DOI: 10.1002/adsc.200606163

New Heterogenized Gold(I)-Heterocyclic Carbene Complexes as Reusable Catalysts in Hydrogenation and Cross-Coupling Reactions

A. Corma,[a,*] E. Gutiérrez-Puebla,[b] M. Iglesias,[b,*] A. Monge,[b] S. Pérez-Ferreras,[b,c] and F. Sánchez[c,*]

[a] Instituto de Tecnología Química, UPV-CSIC, Avda. de los Naranjos, s/n, 46022 Valencia, Spain
Fax: (+49)-6221-487-672; e-mail: acorma@itq.upv.es
[b] Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, 28049 Madrid, Spain
Fax: (+34)-91-372-0623; e-mail: marta.iglesias@icmm.csic.es
[c] Instituto de Química Orgánica General, CSIC, C/Juan de la Cierva, 3, 28006 Madrid, Spain
Fax: (+34)-91-564-4872; e-mail: felix-iqo@iqog.csic.es

Received: April 5, 2006; Accepted: July 11, 2006

Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

Abstract: Mononuclear unsymmetrical N-heterocyclic carbene-gold complexes and the corresponding solid catalysts in which a gold-carbene complex has been immobilized on silica gel, ordered mesoporous silica (MCM-41), and delaminated zeolite (ITQ-2) have been prepared. These new catalysts have been tested in the hydrogenation of alkenes and the Suzuki cross-coupling reaction to afford selectively non-symmetrical biaryls. These reactions were studied with the soluble as well as with the heterogenized counterpart catalysts. The high accessibility introduced by the structure of the supports allows the preparation of highly efficient immobilized catalysts with TOFs up to 400 h^{-1}. Moreover, the heterogenized complexes were reused and no deactivation of the catalysts can be observed.

Keywords: cross-coupling; gold; heterogenized; hydrogenation; NHC ligands

Introduction

Recently there has been a resurgence of interest in the chemistry of gold compounds in general and that of gold(I) compounds in particular. A major driving force for this interest has been the utility of soluble gold compounds, and the observation that gold nanoparticles and supported gold nanoparticles can stabilize cationic gold and this is active, for instance, for CO oxidation,[1] C–C bond formation,[2] and selective oxidation of alcohols.[3] Moreover, the use of Au complexes in homogeneous catalysis has undergone a renaissance as of late and spectacular achievements have recently been reported.[4] Among Au(I) compounds, there has been considerable success in the preparation of alkynylgold complexes.[5] These are among the most stable organogold complexes.[5] One interesting aspect of these complexes has been the ability to exhibit rich photophysical and photochemical behaviour.[6]

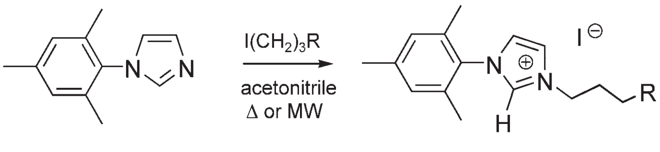
The application of N-heterocyclic carbene (NHC) ligands represents one of the most important developments in the field of metal-mediated catalysis over recent years and valuable contributions have been made to a diversity of reactions.[7] Commonly, NHCs have been described as alternatives to tertiary phosphines in terms of bonding and reactivity,[8] but metal-carbene complexes are often more stable than similar metal-phosphine complexes,[9] and NHCs have been used as alternatives to phosphines as ligands in a broad range of transition metal catalysts owing to their special donor properties.[8] As a result, a large variety of metal-NHC complexes are known, many of which have been successfully used in catalytic applications.[10] Interestingly, most studies focussing on catalysts incorporating NHC ligands have revolved around the platinum metal groups. In numerous instances simple substitution reaction routes involving replacement of phosphines by NHC ligands lead to higher catalytic activity as well as improved thermal stability of the resulting organometallic complex. The common knowledge that NHC ligands should be considered as simple σ donors is being replaced by the idea that NHCs are electronically much more flexible.

Both filled and empty π, π* orbitals on the NHC ring can be deeply involved in the bonding to the metal. They can contribute to stabilize electron-rich metals through a d→π* back-donation scheme, but they are so flexible that they can also stabilize electron-deficient metals through a π→d donation scheme.[11]

Au(I)-carbene complexes have been known since more than a quarter of a century,[12] but chemical reactions have been less studied than those of Au(I)-phosphine complexes. Most publishing works dealing with Au(I)-carbenes concerns oxidative addition reactions.[13] The first example in literature for the use of a gold(I)-carbene complex in homogeneous catalysis was reported for the addition of water to 3-hexyne in the presence of a Lewis acid as co-catalyst.[14] Recently Nolan et al. reported the synthesis and structural characterization of a series of symmetric N-heterocyclic carbene-gold(I) complexes and their application for carbene transfer reactions from ethyl diazoacetate.[15] Herein we report the synthesis, characterization and the catalytic applications of new stable unsymmetrical NHC-gold(I) complexes for the Suzuki cross-coupling and hydrogenation reactions.

