed cross-coupling under Suzuki reaction conditions.^[a]

						
Aryl	2/3-Pd ^{II} Conv. ^[b]	S ^[c]	2/3-Pd ^{II} /(MCM-41) Conv. ^[b]	S ^[c]	2-Au ^I Conv. ^[b]	S ^[c]
Ph	80/87	–	97/100	–	100	–
4-MeOC ₆ H ₄	50/67	100	28/100	100	20	86
3-BrC ₆ H ₄	30/60	100	22/95	100	89	95
4-MeC ₆ H ₄	68	100	–	–	61	100
4-OHCC ₆ H ₄	39	100	–	–	42	100

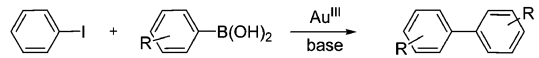
[a] Arylboronic acid (15 mmol), aryl halide (10 mmol), catalyst (30 mol-%), and K₃PO₄ (20 mmol) in xylene at 130 °C. [b] Reaction time: 3 h. [c] Cross-coupling/conversion.



The standard reaction conditions were applied to a series of catalysts, and the conversions are tabulated in Tables 2 and 3. We chose K₃PO₄ as a mild base because longer reaction times were necessary with K₂CO₃ to obtain reasonable conversions. The general utility of the reaction conditions with a variety of arylboronic acid substrates (aryl = Ph, 4-MeOC₆H₄, 3-BrC₆H₄, 4-MeC₆H₄, 4-OHCC₆H₄) and aryl halides (BrPh, IPh) was studied. The optimal reaction conditions were applied to a series of catalysts, and conversions of more than 80% were obtained after 24 h. Complete conversion was obtained with longer reaction times. Au^I complexes are ineffective with phenyl bromide as they form the homocoupling compound as the principal product. The effect of electron-donating and -withdrawing substituents in

the boronic acid on the reactivity can be seen in Table 2. In general, moderate yields and good selectivity for the cross-coupling product are found with Au^I complexes.

Table 3. Yields for the Au^{III}-catalysed homocoupling of arylboronic acids under Suzuki reaction conditions.^[a]

		
R'	2/3-Au ^{III}	2/3-Au ^{III} -(MCM-41)
Ph	95/97	97/99
4-MeOC ₆ H ₄	90/96	94/97
3-BrC ₆ H ₄	93/95	92/95

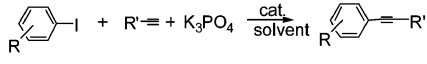
[a] Arylboronic acid (1.5 equiv.), catalyst (15–20 mol-%) and K₃PO₄ (2.0 equiv.) in xylene at 130 °C. Yields determined by GC analysis after 24 h and by isolating samples from the reaction mixture.

Complexes **2**-Pd^{II} were also tested under the same reaction conditions for comparison purposes (Table 2). The results show that the activity and selectivity of **2**-Au^I and **2**-Pd^{II} complexes are similar. Nevertheless, it is interesting to note that Au^I, which has the same d¹⁰ electronic structure as Pd⁰, is able to catalyze the cross-coupling reaction with high selectivity, and that simply changing the charge on the gold atom (**2**-Au^{III}) gives a complex that can selectively catalyze the homocoupling reaction (Table 3).^[13]

Sonogashira Coupling Reaction

As gold(I) has been successfully used to perform the same role as Pd during carbon–carbon bond formation under Suzuki–Miyaura conditions,^[14a] has the same d¹⁰ electronic structure as Cu^I, and can easily and properly interact with an acetylenic group,^[29] it appeared to us that gold could catalyze a copper-free Sonogashira cross-coupling reaction. We therefore studied the homogeneous complexes as catalysts for the Sonogashira cross-coupling of PhI with a series of alkynes containing electron-donating and -withdrawing substituents. The standard reaction conditions were applied with the catalysts [Pd(PPh₃)₄] (Pd⁰), **2**-Pd (Pd^{II}) and [AuCl(PPh₃)] and **2**-Au (both Au^I); the conversions are presented in Table 4. When Au^{III} complexes were tested as catalysts for several of these reactions, the product observed contained 10% of the alkyne homocoupling product along with a very small amount of the iodobenzene

