SUPPLEMENTARY MATERIAL

General Remarks

All preparations of metal complexes were carried out under dinitrogen by conventional Schlenk-tube techniques. Solvents were carefully degassed before use. The silylating agent $OCN(CH_2)Si(OEt_3)$ was obtained from ABCR. C, H and N analysis were carried out by the analytical department of the Instituto de Química Orgánica (C.S.I.C.) with a LECCO apparatus. Metal contents were analysed 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. Diffuse reflectance UV-Vis spectra were recorded on Shimadzu UV-2401 PC spectrophotometer. ^{1}H-NMR, ^{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 90º 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 (54º44') was 4 KHz.[1] Gas chromatography analysis was performed using a Hewlett-Packard 5890. 2-(support), 2Au-(support) has described previously[2]

Synthesis of MCM- 41 materials

The inorganic supports for anchoring were purely siliceous MCM-41, Al-containing MCM-41 (Si/Al ≈ 15) and Sn-containing MCM-41 (~10-12% Sn). MCM-41 materials were synthesized following previous works[3].

Synthesis of pure silica MCM-41 **(MCM-41 pure silica)**

Pure silica MCM-41 was synthesized from a gel having the following molar composition: SiO_2:0.15CTABr:0.26TMAOH:24.3H_2O where CTABr is cetyltrimethylammonium bromide and TMAOH is tetramethylammonium hydroxide.

In a typical procedure, 1.82 g. of CTABr was dissolved in 12.2 g of water and 3.151 g. of TMAOH (25% TMAOH in water, Aldrich) at 40ºC. Then 2 g of SiO_2 (Aerosil, Degussa 200) was added.

The resulting gel was introduced into Teflon-lined stainless steel autoclave, and was heated at 100ºC for 48h under static conditions. The solid was recovered by filtration and then was extensively washed with distilled water and dried in an oven at 100ºC, overnight.

Synthesis of Al- containing MCM-41 **(MCM-41, Si/Al=15)**

Al-MCM-41 sample was synthesized from a gel having the following molar composition: SiO_2:0.15CTABr:0.26TMAOH:0.037Al_2O_3:24.3H_2O.

In a typical procedure, 1.82 g. of CTABr (Aldrich, 99%) was dissolved in 12.2 g of water and 3.151 g. of TMAOH (25% TMAOH in water, Aldrich) at 40ºC. Then, 0.232 g of $Al(OH)_3$ was added, and the resulting mixture was stirred for 5 minutes. Then 2 g of SiO_2 (Aerosil, Degussa 200) was added.

The resulting gel was introduced into Teflon-lined stainless steel autoclave, and was heated at 135ºC for 24h under static conditions. The solid was recovered by filtration and then was extensively washed with distilled water and dried in an oven at 100ºC, overnight.

Synthesis of Sn- containing MCM-41 (**MCM-41-Sn$_s$**)

61.5 g. of an aqueous solution of hexadecyltrimethylamonium hydroxide (C_{16}TAOH, 0.43M) was mixed with 15.7 g. of tetramethylamonium hydroxide solution (TMAOH 25% in water, Aldrich) and an aqueous solution of $SnCl_4.5H_2O$ (2.38 g. of $SnCl_4.5H_2O$ in 7.01 g. of H_2O). After homogenisation, 10 g. of silica (Aerosil, Degussa) was added under continuous stirring.

The final gel composition was the following:

$$1SiO_2: 0.16C_{16}TAOH : 0.26TMAOH : 0.04SnCl_4 : 24.3\ H_2O$$

The homogeneous gel was sealed in Teflon-lined stainless steel autoclaves and heated at 135ºC under static conditions during 24 hours. The resulting solid product was recovered by filtration, washed and dried at 100ºC for 24 hours.

The occluded organic in as-prepared MCM-41 materials (Si-MCM-41, Al-MCM-41 and Sn-MCM-41) was removed by heating the solids at 540ºC for 1 hour in a flow of N_2, followed by 6 hours in air. The final solids present a typical XRD pattern of MCM-41 structure.