Results and Discussion

The symmetrical 1,3-bis-(2,4,6-trimehylphenyl)imidazolium salt **1** was obtained as reported in the literature[16] and the unsymmetrical salts **2** and **3** were synthesized by reacting propyl iodide with 1-(2,4,6-trimethylphenyl)-*1H*-imidazole in acetonitrile (for **2**) or diglyme (for **3**) according to Scheme 1. Alternatively, we have found that microwave activation without solvent affords the imidazolium salts cleanly and quantitatively in 15 seconds at 350 W.[17]



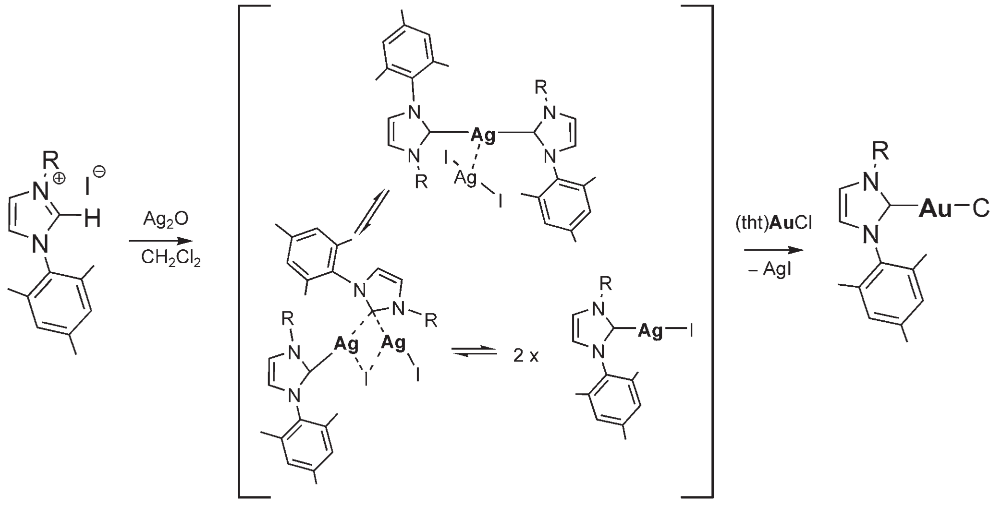
2, 3

2: R = H; **3**: R = Si(OEt)$_3$

Scheme 1. Synthesis of imidazolium salts **2** and **3**.

Wang and Lin[18] reported that simple imidazolium salts react with Ag_2O to yield Ag(I)-bis(carbene) complexes which can then be used as possible transfer agents to synthesize Au(I)-carbene complexes. Therefore the silver(I)-carbene complexes **1–3Ag** were synthesized by stirring imidazolium salts **1–3** in CH_2Cl_2 with Ag_2O for 4 h. Subsequent work-up of the filtered solution afforded the complexes **1–3Ag** ([Ag(carbene)$_2$]$^+$[AgI$_2$]$^-$) in high yield (Scheme 2). The silver(I) complexes (**1–3Ag**) reacted smoothly with the Au(I) precursor [(tht)AuCl] (tht = tetrahydrothiophene) to afford the corresponding carbene-Au(I) chloride **1–3Au** in nearly quantitative yield (80–92%). In a typical reaction the silver complex was stirred with the gold precursor in CH_2Cl_2 solution for 3 h. afterwards the reaction mixture was filtered to remove the precipitated AgI. Complexes **1–3Au(I)** are readily soluble in most common polar organic solvents (dichloromethane, THF), but insoluble in hexane or diethyl ether. The Au-carbene compounds are thermally stable up to >250 °C.

The complexes were characterized by ^{1}H and ^{13}C NMR spectroscopy, elemental analysis and mass spectrometry. The ^{13}C NMR resonances of the carbene atoms in complexes **2–3Au** occur at $\delta = 170.78$ and 171.50, respectively. This signal is shifted down-



1 – 3 **1 – 3Ag** **1 – 3Au**

Scheme 2. Synthesis of gold-carbene complexes.

field compared to the corresponding imidazolium 2-carbon resonance (141.04 for **2**, 140.34 for **3**). For both Au(I)-carbene complexes the most prominent peak in the mass spectra is the $[(NHC)Au]^+$ fragment indicating a molecular structure of the type (NHC)AuX instead of a ionic one of the type $[(NHC)_2Au]^+[AuX_2]^-$ for these compounds. The complexes are colourless with fairly featureless absorption bands deep in the UV. In dichloromethane, the carbene precursor has two absorption bands at 279, 352 nm (**2**) or 299, 366 nm (**3**). The electronic absorption spectra for the Au(I)-carbene complexes show the bands at 302, 368 nm and 315 (**2Au**), 413 nm (**3Au**).

Crystal Structure Studies of Complex 2Au

The structure of **2Au** was confirmed by X-ray diffraction studies (Figure 1). The gold(I) atom is two-coordinate in an essentially linear environment with C–Au–Cl bond angles close to 180° (178.8, 174.6). There are two crystallographically independent molecules in the asymmetric unit, which are bonded to each other by a non-classic hydrogen bond [C(15)-H(15)···Cl(2)] forming dimers. The Au–C(NHC) distances are 1.99(1) Å in both molecules and suggest a single-bond character, in good accordance with their strong σ-donor characteristics, comparable to those reported for other Au(I)(carbene) complexes.[19] The Au–Cl distances lie in the range 2.298–2.323(3) Å. The disposition of the propyl group is directed toward the gold atom. The distance Au···Au (>6.7 Å) indicates that are no aurophilic interactions between the Au atoms.