Table 4. Pd^{II}- and Au^I-catalysed cross-coupling under Sonogashira conditions.^[a]

		
Catalyst	R' = Ph	R' = CH ₂ CH(CO ₂ Me) ₂
[Pd(PPh ₃) ₄]	13	25
2 -Pd ^{II}	17	15
[AuCl(PPh ₃)]	54	10
2 -Au ^I	50	5

[a] Alkyne (15 mmol), aryl halide (10 mmol), catalyst (20 mol-%) and K₃PO₄ (20 mmol) in xylene at 130 °C. Yields (%) calculated after 24 h.

homocoupling product. Pd^{II} and $[\text{Pd}(\text{PPh}_3)_4]$ complexes were also prepared and tested under the same reaction conditions for comparison purposes (Table 4). The results show that the activity of these Pd complexes is similar to that of gold and that their selectivity for the Sonogashira reaction is also high.

Heck Reaction

We studied the performance of Au^{I} , Au^{III} and Pd^{II} complexes in Heck reactions using a biphasic mixture of toluene and ethylene glycol as solvent in the presence of potassium acetate.^[30] Catalysis in two-phase liquid/liquid systems is generally referred to as biphasic catalysis as the catalyst is present in one phase while the reactants and products are present in the other phase. In our case the term “biphasic” refers to the mixture of two immiscible solvents, with the heterogenized catalyst being a third phase.

The reactivity and recyclability of these systems for the Heck reaction of iodobenzene with *n*-butyl acrylate under phosphane-free conditions was studied (Table 5). The complexes are not sensitive to oxygen or moisture, and no change in their activity was observed when the reaction was carried out in an open system. This catalytic system is stable and recyclable, and the reaction products, catalyst and base can easily be separated. In this biphasic vinylation system, the toluene phase contains the reactants and products while the metal complex and potassium acetate are present in the ethylene glycol phase. The reaction should therefore occur in the ethylene glycol phase and at the ethylene glycol/toluene interface, where the base is partly soluble.

Table 5. Heck reaction of iodobenzene with *n*-butyl acrylate using homogeneous and supported palladium catalysts.^[a]

$\text{Ph-I} + \begin{array}{c} \text{R}^1 \\ \\ \text{C} = \text{C} \\ \\ \text{R}^2 \end{array} + \text{Base} \xrightarrow[\text{solvent}]{\text{cat. (5 mol-\%)}} \text{Ph}-\begin{array}{c} \text{R}^1 \\ \\ \text{C} = \text{C} \\ \\ \text{R}^2 \end{array}$	
Catalyst	Conv. [%] ^[b]
2-Pd	7
2-Pd-(MCM-41) (1st run)	10
2-Pd-(MCM-41) (2nd run)	53
2-Pd-(MCM-41) (3rd run)	43
3-Pd	69
3-Pd-(MCM-41) (1st run)	15
3-Pd-(MCM-41) (2nd run)	60
3-Pd-(MCM-41) (3rd run)	75

[a] Olefin (10 mmol), aryl halide (10 mmol), catalyst (20 mol-%) and KOAc (11 mmol) in toluene/ethylene glycol at 140 °C. [b] Yields (%) after 24 h.

Table 5 shows the catalytic performance of various supported complexes for the Heck reaction. The reaction was successful at low metal catalyst loadings (2–5 mol-%), although the reactions did not proceed at concentrations below 2 mol-%. Analogous Au^{III} complexes and gold colloids do not catalyze this reaction under the same reaction conditions. No palladium black was observed after more than 72 h when using the palladium complexes as catalysts.