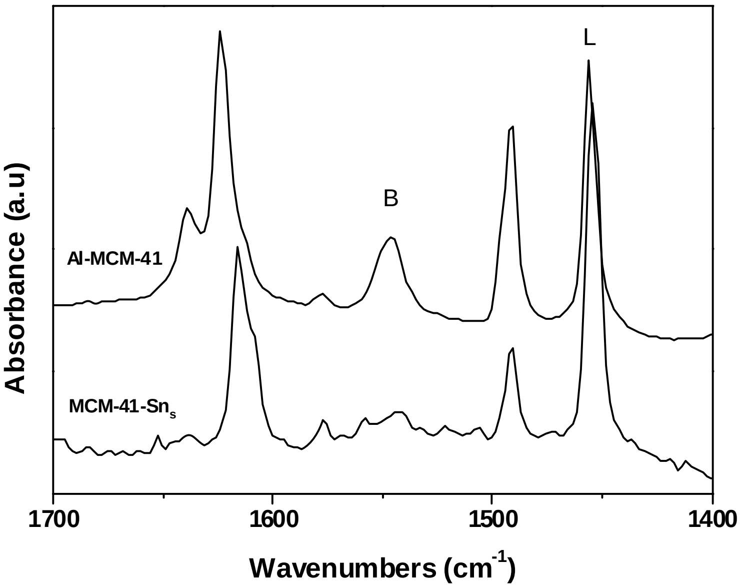
Chemical composition and textural properties of inorganic supports are sumamarized in the following table

	Si/M	BET Area (m^2/g)	V (cc/g)
MCM-41	-	1064	0.66
Al-MCM-41	12	846	0.62
MCM-41-Sn_s	25	925	0.69

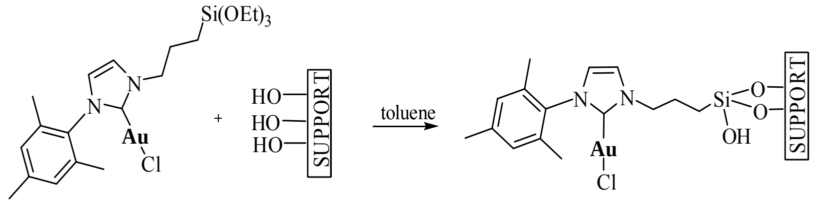
Synthesis of Sn grafted MCM-41 **(MCM-41-Sn_G)**

Sn grafted MCM-41 material was prepared according to previous work[4] using $nBuSnCl_3$ as source of tin. The grafting procedure was carried out as follows. 1 g of extracted pure silica MCM-41(the template was extracted following a two step extraction procedure[5]) was out gassed at 100ºC for 2 hours. Then, 10 g of a solution containing the appropriate amount of $nBuSnCl_3$ (Sn/Si=0.04) in anhydrous toluene was added under N_2 on the dehydrated MCM-41. After 1 hour in aging conditions at room temperature, 2g of a solution containing triethylamine ($nBuSnCl_3/(C_2H_5)_3N=1$, molar relation) in toluene was added under inert atmosphere at room temperature. Next, after 1 hour in aging conditions the solid was filtrated and washed with toluene. Finally, the organic material was removed by calcination at 580ºC for 3 h. in air stream.

Figure S1. IR spectra of MCM-41 materials after adsorption at 673 K in vacuum and desorption at 423 K of pyridine. (B: Brönsted acid sites, L: Lewis acid sites)



Synthesis of Supported carbene gold(I)-complexes[6,]



1Au **1Au-(support)**

Scheme S1. Heterogenization of 1Au complex on MCM-41.

Heterogenization of 1Au (1Au-(MCM-41) support). Scheme S1

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 (**1Au**) (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.

1Au-(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 ($\mathrm{C_{arom}}$-N); 135.1 ($\mathrm{C_{arom}}$-$\mathrm{CH_3}$ *o*-); 129.2 ($\mathrm{C_{arom}}$); 123.0 ($\mathrm{CH_{imin}}$-$\mathrm{N_{alif}}$); 121.7 ($\mathrm{CH_{imin}}$-$\mathrm{N_{arom}}$); 65.8 ($\mathit{C}\mathrm{H_2O}$); 54.8 ($\mathit{C}\mathrm{H_2N}$); 31.0 (-$\mathrm{CH_2}$-); 25.5 ($\mathrm{CH_{3\mathit{o}}}$); 15.5 (-$\mathrm{OCH_2\mathit{C}H_3}$); 13.6 ($\mathrm{CH_{3\mathit{p}\text{-}}}$); 8.2 ($\mathit{C}\mathrm{H_2Si}$). IR (KBr, cm^{-1}): ν = 1631 (C=N), 1089 (Si-O); 325 (Au-Cl). UV-vis (λ, nm): 210, 250, 260, 325, 410, 510.