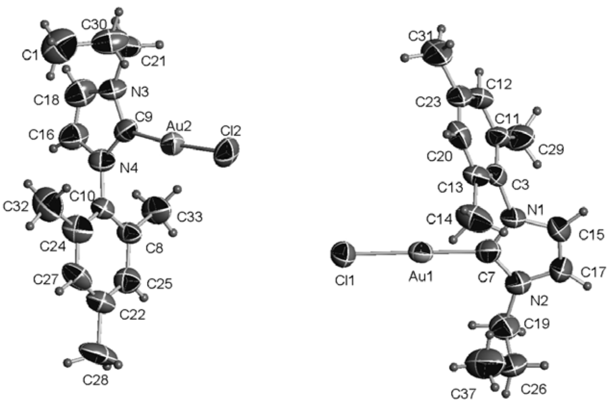
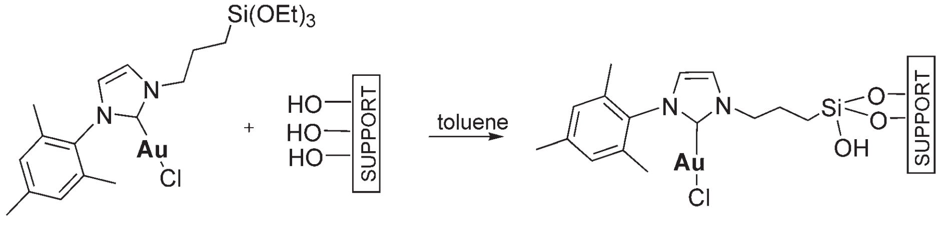


Figure 1. ORTEP representation for **2Au**.

Preparation of Immobilized Complexes

In the last years we have developed a modular system combining functionalized ligands with different supports and linkers in order to have a systematic access to a variety of immobilized chiral catalysts.[20] We have applied this methodology here (Scheme 3) to immobilize unsymmetrical carbene ligands on silica gel (Merck silica, average pore diameter 40 Å), a mesoporous silica support such as MCM-41, [BET surface area ($m^2 \cdot g^{-1}$) = 1030, micropore surface (t-plot $m^2 \cdot g^{-1}$) = 0, external (or mesoporous) surface area ($m^2 \cdot g^{-1}$) = 1030],[21] and delaminated zeolite ITQ-2, [BET surface area ($m^2 \cdot g^{-1}$) = 830, micropore surface (t-plot $m^2 \cdot g^{-1}$) = 130, external (or mesoporous) surface area ($m^2 \cdot g^{-1}$) = 700].[22] Silica and MCM-41 are short-range amorphous materials containing a large number of silanol groups available for grafting. In the case of MCM-41, however, the material presents a long-range ordering with hexagonal symmetry and regular monodirectional channels of 3.5 nm diameter. On the other hand, ITQ-2 delaminated zeolite presents both short- and long-range order, together with a very large, well structured external surface on which the silanol groups act as grafting centers.

The solid was functionalized according to the procedure shown in Scheme 3. Supported complexes, **3Au(support)**, were obtained by refluxing a mixture of the precursor **3Au** and the support, in toluene, for 16 h. These materials were characterized by microanalysis, FT-IR, DFTR and ^{13}C NMR. The catalysts prepared in this way presented metal loadings of 0.20–30 mmol-metal/g support as determined by atomic absorption analysis. The solid was characterized by FT-IR, DFTR and ^{13}C NMR spectroscopy.



3Au

3Au-(Sil, MCM-41, ITQ-2)

Scheme 3. Heterogenization of **3Au** complex on silica, MCM-41 and ITQ-2.

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 bands characteristic of the complexes could, however, be distinguished. Major zeolite framework bands appeared around 1140, 1040, 960, 785 and 740 cm^{-1}. FT-IR spectra are characteristic for the binding of imine nitrogen. The 1600 cm^{-1} frequencies may be assigned to C=C shifted to lower wavenumbers (relative to the free ligands) due to coordination. New bands in the cm^{-1} region at *ca.* 330 cm^{-1} are ascribed to ν(Au–Cl).

The Au-carbene complexes immobilized on supports have been characterized by diffuse reflectance UV spectroscopy. The DFTR spectra for all complexes were obtained in the 200–800 nm range. The complexes show several band maxima in the UV region agreeing with the assignment of the bands as intraligand transitions in the aromatic ring, imidazolium group and charge-transfer transition. The diffuse reflectance spectra of Au(carbene) complexes are almost identical before and after heterogenization process, indicating that the complexes maintain their geometry and their electronic surroundings even after heterogenization without significant distortion.

NMR Spectra

Diamagnetic gold complexes have been characterized by ^{13}C NMR spectroscopy. In all cases, the spectra show the simultaneous occurrence of two sets of signals which are attributable on the one hand to the imidazolium entity and on the other hand to the aliphatic and aromatic part of the ligand. The ^{13}C NMR spectra show the signals assigned to the carbene carbon at $\delta \sim 175$ downfield shifted.

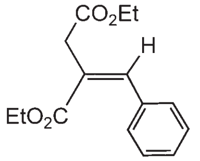
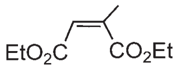
Catalytic Activity

In order to evaluate the catalytic performances of these new soluble and the corresponding heterogenized counterparts gold(I)-carbene complexes we have tested them in the hydrogenation of alkenes and the Suzuki cross-coupling reaction between halobenzene and arylboronic acids.

Catalytic Hydrogenation of Olefins

The Au(I)-carbene complexes enable us to explore the possibilities of these complexes in hydrogenation reactions. Thus, the hydrogenation of diethyl citraconate and diethyl benzylidenesuccinate with (carbene)Au complexes were carried out under the usual conditions (EtOH as the solvent, 4 atm hydrogen pressure, 40 °C). In these hydrogenation reactions we have paid special attention to the influence of the nature of the support, and the comparison of the activity and stability of the supported catalysts with respect to their homogeneous counterparts and the possibilities of recycling the supported catalysts. Table 1 and Figure 1 summarize the catalytic results obtained for homogeneous catalysts compared with those of corresponding carbene complexes immobilized on MCM-41. The results show that the homogeneous systems lead to quantitative conversion of olefins under the hydrogenation conditions. While it is common to characterize the steric demand of PR_3 ligands using the Tolman cone angle, in the case of NHC ligands Jacobsen et al. reported[11] that the use of the $\% V_{Bur}$ molecular descriptor (amount of volume of a sphere centered on the metal, buried by overlap with atoms of the various NHC ligands) is a convenient method. The $\% V_{Bur}$ for PPh_3 is 27 or 22 and **1** presents a similar value (26, 20). The better reactivity found for carbene-gold complexes compared with phosphine-gold chloride could be explained by electronic effects being more important than steric factors in this case.