Recycling of Heterogenized Catalysts

The major advantage of using heterogenized metal complexes as catalysts is the ease with which they can be recovered as stable species from the reaction mixture (by simple filtration) and then reused. We carried out the heterogeneous asymmetric hydrogenation of olefins until completion, filtered and washed the heterogenized catalyst, then added fresh substrate and solvent without further addition of catalyst several times and found that both yield and activity are retained. A portion of supported catalyst was analyzed after each experiment to determine the concentration of metal still present on the support. The filtrate was used in a new reaction and was found not to catalyze the hydrogenation. The catalysts were re-used three times (to test their recyclability) and the results show that reproducibility is high. Hot filtration experiments and ICP (inductively coupled plasma) measurements were carried out independently to rule out the possibility of leaching.

The recycling experiments for Heck reactions were performed by separating the ethylene glycol phase and reusing this together with fresh toluene and base. Since the stability of supported complexes towards dissolution during the reaction is a common problem for most anchored catalysts,^[31] and considering the leaching observed with palladium supported on polymer beads, quantitative analysis by atomic absorption spectroscopy (AAS) was employed to determine the amount of metal in the final reaction solution. We observed that the catalyst could be recycled at least three times without significant loss of activity (Table 5).

In order to check the stability of the metal complexes supported on the solid matrix, we characterised the solid before and after the reaction. As can be seen from the IR, ^{13}C NMR and UV/Vis spectra, the nature of supported species is very similar and the most important signals for the Schiff-base ligands appear in the same position after the reaction.

Conclusions

Palladium and gold catalysts supported on mesoporous silica have been successfully prepared by sequential grafting of organic functional groups. The catalysts are active in hydrogenation and C–C coupling reactions (Suzuki, Sonogashira and Heck) and, more importantly, are stable under the reaction conditions employed and can be recycled without loss of activity. Au^{III} – and Pd^{II} –Schiff-base complexes are very active hydrogenation catalysts, and their activity increases when they are supported on MCM-41. Gold(III) homogeneous or heterogenized complexes catalyze the homocoupling of arylboronic acids or alkynes to afford symmetrical biaryls, whereas the respective gold(I) and palladium(II) complexes catalyze the corresponding cross-coupling reaction. The fact that no inert gas and no additional ligands or co-catalyst are necessary, their easy separation, and their easy availability make the supported catalysts an interesting alternative to homogeneous catalysts, and we have shown here that it is possible to obtain a selec-

tive catalytic system for a specific reaction by choosing the appropriate combination of metal, ligand and support.

Experimental Section

General Remarks: All preparations of metal complexes were carried out under nitrogen using conventional Schlenk-tube techniques. Solvents were carefully degassed before use. The silylating agent $\text{OCN}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$ was obtained from ABCR. C, H, N analyses were carried out by the analytical department of the Instituto de Química Orgánica (CSIC) with a Lecco apparatus. Metal contents were analysed by atomic absorption spectroscopy using a Perkin–Elmer AAnalyst 300 atomic absorption apparatus and plasma ICP Perkin–Elmer 40 instrument. IR spectra were recorded with a Bruker IFS 66v/S spectrophotometer (range 4000–200 cm^{-1}) for KBr pellets. ^1H and ^{13}C NMR spectra were recorded with Varian XR300 and Bruker 200 spectrometers. Chemical shifts are quoted relative to tetramethylsilane as internal standard. High-resolution ^{13}C MAS or CP/MAS NMR spectra of powdered samples, which in some cases also included a Toss sequence to eliminate the spinning side-bands, were recorded at 100.63 MHz (6 μs 90° pulse width, 2 ms contact time and 5–10 s recycle delay) with a Bruker MSL 400 spectrometer equipped with an FT unit. The spinning frequency at the magic angle (54°44′) was 4 kHz.^[32] Optical rotation values were measured at the sodium-D line (589 nm) with a Perkin–Elmer 241 MC polarimeter. GC analysis was performed with a Hewlett–Packard 5890 instrument. The enantiomeric excess was measured by HPLC using a chiralcel OD chiral column. The inorganic supports for anchoring were purely siliceous MCM-41^[33] and Al-containing MCM-41 (Si/Al $\approx$ 15).