1Au-(MCM-41-Sn$_{\mathrm{G}}$): 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 ($\mathrm{C_{arom}}$-N); 135.4 ($\mathrm{C_{arom}}$-$\mathrm{CH_3}$ *o*-); 129.0 ($\mathit{C}_{\mathrm{arom}}$); 123.2 ($\mathrm{CH_{imin}}$-$\mathrm{N_{alif}}$); 121.8 ($\mathrm{CH_{imin}}$-$\mathrm{N_{arom}}$); 65.6 ($\mathit{C}\mathrm{H_2O}$); 54.5 ($\mathit{C}\mathrm{H_2N}$); 31.2 (-$\mathrm{CH_2}$-); 25.3 ($\mathrm{CH_{3\mathit{o}}}$); 15.2 (-$\mathrm{OCH_2\mathit{C}H_3}$); 13.8 ($\mathrm{CH_{3\mathit{p}\text{-}}}$); 8.3 ($\mathit{C}\mathrm{H_2Si}$). IR (KBr, cm^{-1}): ν = 1631 (C=N), 1095 (Si-O); 313 (Au-Cl). UV-vis (λ, nm): 215, 247, 263, 323, 416, 516.

IR spectrum (Figure S2) shows the vibration of O-H groups in the range 3700-3300 cm^{-1}. IR associated to zeolite framework appears at 1140, 1040, 960, 785 and 740 cm^{-1}. The 1600 cm^{-1} frequencies can be assigned to C=C shifted to lower wavenumbers relative to the free ligands. New bands in the cm^{-1} region at ca. 330 cm^{-1} are ascribed to ν(Au-Cl).

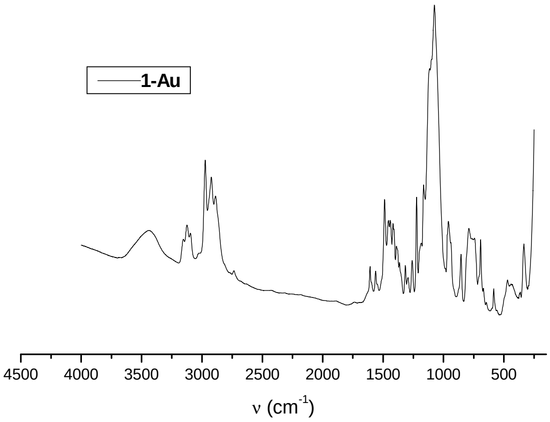


Figure S2. IR spectrum for 1Au

The complexes show several band maxima in the UV region (Fig S3, S4) with the assignment of the bands as intraligand transitions in the aromatic ring, imidazolium group and charge-transfer transition. The spectrum shows the signals attributable to the imidazolium entity and to the aliphatic and aromatic part of the ligand. The ^{13}C NMR spectra give the signals assigned to the carbene carbon at δ ~ 175 downfield shifted.

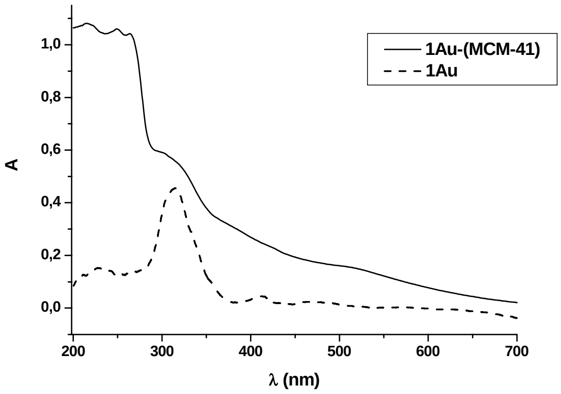


Figure S3. DFTR spectra for 1Au complexes

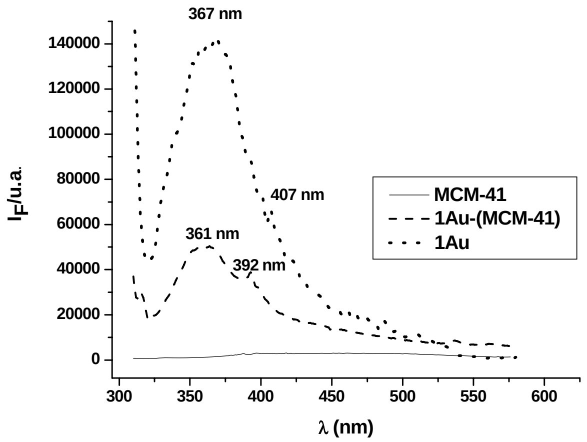


Figure S4. Emision spectra for soluble 1Au and heterogenized 1Au-(MCM-41) complexes (λ = 302 nm)

Synthesis of supported Schiff base gold(III)-complexes[2,7]