Table 1. Turnover rates[a] for the catalytic hydrogenation of diethyl citraconate and diethyl benzylidensuccinate with Au-carbene catalysts.[b]

Catalyst				
	Conv.(%) [h]	TOF[a]	Conv.(%) [h]	TOF[a]
$(PPh)_3AuCl$	100 [3][c]	25	50 [6]	6
1Au	97 [3]	50	55 [7]	20
2Au	97 [3]	225	75 [7]	75
3Au-(Sil)	100 [1]	250	90 [6]	100
3Au-(MCM-41)	100 [3]	300	95 [7]	170
3Au-(ITQ-2)	100 [2]	425	90 [6]	300

[a] TOF: mmol subs./mmol cat. h.

[b] Conditions: 4 atm, 40 °C. S/C ratio 500:1.

As Table 1 shows, the heterogenized catalysts had, in general, higher activities than the homogeneous ones (see also Figure 2). These results indicate that either the support or the metal complexes have a considerable effect on the catalytic process, because of the stability of the active metallic species formed. The fact that the heterogenized catalysts have higher reaction rate is one of the expected advantages of using heterogenized catalysts and is in good agreement with our former results.[23] In different systems we have ob-

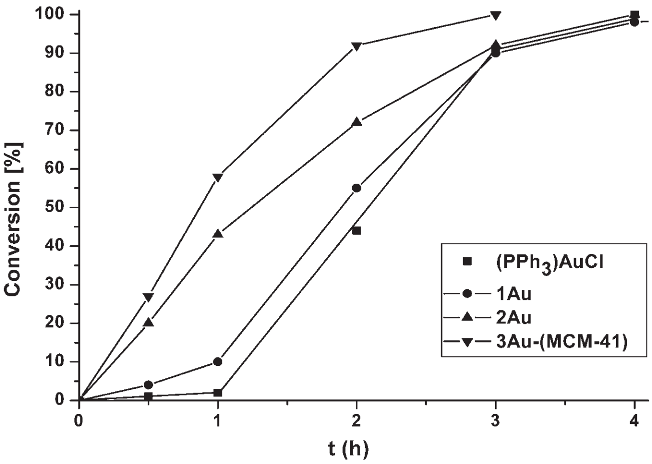


Figure 2. Comparison of the catalytic activities (homogeneous and heterogenized complexes) on the hydrogenation reaction of diethyl citraconate.

served higher reaction rates on heterogenized samples. The explanation could be that in the homogeneous condition the reaction rate is decreased by the poor solubility of these complexes in most organic solvents and by self-degradation. If we eliminate these factors by heterogenizing the complex we can expect a higher reaction rate. The site isolation effect which works on the heterogenized condition may also be an explanation for the higher rate, since the complex is in a molecularly dispersed form and because of this, is not subject to self-degradation. After prolonged storage at room temperature our heterogenized catalysts showed the same features as the freshly prepared catalysts in the standard hydrogenation reaction.

From the above work it appeared to us that mesostructured solids could be suitable supports for immobilizing homogeneous hydrogenation catalysts, since they could avoid the mass transfer limitations of the previously reported support. Moreover, the fact that we could control, up to a certain point, the polarity (acidity) of the catalyst surface, could introduce an additional benefit from the point of view of increasing reactant concentration at the surface, and/or stabilizing reaction transition states. Therefore, we should not see the support only as a tool to immobilize and disperse the metal complexes, but, if properly designed, it can contribute in a collaborative way to the final activity and selectivity observed.[24]

The accumulated evidence concerning the mechanisms of homogeneously catalyzed hydrogenation indicates that three principal modes of hydrogen activation are suitable: oxidative addition, and homolytic or heterolytic hydrogen cleavage. In the case of these Au complexes, heterolytic cleavage is preferred to give a hydride intermediate which involve charge separation without any oxidation of the metal. Heterolytic cleavage of hydrogen by Au complexes have been reinforced from our experiments using more polar and protonic acid media which produces a significant increase of reaction rate, probably favouring charge separation in the step of formation of intermediate.

Recycling of Heterogenized Catalysts

The major advantage of the use of 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 reused. We have carried out the heterogeneous hydrogenation of olefins until completion, filtered and washed the heterogenized catalyst, then added fresh substrate, and solvent without further addition of catalyst, for several consecutive experiments and have found that both yield and activity are retained (Figure 3). After each experiment a portion of the supported catalyst was analyzed to determine the concentration of metal still present in the support. The filtrate has been used in a new reaction and was found not to catalyze hydrogenation.