Synthesis of Ligands: The soluble ligand **2** was synthesised in high yield by a similar method to that described previously.^[16] Ligand **3** was obtained by reported methods.^[34]

(R)-2-[(2′-Amino-1,1′-binaphthyl-2-ylimino)methyl]-6-tert-butyl-4-methylphenol (2): 1,1-Binaphthyl-2,2′-diamine (568 mg, 2 mmol) was added to a solution of 3-tert-butyl-5-methylsalicylaldehyde (**1**; 384 mg, 2 mmol) in acetonitrile (20 mL), and the mixture was stirred under reflux for 10 h. The solvent was then removed under vacuum and the residue purified by flash chromatography (hexane) to give an orange solid. Yield: 690 mg (75%). M.p. 52–55 °C. $[\alpha]_{\text{D}}^{25} = -134$ ($c = 0.6$, CHCl_3). $\text{C}_{32}\text{H}_{30}\text{N}_2\text{O}$ (458); calcd. C 83.8, H 6.6, N 6.1; found C 83.0, H 6.4, N 5.9. IR (KBr): $\tilde{\nu} = 3468$ (OH); 3381 (NH); 1618, 1578 ($\text{C}=\text{C} + \text{C}=\text{N}$) cm^{-1} . UV/Vis: $\lambda = 360$, 325, 295, 232 nm. ^1H NMR (CDCl_3): $\delta = 8.59$ (s, $\text{CH}=\text{N}$), 8.03–6.85 (m, H_{arom}), 3.70–3.56 (br, NH_2), 2.22 (s, CH_3), 1.27 [s, $\text{C}(\text{CH}_3)_3$] ppm. ^{13}C NMR (CDCl_3): $\delta = 167.43$ ($\text{CH}=\text{N}$); 158.36 (COH); 137.17, 134.59, 133.95, 133.31, 132.67, 131.17, 130.92, 130.04, 129.74, 129.48, 129.31, 128.33, 128.19, 128.00, 127.17, 126.76, 126.44, 125.93, 123.92, 122.05, 118.59, 118.30, 118.16, 118.11, 118.02 (C_{arom}); 34.59 [$\text{C}(\text{CH}_3)_3$]; 29.08 [$\text{C}(\text{CH}_3)_3$]; 20.57 (CH_3) ppm. MS (EI): m/z (%) = 458 (100) [M], 443 (82) [M – 15], 267 (53) [M – 191].

Synthesis of Heterogenized Ligands: The heterogenized ligands **2**-(MCM-41) were synthesised in high yields according to a similar method to that described previously.^[18] Thus, a stirred slurry containing 1 mmol of the corresponding anchored hydroxy aldehyde was prepared in acetonitrile (10 mL) under argon at room temperature. After 10 min, 125 mg (1.1 mmol) of the amine was added and the mixture stirred for 16 h. It was then cooled and the deep yellow solid filtered off and washed thoroughly with ethanol and diethyl ether. The resultant solid was dried under vacuum to afford the

corresponding anchored ligands. The heterogenized ligands **3**-(MCM-41) were synthesised as follows. A stirred slurry containing 1 mmol of the corresponding anchored hydroxy aldehyde was prepared in acetonitrile (15 mL) under argon at room temperature. After 10 min, 125 mg (1.2 mmol) of the amine was added and the mixture stirred at reflux for 1 h. 3-tert-Butyl-5-methylsalicylaldehyde (1 mmol) was then added and the mixture stirred for 3 h. The mixture was cooled, and the deep yellow solid was filtered off and washed thoroughly with ethanol and diethyl ether.