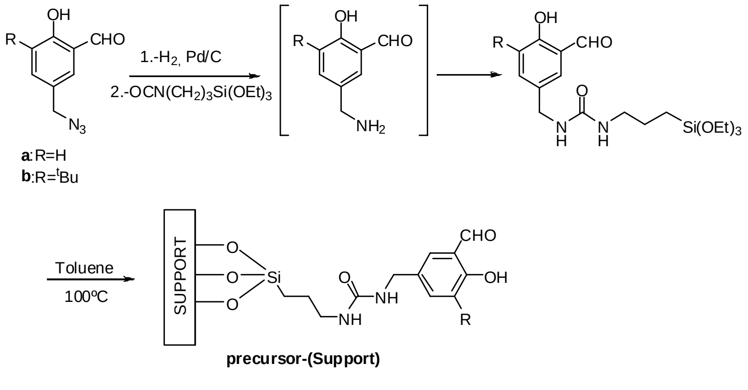
a) Synthesis of 2Au(III) complex on MCM-41 suppports.

The heterogeneized ligands 2Au(III)-(MCM-41) were synthesised according a similar method to that described previously.[2]

b) Synthesis of 3Au(III) complex on MCM-41 supports.

General heterogenization of hydroxyaldehydes: Scheme S2

Typically, to a suspension of silica or the corresponding support MCM-41, MCM-41(Sn) (2 g) in toluene (25 ml), stirred at room temperature for 30 minutes, a solution of 2 mmol of the aldehyde in toluene (5 ml) and 400μl of water were added. The slurry was heated at 100ºC for 16 h and the yellow solid was filtered off and washed successively with toluene, petroleum ether, ethanol and ether. The solid was dried under vacuum for 24 hours to afford the anchored precursors **precursor-(support)**. The loadings are based on the percent of nitrogen obtained from the elemental analysis data.



Scheme S2. Synthesis of heterogenized precursor.

precursor-(MCM-41): anal. found: C 13.4, H 2.8, N 1.5%; (0.55 mmol/g). IR (KBr, cm^{-1}): ν = 3421 (NH), 1642, 1564 (CO, C=C). UV-vis (λ, nm): 360, 425. ^{13}C-NMR (solid): δ = 199.29 (*C*HO); 160.58 (NH*C*ONH); 147.84 (*C*OH); 138.13 (*C*-CHNH-); 130.98 (*C*H$_{arom}$); 120.18 (*C*-CHO); 57.45 (CH$_3$*C*H$_2$O-); 54.29 (NH*C*H$_2$Ph); 42.04 (NH*C*H$_2$CH$_2$-); 27.60 (*C*(*C*H$_3$)$_3$); 18.99 (*C*H$_3$CH$_2$O-); 9.64 (*C*H$_2$Si-).

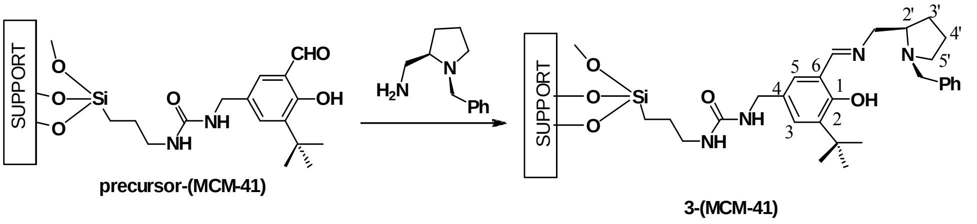
precursor-(MCM-41, Si/Al ≈15): anal. found: C 36.2, H 3.3, N 1.4%; (0.47 mmol/g). IR (KBr, cm^{-1}): ν = 3407 (NH), 1639, 1512 (CO, C=C). UV-vis (λ, nm): 349, 264, 223. ^{13}C-NMR (solid): δ = 199.00 (*C*HO); 161.02 (NH*C*ONH); 147.41 (*C*OH); 137.83 (*C*-CHNH-); 131.26 (*C*H$_{arom}$); 120.03 (*C*-CHO); 57.31 (CH$_3$*C*H$_2$O-); 54.05 (NH*C*H$_2$Ph); 42.00 (NH*C*H$_2$CH$_2$-); 27.43 (C(*C*H$_3$)$_3$); 19.12 (*C*H$_3$CH$_2$O-); 9.58 (*C*H$_2$Si-).

precursor-(MCM-41, Sn$_{synth}$): anal. found: C 20.3, H 3.1, N 3.3%; (1.2 mmol/g). IR (KBr, cm^{-1}): ν = 3394 (NH), 1644, 1565 (CO, C=C). UV-vis (λ, nm): 224, 265, 343 432.

precursor-(MCM-41, Sn$_{graft}$): anal. found: C 17.6, H 2.6, N 2.5%; (0.9 mmol/g). IR (KBr, cm $^{-1}$): ν = 3428 (NH), 1640, 1566 (CO, C=C). UV-vis (λ, nm): 227, 267, 347 426. ^{13}C-NMR (solid): δ = 198.65 (*C*HO); 160.32 (NH*C*ONH); 147.75 (*C*OH); 138.00 (*C*-CHNH-); 131.04 (*C*H$_{arom}$); 120.43 (*C*-CHO); 57.00 (CH$_3$*C*H$_2$O-); 54.32 (NH*C*H$_2$Ph); 41.86 (NH*C*H$_2$CH$_2$-); 27.22 (C(*C*H$_3$)$_3$); 19.05 (*C*H$_3$CH$_2$O-); 9.21 (*C*H$_2$Si-).