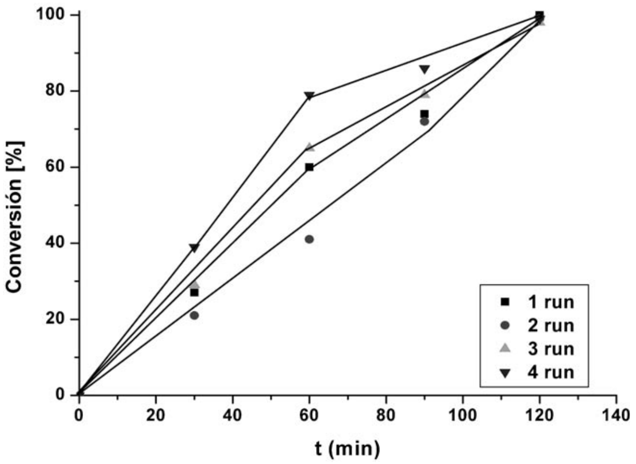


Figure 3. Recycling of **3Au-(MCM-41)** in the hydrogenation of diethyl citraconate

Catalytic Suzuki Coupling

The carbene Au(I) complexes were also studied for the Suzuki cross-coupling of Br-Ph and I-Ph with a series of arylboronic acids. The standard reaction conditions were applied to a series of catalysts and the conversions are tabulated in Table 2. In our experiments, we have chosen K_3PO_4 as mild base because with K_2CO_3 longer reaction times were necessary to obtain reasonable conversions.

Table 2. Influence of ligands on Au(I) reactivity for Suzuki cross-coupling reactions.[a].

$$\text{Ph-I} + \text{Ar-B(OH)}_2 \longrightarrow \text{Ph-Ar} + \text{Ar-Ar}$$

Catalyst	4-BrPh Conv. % [h]	Sel.[b,c] [%]	4-MeOPh Conv. % [h]	Sel.[b,c] [%]
1Au	30 [6]/51 [22]	100	25 [6]/62 [22]	100
2Au	65 [6]/79 [24]	100	53 [6]/72 [24]	100
(PPh$_3$)AuCl	70 [6]/85 [22]	100	55 [6]/62 [22]	100

[a] Ratio catalyst:IPh = 1:30, IPh (1 mmol), arylboronic (1.5 mmol), K_3PO_4 (2 mmol).

[b] Cross-coupling/conversion.

[c] Reaction with K_2CO_3 as base gives 20% cross-coupling with selectivity 100%.

The general utility of the reaction conditions with a variety of arylboronic acid substrates (aryl = Ph, 3- and 4-BrC_6H_4, 4-$MeOC_6H_4$) and aryl halides (BrPh, IPh) was studied. Au(I) complexes are ineffective with phenyl bromide. On the other hand, the gold(I) complex with ligand **1** gives lower activity towards the Suzuki reaction (Table 2). The effect of electron-donating and electron-withdrawing substituents in the boronic acid on reactivity can be seen in Table 2. In general, moderate yields (calculated with respect to PhI) and 100% selectivity towards the cross-coupling product were found with Au(I)-carbene complexes (homogeneous and heterogenized) (only traces of boronic homocoupling were detected).

For comparison purposes **(PPh$_3$)AuCl** has also been prepared and tested under the same reaction conditions (Table 2). The results show that activity and selectivity of **2Au(I)** and **(PPh$_3$)AuCl** complexes are similar, though the **(PPh$_3$)AuCl** is systematically more active. These results are in accordance with previous obtained in our group with Au(I)-Shiff base complexes,[25] the respective Au(III) complexes only give boronic homocoupling.[26]

Conclusions

We were able to successfully employ [(carbene)AuCl] as catalysts for the hydrogenation of diethyl succinates and the Suzuki coupling between PhI and arylboronic acids (Ar = 4-Br, 4-OMe). We have shown that it is possible to boost the activity of a transition metal complex catalyst by using an adequate support. We have seen that by using mesostructured silicates as carriers, with very high surface areas and accessibility to reactants, together with high adsorption capacity, the activities of the grafted Au complexes in the hydrogenation reactions were higher than with the homogeneous counterpart catalysts.

Experimental Section

General Remarks

All preparations of metal complexes were carried out under dinitrogen by conventional Schlenk-tube techniques. Solvents were carefully degassed before use. The (tht)gold(I) chloride was prepared by known methods.[27] 1,3-(2,4,6-Trimethylphenyl)-*1H*-imidazol-3-ium chloride (**1**) and the respective Au((I)-carbene complex (**1Au**) were prepared according with published methods.[16,19] Metal contents were analyzed by atomic absorption using a Perkin–Elmer AAnalyst 300 atomic absorption apparatus and plasma ICP Perkin–Elmer 40. IR spectra were recorded on a Bruker IFS 66v/S spectrophotometer (range 4000–200 cm^{-1}) in KBr pellets. ^{1}H NMR and ^{13}C NMR, spectra were taken on Varian XR300 and Bruker 200 spectrometers. Chemical shifts being referred to tetramethylsilane (internal standard). High resolution ^{13}C MAS or CP/MAS NMR spectra of powdered samples, in some cases also with a Toss sequence in order to eliminate the spinning side bands, were recorded at 100.63 MHz, 6 μs 90° pulse width, 2 ms contact time and 5–10 recycle delay, using a Bruker MSL 400 spectrometer equipped with an FT unit. The spinning frequency at the magic angle (54°44′) was 4 kHz. Gas chromatography analysis were performed in a Hewlett–Packard 5890 II with a flame ionization detector or/and in a Hewlett–Packard G1800 A with a quadrupole mass detector using a cross-linked methylsilicone column.[28] The inorganic supports for anchoring were silica gel [Merck silica, average pore diameter 40 Å], purely siliceous MCM-41,[21] and delaminated zeolites ITQ-2.[22]

Synthesis of Ligands: 1-(2,4,6-Trimehylphenyl)-3-propyl-*1H*-imidazol-3-ium Iodide (2)

Method A: To a solution of 3 g (0.016 mol) of 1-(2,4,6-trimehylphenyl)-*1H*-imidazole in acetonitrile (100 mL) was added dropwise 1.61 mL (1,016 mol) of propyl iodide. The reaction mixture was refluxed for 12 h, the solvent removed under reduced pressure and the resulting solid washed with Et_2O and dried under vacuum; yield: 80–95%