2-(MCM-41): Found C 13.9, H 2.4, N 1.8 (0.32 mmol g^{-1}). IR (KBr): $\tilde{\nu} = 1646$, 1630, 1557 ($\text{C}=\text{N}$, $\text{C}=\text{O}$, $\text{C}=\text{C}$) cm^{-1} . UV/Vis: $\lambda = 347$, 265, 224 nm. ^{13}C NMR (solid): $\delta = 159.43$ ($\text{CH}=\text{N}$); 154.96 (NHCONH); 152.62 (COH); 137.25, 128.37, 119.58, 110.27 (C_{arom}); 42.48 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$); 33.68 [$\text{C}(\text{CH}_3)_3$]; 27.57 [$\text{C}(\text{CH}_3)_3$]; 15.78 ($\text{CH}_2\text{CH}_2\text{Si}$); 8.64 (CH_2Si) ppm.

2-(MCM-41) (Si/Al $\approx$ 15): Found C 20.3, H 2.8, N 3.1 (0.55 mmol g^{-1}). IR (KBr): $\tilde{\nu} = 1647$, 1630 ($\text{C}=\text{N}$, $\text{C}=\text{O}$, $\text{C}=\text{C}$) cm^{-1} . UV/Vis: $\lambda = 346$, 264, 222 nm.

3-(MCM-41): Found C 15.6, H 2.5, N 2.3 (0.41 mmol g^{-1}). IR (KBr): $\tilde{\nu} = 1642$ –1599 ($\text{C}=\text{N}$, $\text{C}=\text{O}$, $\text{C}=\text{C}$) cm^{-1} . UV/Vis: $\lambda = 349$, 282, 235 nm. ^{13}C NMR (solid): $\delta = 160.30$ (NHCONH, $\text{CH}=\text{N}$), 128.71–120.26 (C_{arom}), 43.58 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 34.36 [$\text{C}(\text{CH}_3)_3$], 28.73 [$\text{C}(\text{CH}_3)_3$], 23.78 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$, CH_3), 9.85 (CH_2Si) ppm.

3-(MCM-41) (Si/Al $\approx$ 15): Found C 20.8, H 3.1, N 3.2 (0.56 mmol g^{-1}). IR (KBr): $\tilde{\nu} = 1639$ ($\text{C}=\text{N}$, $\text{C}=\text{O}$, $\text{C}=\text{C}$) cm^{-1} . UV/Vis: $\lambda = 348$, 264, 222 nm.

Synthesis of Metal Complexes: The homogeneous chiral complexes were synthesised and used as catalysts to compare the catalytic activities and to evaluate the relationship between the structural features of the ligands and the activity of the complexes. Soluble complexes were obtained as follows. An ethanolic solution of Pd(OAc)₂ or HAuCl₄·3H₂O (0.5 mmol/15 mL) was added to a solution of the ligand (50 mg, 1 mmol) in EtOH (15 mL) at room temperature. The resulting mixture was stirred under reflux for 4 h, then cooled to room temperature and concentrated under vacuum. The residue was washed several times with diethyl ether, dried and filtered to afford the respective complexes in almost quantitative yields.

2-Pd: Brick-red solid. Yield: 61 mg (90%). M.p. > 230 °C. $[\alpha]_{\text{D}}^{25} = -92$ ($c = 0.02$, MeOH). $\text{C}_{34}\text{H}_{32}\text{N}_2\text{O}_3\text{Pd}$ (623.04); calcd. C 65.5, H 5.2, N 4.5, Pd 17.1; found C 65.2, H 5.6, N 4.3, Pd 16.9. IR (KBr): $\tilde{\nu} = 1620$, 1584 (CO); 1522 ($\text{C}=\text{N}$); 552 (Pd–O) cm^{-1} . UV/Vis: $\lambda = 467$, 326, 299, 229, 214 nm. ^1H NMR (CDCl_3): $\delta = 8.04$ –7.91 (m, 1 H, $\text{CH}=\text{N}$), 7.60–7.50 (H_{arom}), 7.47–7.17 (H_{arom}), 7.00–6.74 (H_{arom}), 2.32 (s, 3 H, OCH_3), 2.13 (s, 3 H, CH_3), 1.46 [s, 9 H, $\text{C}(\text{CH}_3)_3$] ppm. ^{13}C NMR (CDCl_3): $\delta = 196.97$ (OCOCH_3); 164.62 (COPd); 162.68 ($\text{CH}=\text{N}$); 146.90, 141.40, 135.35, 134.33, 133.23, 132.81, 131.41, 130.82, 130.22, 128.35, 127.03, 126.03, 125.94, 125.81, 124.58, 123.43, 123.24 (C_{arom}); 35.77 [$\text{C}(\text{CH}_3)_3$]; 29.75 [$\text{C}(\text{CH}_3)_3$]; 20.51 (CH_3); 20.25 (OCH_3) ppm. MS: $m/z = 564$ [M – OAc; ^{106}Pd].