Synthesis of heterogenized ligands: Scheme S3

Typically, stirred slurry of 1 mmol of the corresponding anchored hydroxyaldehyde **precursor-(support)** was prepared in ethanol (10 ml) under argon at room temperature. After 10 min. 125 mg (1.1 mmol) of the amine were added and stirred for 16 hours. Then, the mixture was allowed to cool and the deep yellow solid was filtered off and washed thoroughly with ethanol and then with ether. The solid was dried under vacuum to afford the corresponding anchored ligands **ligand-(support)**.



Scheme S3. Synthesis of heterogenized ligands

3-(MCM-41): anal. found: C 16.3, H 3.0, N 2.5%; (0.44 mmol/g). IR (KBr, cm^{-1}): ν = 1630, 1557 (C=N, C=O, C=C). UV-vis (λ, nm): 224, 264, 347, 419. ^{13}C-NMR (solid): δ = 166.60 (*C*H=N); 160.53 (NH*C*ONH); 153.62 (*C*-OH); 136.99 (C_6, C_{arom}, C_4, C_2) 128.74 (C_{arom}, C_3, C_5); 66.50 ($C_{2'}$, CH=NCH_2); 58.98 (CH_2Ph); 53.64 ($C_{5'}$); 42.48 ($CH_2CH_2CH_2Si$, CCH_2NH); 28.40 (C(CH_3)$_3$, $C_{3'}$); 22.09 (CH_2CH_2Si, $C_{4'}$); 8.02 (CH_2Si).

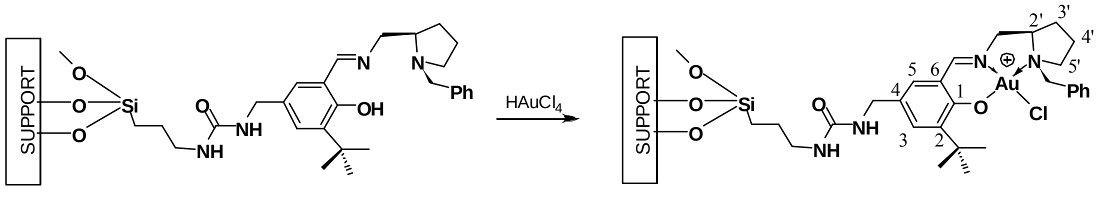
3-(MCM-41, Si/Al ≈ 15): anal. found: C 17.4, H 2.4, N 2.7%; (0.5 mmol/g). IR (KBr, cm^{-1}): ν = 1630 (C=N). UV-vis (λ, nm): 420, 337, 264, 223.

3-(MCM-41, Sn_{synth}): anal. found: C 21.4, H 3.0, N: 3.5%; (0.6 mmol/g). IR (KBr, cm^{-1}): ν = 1638 (C=N). UV-vis (λ, nm): 429, 338, 266, 228.

3-(MCM-41, Sn_{graft}): anal. found: C 19.0, H 3.1, N 3.1%; (0.5 mmol/g). IR (KBr, cm^{-1}): ν = 1634 (C=N). UV-vis (λ, nm): 431, 335, 264, 228. ^{13}C-NMR (solid): δ = 165.70 (*C*H=N); 160.21 (NH*C*ONH); 154.04 (*C*-OH); 137.32 (C_6, C_{arom}, C_4, C_2) 128.50 (C_{arom}, C_3, C_5); 66.65 ($C_{2'}$, CH=NCH_2); 59.14 (CH_2Ph); 53.75 ($C_{5'}$); 42.52 ($CH_2CH_2CH_2Si$, CCH_2NH); 28.35 (C(CH_3)$_3$, $C_{3'}$); 22.00 (CH_2CH_2Si, $C_{4'}$); 8.00 (CH_2Si).