Method B (Microwave heating):[17] In a 15-mL round-bottomed flask 7 mL (0.072 mol) of propyl iodide and 2.0 g (0.011 mol) of 1-mesityl-*1H*-imidazole were added. The flask was closed and three cycles of 350 Watt were done for 5 seconds each. Two phases appeared and the product was precipitated by addition of AcOEt; yield: 95%; mp 128 °C. Anal. calcd. for $C_{15}H_{21}N_2I$ (356): C 50.6, H 5.9, N 7.9; found: C 50.2, H 5.8, N: 7.9%; ^{1}H NMR ($CDCl_3$): $\delta = 9.80$ (dd, 1H, H_3, $J_{31} = 1.7$ Hz, $J_{32} = 1.6$ Hz), 8.00 (dd, 1H, H_1, $J_{12} = 1.7$ Hz, $J_{13} = 1.7$ Hz), 7.21 (dd, 1H, H_2, $J_{21} = 1.7$ Hz, $J_{23} = 1.6$ Hz), 6.89 (s, 2H_{arom}), 4.54 (t, 2H, -CH_2-*N*-; $J = 7.08$ Hz), 2.23 (s, 3H, CH_3 *para*), 1.96 (s, 6H, CH_3 *ortho*), 1.94 (m, 2H, -CH_2-), 0.89 (t, 3H, CH_3-CH_2); ^{13}C NMR ($CDCl_3$): $\delta = 141.04$ ($C_{carbene}$), 136.68 (C_{arom}-CH_3 *para*), 133.92 (C_{arom}-CH_3 *o*rtho), 129.61 (CH_{arom}), 130.29 (C_{arom}-N), 123.57 (CH_{imin}-N_{aliph}), 123.30 (CH_{imin}-N_{arom}), 51.45 (-CH_2-N), 23.72 (-CH_2-), 20.85

(CH$_3$ *para*), 17.54 (CH$_3$ *ortho*), 10.24 (-CH$_2$-*C*H$_3$); IR (KBr): ν = 3116, 3080 (C=H), 3000–2800 (C-H), 1606 (C=H); 1559, 1544 (C=N), 1483, 1452 (C=N), 1203, 1160, 1067 cm^{-1} (C-N); UV-vis: λ = 279, 352 nm; MS (IE): *m/z* (%) = 255 (M$^+$–I, 7); 229 (75); 227 (M$^+$–I–2H; 100), 200 (42), 185 (53), 158 (30).

1-(2,4,6-Trimehylphenyl)-3-(3-(triethoxysilyl)propyl)-1*H*-imidazol-3-ium Iodide (3)

To a solution of 1 g (5.38 mmol) of 1-(2,4,6-trimehylphenyl)-1*H*-imidazole in diglyme (15 mL) was added 1.87 g (6.58 mmol) of iodopropyltriethoxysilane. The reaction mixture was stirred at 160 °C for 24 h. After that the solvent was removed under reduced pressure and the crude material was purified using a mixture of AcOEt:MeOH (4:1); yield: 90%. Anal. calcd. for $C_{21}H_{35}IN_2O_3Si$ (518.5): C 48.6, H 6.8, N 5.4; found: C 48.2, H 6.5, N 5.6%; ^{1}H NMR (CDCl$_3$): δ = 9.51 (s, 1H, H$_3$), 7.72 (t, 1H, H$_1$, J_{12} = 1.8 Hz), 7.16 (dd, 1H, H$_2$, J_{21} = 1.8 Hz, 6.76 (s, 2H$_{\text{arom}}$), 4.63 (t, 2H, -CH$_2$-*N*-, *J* = 6.8 Hz), 3.76 (c, 6H, CH$_3$-C*H*$_2$-O-, *J* = 7.0 Hz), 2.27 (s, 3H, CH$_3$ *para*), 2.02 (m, 8H, 2CH$_3$ *ortho*, -CH$_2$-), 1.14 (t, 9H, C*H*$_3$-CH$_2$-O-, *J* = 7.0 Hz), 0.58 (t, 2H, -CH$_2$-Si-, *J* = 7.9 Hz); ^{13}C NMR (CDCl$_3$): *δ* = 140.34 (C$_{\text{carbene}}$), 135.96 (*C*$_{\text{arom}}$-CH$_3$ *para*), 133.35 (*C*$_{\text{arom}}$-CH$_3$ *ortho*), 128.95 (CH$_{\text{arom}}$), 128.24 (*C*$_{\text{arom}}$-N), 123.00 (CH$_{\text{imin}}$-N$_{\text{aliph}}$), 122.86 (CH$_{\text{imin}}$-N$_{\text{arom}}$), 57.73 (CH$_3$*C*H$_2$O-), 51.25 (-CH$_2$-N), 23.64 (-CH$_2$-), 20.23 (CH$_3$ *para*), 17.46 (*C*H$_3$CH$_2$O-), 16.87 (CH$_3$ *ortho*), 6.00 (-CH$_2$-Si-); IR (KBr): ν = 1608 (C=C), 1563, 1546 (C=N), 1075 (Si-O), 782 cm^{-1} (Si-C); UV-vis: λ = 299, 366 nm; MS (IE): *m/z* (%) = 391 (M$^+$–I; 100), 227 (4), 213 (11), 200 (21), 163 (28), 119 (13).