2-Au: Dark brown. Yield: 68 mg (91%). M.p. > 230 °C. $[\alpha]_{\text{D}}^{25} = -92$ ($c = 0.05$, MeOH). $\text{C}_{32}\text{H}_{28}\text{AuClN}_2\text{O}$ (689.01); calcd. C 55.8, H 4.1, Au 28.6, N 4.1; found C 55.6, H 4.0, Au 28.3, N 3.8. IR (KBr): $\tilde{\nu} = 1615$, 1555 ($\text{C}=\text{N}$) cm^{-1} . UV/Vis: $\lambda = 482$, 345, 328, 230 nm. ^1H NMR (CD_3OD): $\delta = 7.89$ –6.37 (H_{arom} , $\text{CH}=\text{N}$), 1.96 (s, 3 H, CH_3), 1.20 [s, 9 H, $\text{C}(\text{CH}_3)_3$] ppm. ^{13}C NMR (CD_3OD): $\delta = 167.34$ (COAu); 156.00 ($\text{CH}=\text{N}$); 135.46, 134.96, 134.53, 133.52, 132.87, 132.35, 131.54, 131.32, 130.63 (C_{arom}); 35.22 [$\text{C}(\text{CH}_3)_3$]; 30.04 [$\text{C}(\text{CH}_3)_3$]; 20.00 (CH_3) ppm. MS: $m/z = 654$ [M – Cl].

3-Pd: Brick-red solid. Yield: 176 mg (92%). M.p. > 230 °C. $[\alpha]_D^{25} = +289$ ($c = 0.36$, CH_2Cl_2). $\text{C}_{44}\text{H}_{42}\text{N}_2\text{O}_5\text{Pd}$ (737.23): calcd. C 71.7, H 5.7, N 3.8, Pd 14.4; found C 71.5, H 5.6, N 3.7, Pd 14.1. IR (KBr): $\tilde{\nu} = 1607, 1504$ (C=N, C=C) cm^{-1} . UV/Vis: $\lambda = 438, 318, 298, 231$ nm. ^1H NMR (CDCl_3): $\delta = 8.20\text{--}7.78$ (H_{arom}), 7.60–6.82 (H_{arom} , CH=N), 6.74–6.63 (H_{arom}), 2.09 (s, 3 H, CH_3), 1.35 [s, 9 H, $\text{C}(\text{CH}_3)_3$] ppm. ^{13}C NMR (CD_3Cl): $\delta = 169.34$ (COPd); 158.00 (CH=N); 135.63, 134.89, 134.65, 133.73, 133.50, 132.25, 131.97, 131.65, 130.58, 129.28 (C_{arom}); 35.42 [$\text{C}(\text{CH}_3)_3$]; 30.09 [$\text{C}(\text{CH}_3)_3$]; 20.10 (CH_3) ppm. MS: $m/z = 737$ [M; ^{106}Pd].