Synthesis of Schiff base gold(III)-complexes. Scheme S4

The homogeneous chiral complexes were also synthesized and used as catalysts to compare the catalytic activities and to evaluate the relations between the structural features of ligands and activity. Heterogenized complexes were synthesized following the general method: to a suspension of heterogenized ligand in toluene (20 ml), at room temperature was added an ethanolic solution of $HAuCl_4$ (0.5 mmol/15 ml). The resulting mixture was stirred under reflux for 12 h, cooled to room temperature and filtered. The solid was washed several times with ethanol, dried and filtered to afford the respective heterogenized complexes, **complex-(support)**, in almost quantitative yields.



3-(support) **3Au-(support)**

Support: MCM-41, MCM-41(Si/Al = 15), MCM-41 (Sn)

Scheme S4. Synthesis of heterogenized complexes

3Au-(MCM-41): anal. found: C 15.0, H 2.0, N 2.2, Au 2.9%; (0.27 mmol/g). IR (KBr, cm^{-1}): ν = 1632-1558 (C=N, C=O, C=C), 462 (Au-O). UV-vis (λ, nm): 225, 352, 410. ^{13}C-NMR (solid): δ = 160.07 (NH*C*ONH, *C*-O-Au); 155.30 (*C*H=N) 137.61 (C_2); 128.70 (C_{arom}, C_5, C_3); 120.00 (C_6); 70.60 (CH=N*C*H$_2$, $C_{2'}$); 63.21 (*C*H$_2$Ph); 58.64 ($C_{5'}$); 42.97 (*C*H$_2$CH$_2$CH$_2$Si, C*C*H$_2$NH); 34.50 (*C*(CH$_3$)$_3$); 28.20 (C(*C*H$_3$)$_3$, $C_{3'}$); 23.34 ($C_{4'}$, CH$_2$*C*H$_2$CH$_2$Si); 11.23 (*C*H$_2$Si).

3Au-(MCM-41, Si/Al ≈ 15): anal. found: C 15.7, H 2.0, N 2.5, Au 4.3%; (0.4 mmol/g). IR (KBr, cm $^{-1}$): ν = 1630 (CO), 1564(C=N), 454 (Au-O). UV-vis (λ, nm): 229, 255, 289, 343, 408.

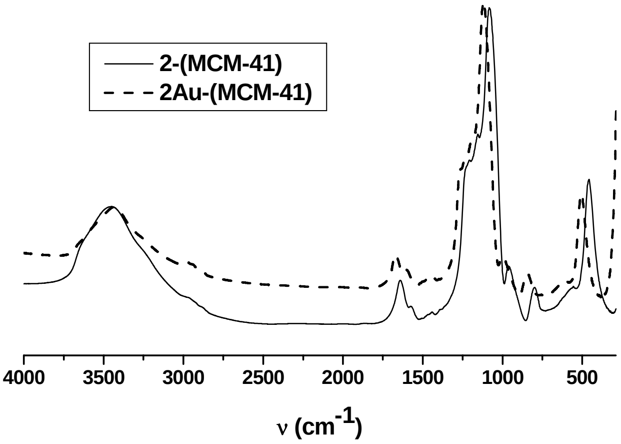
3Au-(MCM-41, Sn$_{synth}$): anal. found: C 22.7, H 2.7, N 2.7, Au 5.9%; (0.6 mmol/g). IR (KBr, cm $^{-1}$): ν = 1630 (CO), 1571 (C=N), 461 (Au-O). UV-vis (λ, nm): 229, 271, 351, 450, 538.

3Au-(MCM-41, Sn$_{graft}$): anal. found: C 31.9, H 5.9, N 5.5, Au 1.3%; (0.1 mmol/g). IR (KBr, cm $^{-1}$): ν = 1634 (CO), 1582 (C=N), 460 (Au-O). UV-vis (λ, nm): 229, 267, 357, 459, 608.

The IR spectra of supported Schiff base-gold(III) complexes show the O-H vibration in the range 3700-3300 cm^{-1}. Some of the bands characteristic of the complexes could be distinguished. Major zeolite framework bands appeared at 1140, 1040, 960, 785 and 740 cm^{-1}. The 1600 cm^{-1} frequencies may be assigned to C=C and azomethine C=N vibrations, shifted to lower wavenumbers (relative to the free ligands) due to N-coordination of the imine (Figure S5). The DFTR spectra show several band maxima in the UV region agreeing with the assignment of the bands as intraligand transitions in the aromatic ring, azomethine group and charge-transfer transition (Figure S6). The ^{13}C NMR spectra show two set of signals which are attributable on the one hand to the substituted benzaldimine entity and on the other hand to the aliphatic part of the ligand. The ^{13}C NMR spectra showed the signals assigned to the C=N carbon high field shifted and C-O at $\delta \sim 162$ downfield shifted confirming that metallation occurred (Figure S7).