(Carbene)gold(I) Chloride Complexes (1–3Au)

General Method:[19] A mixture of 100 mg of the imidazolium salt (**1**–**3**) and 0.58 mmol of silver(I) oxide was taken up in 20 mL of dichloromethane and stirred for 4 h. The solution was filtered and tetrahydrothiophene-gold(I) chloride (1 mmol) was added to the filtrate. After 3 h, active carbon was added and the reaction mixture was filtered through celite. The solvent was removed under vacuum until *ca.* 5 mL remained, and hexane was added, causing a precipitate to form.

[1-(2,4,6-Trimehylphenyl)-3-propyl-2,3-dihydro-1*H*-imidazol-2-yl)gold(I) chloride (2 Au)

Yield = 92%. $C_{15}H_{21}AuClN_2$ (461.8): calcd. C: 39.0; H: 4.6; N: 6.1; found C: 39.2; H: 4.6; N: 6.3%. ^{1}H NMR (CDCl$_3$) δ-(ppm): 7.18 (s, 1H, H$_1$); 6.93 (s, 2H$_{\text{arom}}$); 6.85 (s, 1H, H$_2$); 4.28 (t, 2H, -CH$_2$-*N*-; *J* = 7.1 Hz); 2.31 (s, 3H, CH$_{3p-}$); 1.95 (s, 8H, CH$_{3o-}$, -CH$_2$-); 0.98 (t, 3H, -CH$_2$-C*H*$_3$; *J* = 7.1 Hz). ^{13}C NMR (CDCl$_3$) δ(ppm): 170.78 (C-Au); 138.60 (*C*$_{\text{arom}}$-N); 133.88 (*C*$_{\text{arom}}$-CH$_{3o}$); 128.86 (CH$_{\text{arom}}$-CH$_{3p}$); 128.37 (CH$_{\text{arom}}$); 121.29 (CH$_{\text{imin}}$-N$_{\text{alif}}$); 119.43 (CH$_{\text{imin}}$-N$_{\text{arom}}$); 51.95 (-CH$_2$-N); 23.34 (CH$_{3o}$); 20.09 (CH$_{3p-}$); 16.74 (-CH$_2$); 16.56 (-CH$_2$-*C*H$_3$). IR (KBr, cm^{-1}): ν = 326 (Au-Cl). UV-vis (λ, nm): 270, 302, 368. EM (ES) (*m/z*;%): 425 (M$^+$–Cl); 418 (M$^+$–propyl). Suitable crystals for crystallographic study were grown by slow evaporation of a solution of dichloromethane-diethyl ether.

[1-(2,4,6-Trimehylphenyl)-3-(3-triethoxysilyl)propyl-2,3-dihydro-1*H*-imidazol-2-yl]gold(I) Chloride (3Au)

Yield: 80%; anal. calcd. for $C_{21}H_{35}AuClN_2O_3Si$ (624): C 40.4, H 5.6, N 4.5; found: C 40.6, H 5.5, N 4.3%; ^{1}H NMR (CDCl$_3$): δ = 6.92–6.85 (m, 2H$_{\text{im}}$, 2H$_{\text{arom}}$), 4.30 (br, -CH$_2$-*N*-), 3.68 (q, 6H, -OCH$_2$CH$_3$, *J* = 6.84 Hz), 2.29 (s, 3H, CH$_3$ *para*), 1.99 (s, 2H, -CH$_2$-), 1.98 (s, 6H, 2CH$_3$ *ortho*), 1.20 (t, 9H, -OCH$_2$CH$_3$, *J* = 6.84 Hz), 0.86–0.82 (m, 2H, -CH$_2$-Si-); ^{13}C NMR (CDCl$_3$): δ = 171.50 (C-Au), 139.34 (C$_{\text{arom}}$-N), 134.67 (C$_{\text{arom}}$-CH$_3$ *ortho*), 129.83 (C$_{\text{arom}}$-CH$_3$ *para*), 129.23 (CH$_{\text{arom}}$), 122.49 (CH$_{\text{imin}}$-N$_{\text{aliph}}$), 121.99 (CH$_{\text{imin}}$-N$_{\text{arom}}$), 58.22 (-OCH$_2$*C*H$_3$), 53.41 (-CH$_2$-*N*-), 29.59 (-CH$_2$-), 21.01 (CH$_3$ *ortho*), 18.32 (-OCH$_2$*C*H$_3$), 17.81 (CH$_3$ *para*), 17.26 (CH$_2$-Si-); IR (KBr), ν = 1608 (C=C), 1076 (Si-O), 782 (Si-C), 334 cm^{-1} (Au-Cl); UV-vis: λ = 154, 315, 413 nm; MS (EI): *m/z* (%) = 405 (M$^+$–3EtO–Cl), 219, 187, 119.

Heterogenization of 3Au [3 Au-(Support)]

Heterogenized complexes were synthesized following the general method: to a suspension of the support in toluene (20 mL), at room temperature, was added a dichloromethane solution of (1-(2,4,6-trimehylphenyl)-3-(3-triethoxysilyl)propyl-2,3-dihydro-*1H*-imidazol-2-yl)gold(I) chloride complex (**3Au**) (20% in weight). The resulting mixture was stirred under reflux for 12 h, cooled to room temperature and filtered. The solid was washed several times with dichloromethane, dried and filtered to afford the respective heterogenized complexes, **complex-(support)**, in almost quantitative yields. The loadings are based on the percent of metal obtained from the elemental analysis data.