3-Au: Black solid. Yield: 197 mg (88%). M.p. > 230 °C. $[\alpha]_D^{25} = -35$ ($c = 0.06$, MeOH). $\text{C}_{44}\text{H}_{42}\text{AuClN}_2\text{O}_2$ (863): calcd. C 61.2, H 4.9, Au 22.8, N 3.2; found C 61.0, H 4.6, Au 22.6, N 3.4. IR (KBr): $\tilde{\nu} = 1638$ (C=N), 555 (Au–O) cm^{-1} . UV/Vis: $\lambda = 493, 343, 326, 227$ nm. ^1H NMR (CD_3OD): $\delta = 8.01\text{--}7.15$ (H_{arom}), 2.00 (s, 3 H, CH_3), 1.25 [s, 9 H, $\text{C}(\text{CH}_3)_3$] ppm. ^{13}C NMR (CD_3OD): $\delta = 162.41$ (COAu); 159.98 (CH=N); 123.19, 119.35, 112.44 (C_{arom}); 35.40 [$\text{C}(\text{CH}_3)_3$]; 29.72 [$\text{C}(\text{CH}_3)_3$]; 20.34 (CH_3) ppm. MS: $m/z = 820$ [M – Cl].

Synthesis of Metal Complexes: The heterogenized complexes were synthesised as follows. An ethanolic solution of $\text{Pd}(\text{OAc})_2$ or $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (0.5 mmol/15 mL) was added to a suspension of heterogenized ligand in toluene (20 mL) at room temperature, and the resulting mixture was stirred under reflux for 12 h, then cooled to room temperature and filtered. The solid was washed several times with ethanol, dried and filtered to afford the respective heterogenized complexes in almost quantitative yields.

2-Pd-(MCM-41): Found C 11.0, H 2.1, N 1.7, Pd 10.6 (1.0 mmol g^{-1}). IR (KBr): $\tilde{\nu} = 1634$ (CO), 1576 (C=N), 586 (Pd–O) cm^{-1} . UV/Vis: $\lambda = 432, 346, 263, 217$ nm. ^{13}C NMR (solid): $\delta = 197.40$ (OCOCH₃), 160.14 (NHCONH, COPd), 155.58 (CH=N), 130.70–118.41 (C_{arom}), 44.30 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 33.90 [$\text{C}(\text{CH}_3)_3$], 27.80 [$\text{C}(\text{CH}_3)_3$], 24.00 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$, CH_3), 20.66 (OCOCH₃), 10.20 (CH_2Si) ppm.

2-Pd-(MCM-41) (Si/Al $\approx$ 15): Found C 18.0, H 2.5, N 2.7, Pd 1.7 (0.49 mmol g^{-1}). IR (KBr): $\tilde{\nu} = 1649, 1568$ (C=N, CO, C=C) cm^{-1} . UV/Vis: $\lambda = 346, 264, 222$ nm.

2-Au-(MCM-41): Found C 7.5, H 1.7, Au 0.6, N 0.7 (0.21 mmol g^{-1}). IR (KBr): $\tilde{\nu} = 1635, 1580$ (C=N, C=C); 556 (Au–O) cm^{-1} . UV/Vis: $\lambda = 526, 389, 302$ nm. ^{13}C NMR (solid): $\delta = 167.68$ (NHCONH, COAu), 153.67 (CH=N), 138.60–113.00 (C_{arom}), 44.00 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 30.86 [$\text{C}(\text{CH}_3)_3$], 23.14 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}$), 22.10 (CH_3), 8.78 (CH_2Si) ppm.

2-Au-(MCM-41) (Si/Al $\approx$ 15): Found C 11.8, H 1.9, Au 2.5, N 1.9 (0.48 mmol g^{-1}). IR (KBr): $\tilde{\nu} = 1644, 1557$ (C=N, C=C) cm^{-1} . UV/Vis: $\lambda = 507, 349, 264, 221$ nm.

3-Pd-(MCM-41): Found C 12.2, H 2.2, N 1.7, Pd 1.2 (0.32 mmol g^{-1}). IR (KBr): $\tilde{\nu} = 1637, 1574$ (CO, C=N, C=C); 558 (Pd–O) cm^{-1} . UV/Vis: $\lambda = 700, 448, 322, 285$ nm.