c) Spectroscopic characterization for some complexes

Figure S5. IR spectra for heterogenized complexes



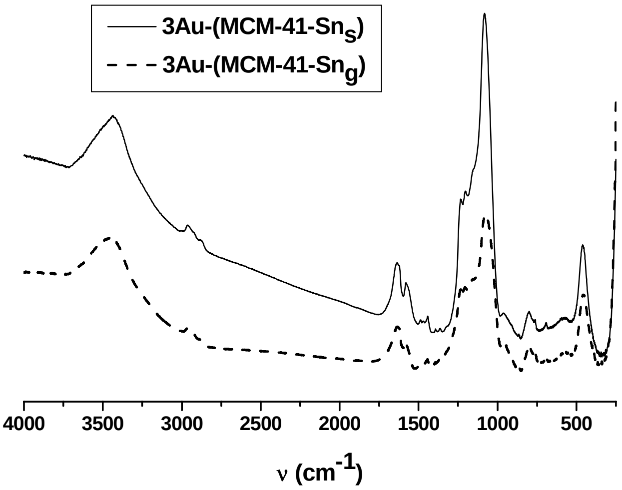
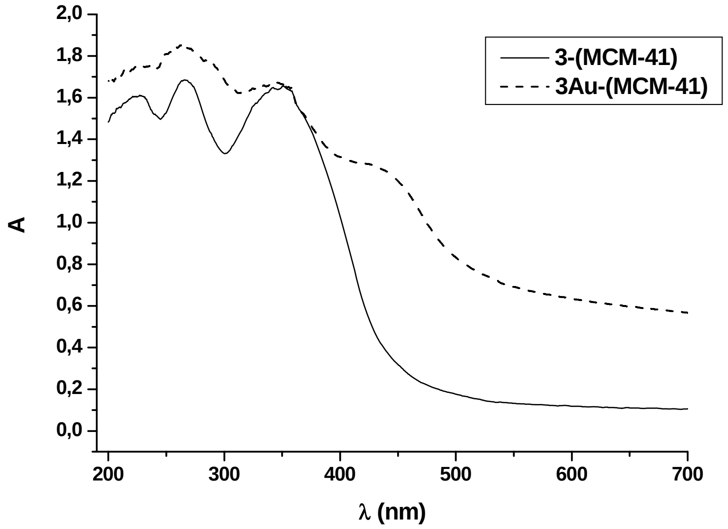


Figure S6. UV-vis spectra for heterogenized complexes.