3Au-(MCM-41): anal. found: C 9.1, H 1.8, N, 0.6, Au 0.6% (0.21 mmol/g); ^{13}C NMR (solid): *δ* = 174.3 (C-Au), 138.5 (C$_{\text{arom}}$-N), 135.1 (C$_{\text{arom}}$-CH$_3$ *ortho*), 129.2 (*C*$_{\text{arom}}$), 123.0 (CH$_{\text{imin}}$-N$_{\text{aliph}}$), 121.7 (CH$_{\text{imin}}$-N$_{\text{arom}}$), 65.8 (*C*H$_2$O), 54.8 (*C*H$_2$N), 31.0 (-CH$_2$-), 25.5 (CH$_3$ *ortho*), 15.5 (-OCH$_2$*C*H$_3$), 13.6 (CH$_3$ *para*), 8.2 (*C*H$_2$Si); IR (KBr): ν = 1631 (C=N), 1089 (Si-O), 325 (Au-Cl); UV-vis: λ = 216, 249, 262, 324, 414, 514 nm.

3Au-(Sil): anal. found: C 5.3, H 1.5, N 0.6, Au: 0.7% (0.20 mmol/g); ^{13}C NMR (solid): *δ* = 174.1 (C-Au). 138.0 (C$_{\text{arom}}$-N). 135.4 (C$_{\text{arom}}$-CH$_3$ *ortho*), 129.0 (*C*$_{\text{arom}}$), 123.2 (CH$_{\text{imin}}$-N$_{\text{aliph}}$), 121.8 (CH$_{\text{imin}}$-N$_{\text{arom}}$), 65.6 (*C*H$_2$O), 54.5 (*C*H$_2$N), 31.2 (-CH$_2$-), 25.3 (CH$_3$ *ortho*), 15.2 (-OCH$_2$*C*H$_3$), 13.8 (CH$_3$ *para*), 8.3 (*C*H$_2$Si); IR (KBr): ν = 1631 (C=N), 1095 (Si-O), 313 cm^{-1} (Au-Cl); UV-vis: λ = 215, 247, 263, 323, 416, 516 nm.

3Au-(ITQ-2): anal. found: C: 9.9, H 2.1, N 0.6, Au: 0.6% (0.21 mmol/g); ^{13}C NMR (solid): *δ* = 174.5 (C-Au), 138.1 (C$_{\text{arom}}$-N), 135.0 (C$_{\text{arom}}$-CH$_3$ *ortho*), 129.0 (*C*$_{\text{arom}}$), 123.3 (CH$_{\text{imin}}$-N$_{\text{aliph}}$), 122.0 (CH$_{\text{imin}}$-N$_{\text{arom}}$), 65.5 (*C*H$_2$O), 55.0 (*C*H$_2$N), 31.2 (-CH$_2$-), 24.9 (CH$_3$ *ortho*), 15.2 (-OCH$_2$*C*H$_3$), 13.3 (CH$_3$ *para*), 8.0 (*C*H$_2$Si); IR (KBr): ν = 1630 (C=N), 1094 (Si-O), 325 cm^{-1} (Au-Cl); UV-vis: λ = 213, 248, 262, 321, 422, 518 nm.

Catalytic Activity: Hydrogenation of Alkenes

The catalytic properties, in hydrogenation reactions, of the complexes were examined under conventional conditions for batch reactions in a reactor (Autoclave Engineers) of 100 mL capacity at 40 °C temperature, 4 atm dihydrogen pressure and 1/500, metal/substrate molar ratio. The evolution of the reaction of hydrogenated product was monitored by gas-chromatography.

Suzuki C−C Coupling

Typical procedure: The reaction was carried out in a 25 mL vessel, at 130 °C during a period of time ranging from 20 to 180 min. In a typical run, a mixture of aryl halide (10 mmol), boronic acid (15 mmol), aqueous potassium carbonate or phosphate (20 mmol) and catalyst (0.3 mmol) in 3 mL of *o*-xylene was stirred for the desired time. The solution was allowed to cool, and a 1:1 mixture of ether/water (20 mL) was added. The organic layer was washed, separated, further washed with another 10 mL portion of diethyl ether, dried with anhydrous $MgSO_4$ and filtered. The solvent and volatiles were completely removed under vacuum to give the crude product which subjected to column chromatographic separation which resulted in pure compounds. The reaction was followed by GC-MS.

Recovery and Recycling of Catalysts

At the end of the catalytic process, the reaction mixture was filtered; the residue of zeolite-containing catalyst was washed with CH_2Cl_2 to completely remove the remains of products and/or reactants and used again.

X-Ray Crystallographic Study

A yellow crystal of **2Au** showing well defined faces was mounted on a Bruker-Siemens Smart CCD diffractometer equipped with a normal focus, 2.4 kW sealed tube X-ray source (molybdenum radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 30 mA. Room temperature data were collected over a hemisphere of the reciprocal space by a combination of three frame sets. The cell parameters were determined and refined by least-squares fit of all reflections collected. Each frame exposure time was of 20 s covering 0.3° in ω. The crystal to detector distance was 4.979 cm. Coverage of the unique set was over 93.3 % complete to at least 29.26° in θ. The first 100 frames were recollected at the end of the data collection showing no crystal decay. In spite of the crystal showing well-defined faces it gave a poor spectrum, especially at high angles, but good enough to solve the structure, which was solved by Multan and Fourier methods using SHELXTL.[29] Full matrix least-square refinement was carried out using SHELXTL minimizing $w(F^2_0\text{-}F^2_c)^2$. Weighted *R* factors (*Rw*) and all goodness of fit S are based on F^2, conventional *R* factors (*R*) are based on *F*. The Supporting Information contains the crystallographic data for **2Au** (crystal data, distances and angles).

CCDC-602942 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44–1223/336–033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgements

Financial support by the Dirección General de Investigación Científica y Técnica of Spain (Project MAT2003–07945-C02–01 and 02) and Ministerio de Educación y Ciencia (S.P.F.) is gratefully acknowledged.

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