3-Pd-(MCM-41) (Si/Al $\approx$ 15): Found C 17.8, H 2.3, N 2.8, Pd 5.9 (0.52 mmol g^{-1}). IR (KBr): $\tilde{\nu} = 1637, 1572$ (C=N, CO, C=C) cm^{-1} . UV/Vis: $\lambda = 445, 349, 270, 224$ nm.

3-Au-(MCM-41): Found C 11.0, H 2.1, Au 0.3, N 1.2 (0.31 mmol g^{-1}). IR (KBr): $\tilde{\nu} = 1646, 1589$ (CO, C=N, C=C); 561 (Au–O) cm^{-1} . UV/Vis: $\lambda = 518, 424, 348, 264, 212$ nm.

3-Au-(MCM-41) (Si/Al $\approx$ 15): Found C 11.3, H 1.9, Au 4.7, N 2.5 (0.26 mmol g^{-1}). IR (KBr): $\tilde{\nu} = 1633, 1540$ (C=N, C=C) cm^{-1} . UV/Vis: $\lambda = 512, 346, 262, 223$ nm.

Catalytic Experiments

Hydrogenation Reactions: The catalytic properties (alkenes: diethyl succinates; imine: 5-phenyl-3,4-dihydro-2H-pyrrole) of the Pd and Au complexes were examined under conventional conditions for batch reactions in a 100 mL reactor (Autoclave Engineers) at 40 °C and 4 atm of H_2 pressure with a metal/substrate molar ratio of 1:1000. Formation of the hydrogenated product was monitored by GC.

Recycling Experiments: At the end of the hydrogenation process, the reaction mixture was filtered, and the zeolite-containing catalyst residue was washed to completely remove any remaining products and/or reactants and used again. A portion of supported catalyst was analysed after each experiment to determine the concentration of metal still present on the support. The filtrate was also used in a new reaction and was found to not catalyze hydrogenation.

C–C Coupling Reactions

Suzuki Reaction: The reaction was carried out in a 25 mL vessel at 130 °C for a reaction time of 20–180 min. In a typical run, a mixture of aryl halide (10 mmol), boronic acid (15 mmol), aqueous potassium phosphate (20 mmol) and catalyst (0.3 mmol) in 3 mL of *o*-xylene was stirred for the desired time. The solution was cooled, and a 1:1 mixture of diethyl ether/water (20 mL) was added. The organic layer was washed, separated, further washed again with another 10 mL portion of diethyl ether, dried with anhydrous MgSO_4 and filtered. The solvent and volatiles were removed completely under vacuum to give the crude product, which was subjected to column chromatographic separation to give pure compounds. The reaction was monitored by GC-MS. At the end of the process, the reaction mixture was filtered and the zeolite-containing catalyst residue washed to completely remove any remaining products and/or reactants and used again. A portion of supported catalyst was analysed after each experiment to determine the concentration of metal still present on the support.

Sonogashira Reaction: The reaction was carried out in a 25 mL vessel at 130 °C for 24 h. In a typical run, a mixture of aryl halide (10 mmol), alkyne (15 mmol), aqueous potassium carbonate or phosphate (20 mmol) and catalyst (0.5 mmol) in 3 mL of *o*-xylene was stirred for the desired time.

Heck Reaction: In a typical experiment, the catalyst (0.03 mmol, 5%) was suspended in a mixture of ethylene glycol and toluene (1:1, 6 mL), then iodobenzene (1 mmol), *n*-butyl acrylate (1 mmol) and potassium acetate (1.14 mmol) were added with stirring. The mixture was refluxed, and the reaction progress was monitored by GC. The recycling experiments were performed by separating the ethylene glycol phase and reusing this together with fresh toluene and base.

Supporting Information (see also the footnote on the first page of this article): Representative experimental procedures and characterization for all new compounds.

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