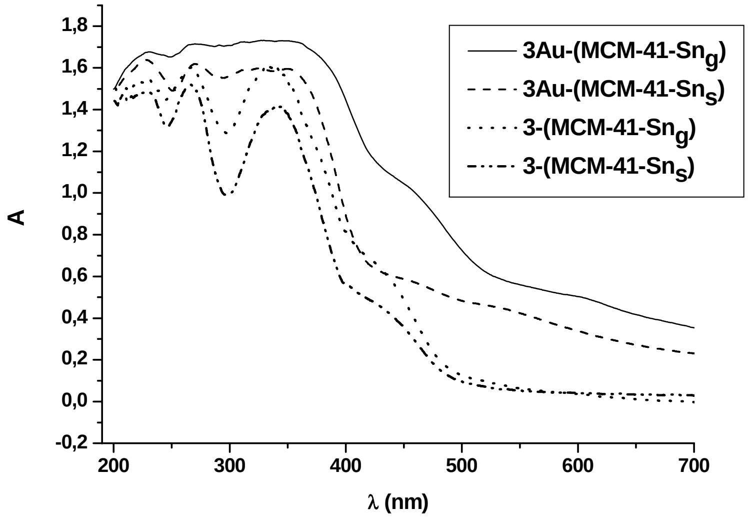


Figure S7. ^{13}C NMR spectra for heterogenized complexes

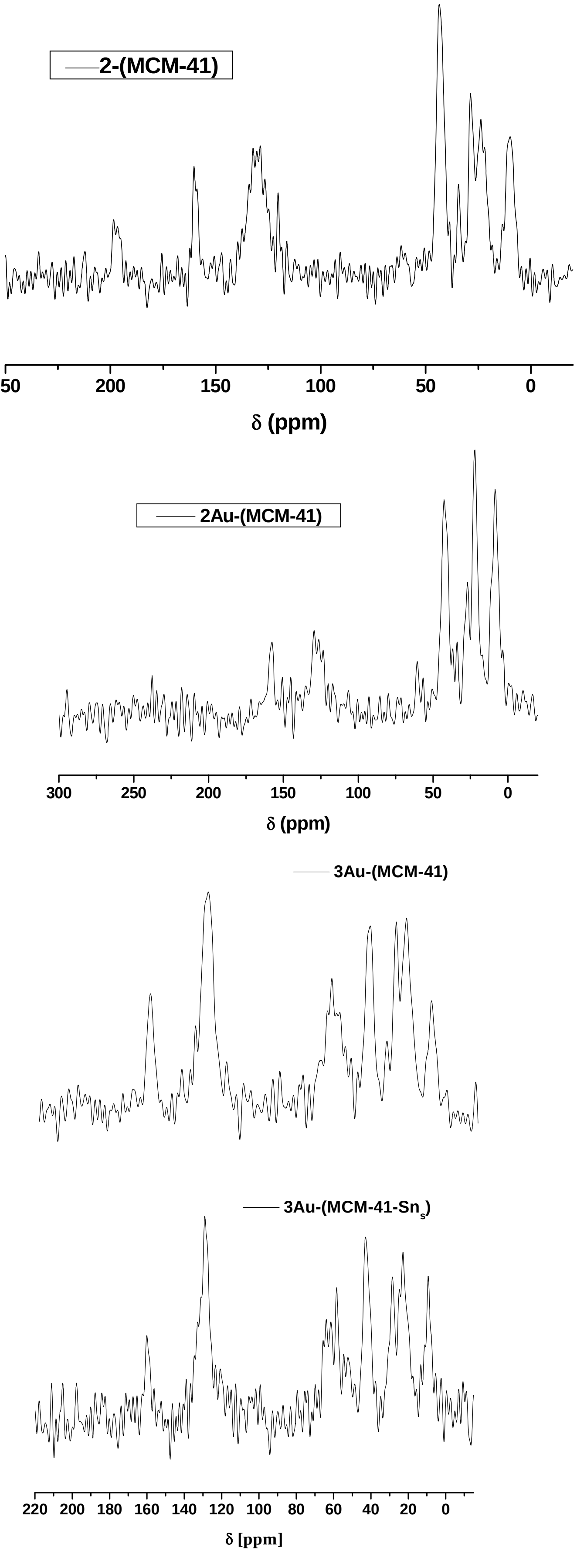


Table 1. Homogeneous Gold-Catalyzed Hydroamination of alkynes[a]

Cat.	Cat.	R	R’	R″	t (h)	Yield. (%)[b]
1	1Au(I)	Ph	H	H	15	50
2	$[1Au(I)]^+$	Ph	H	H	15	95
3	2Au(III)	Ph	H	H	0.3	100[c]
4	3Au(III)	Ph	H	H	1	100
5	2Au(III)	Ph	Br	H	15	60
6	2Au(III)	Ph	H	CH_3	15	100
7	2Au(III)	Ph	H	OMe	4	100
8	2Au(III)	Ph	H	NO_2	15	100
9	2Au(III)	*p*-CH_3Ph	H	H	15	50
10	2Au(III)	C_6H_{13}	H	H	15	100
11	2Au(III)	$C(CH_3)_2OH$	H	H	15	100
12	Au(0) (coll.)	Ph	H	H	15	0

[a] Reaction conditions: 1.0 mmol of alkyne, 1.2 equiv. of amine, 5 mol% of NH_4PF_6 and catalyst (gold(I) 10%, gold(III) 5%) in thf at 70 ºC. [b] Determined by GC and ^{1}HNMR. [c] With $Sn(Bu)_3Cl$ as promoter conversion = 0%.

Table S1. Homogeneous Gold-Catalyzed Hydroamination of alkenes[a]

Entry	**Cat.**	**R**	**R'**	**R″**	**t (h)**	**Conv. (%)[b]**
1	1Au(I)	Ph	CH_3	H	1	100
2	$[1Au(I)]^+$	Ph	H	H	0.5	100
3	2Au(III)	Ph	H	H	3	100
4	3Au(III)	Ph	H	H	5	100
5	2Au(III)	Ph	CH_3	H	0.5	100
6	2Au(III)	$(CH_2)_6$	H	H	15	15
7	2Au(III)	C_8H_{17}	H	H	15	100
8	2Au(III)	Ph	H	CH_3	15	100
9	2Au(III)	Ph	H	NO_2	15	85

[a] Reaction conditions: 1.0 mmol of alkyne, 1.2 equiv. of amine, 5 mol% of NH_4PF_6 and catalyst (gold(I) 10%, gold(III) 5%) in thf at 70 ºC. [b] Determined by GC and ^{1}HNMR.

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[1] Due to the similarity of spectra for supported catalysts in each series of ligands, only completed data from some compounds were given. Data for all compounds can be obtained from authors.

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