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Well-Defined Noble Metal Single Sites in Zeolites as an Alternative to Catalysis by Insoluble Metal Salts

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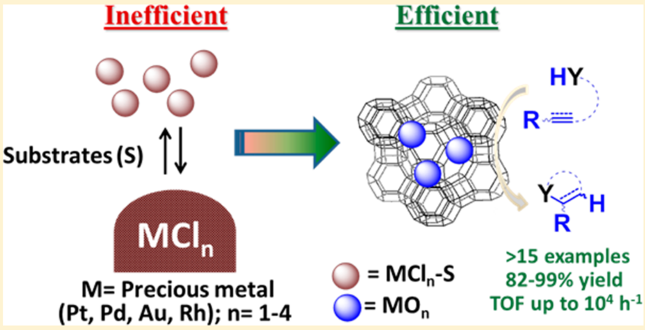
Supporting Information

ABSTRACT: Insoluble precious metal chlorides in polymeric form (i.e., $PtCl_2$, $PdCl_2$, AuCl, $RhCl_3$) are commonly used as catalysts for a plethora of organic reactions in solution. Here we show that only the minor soluble fraction of these precious metal chlorides (typically 5–30%) is catalytically active for the hydroamination, hydroalkoxylation, hydrosilylation, and cycloisomerization of alkynes and alkenes, and that the resting insoluble metal is catalytically useless. To circumvent this waste of precious metal and follow a rational design, we generate here well-dispersed Pt(II) and Pd(II) single sites on zeolite Y, with an exquisite control of the Lewis acidity, to catalyze different hydroaddition reactions to alkynes and alkenes with up to 10^4 catalytic cycles (at least 2 orders of magnitude superior to precious metal chlorides) and with high isolated yields (82–99%, >15 examples).



INTRODUCTION

Catalysis by late transition metals is a cornerstone of modern organic synthesis, and for instance, the polymeric precious metal chlorides $PtCl_2$, $PdCl_2$, $AuCl_3$, and $RhCl_3$ (0.5–5 mol % respect to reactants) are the catalysts of choice for many hydroaddition reactions to alkenes and alkynes (see Supporting Information, Table S1),[1−3] with industrial implementation in some cases.[4] Typically, these reactions are carried out in common organic solvents, despite a significant part of the precious metal chloride remaining at the bottom of the flask, apparently unaltered. This fact makes one wonder if the metal chloride acts as a homogeneous or heterogeneous catalyst, a nontrivial issue considering the high price of precious metals and, furthermore, the potential mechanistic implications for these reactions.

Here we show that the catalytically active species in a variety of hydroaddition reactions to alkynes and alkenes is a minor soluble fraction (<5–30%) of the starting precious metal chloride. With the exact nature of the catalytically active species in hand, we design an atomically efficient Pt(II) catalyst based on well-dispersed precious metal single sites[5] on zeolite Y, after fine-tuning the Lewis acidity of Pt(II) with the zeolite framework. This "ligand-free" Pt(II) (or Pd(II)) solid catalyst is, at least, 2 orders of magnitude more active than the state-of-the art precious metal salt catalysts, not only for the hydroamination of alkynes but also for a variety of hydroaddition reactions to alkynes and alkenes. Besides that, the catalyst can be recovered and reused at least 10 times.

RESULTS AND DISCUSSION

Correlation between the Solubility of the Precious Metal Chloride and Its Catalytic Activity for the Hydroaddition Reaction to Alkynes and Alkenes. Figure 1 shows the solubility of $PtCl_2$, $PdCl_2$, AuCl, and $RhCl_3 \cdot nH_2O$ (0.1 mmol, 20–30 mg) with some representative organic compounds in toluene (5 mol % in Pt, 0.25 M solution), after 2 h at 80 °C.

With minor variations, the amount of precious metal chloride dissolved in aromatic, ether, nitrile, silane, alkene, alcohol, acetate, and alkyne solutions is always <20%, and only carbon monoxide, the strong chelating ligand 1,5-cyclooctadiene (1,5-COD), and the primary alkyl amine cyclohexylamine are able to dissolve >40% of the starting precious metal, at the expense of forming the well-known metal complexes $MCl_2(L)_2$ (L = 1,5-COD, *c*Hex-NH_2) for the latter.[6]

Figure 2 shows that the intramolecular hydroamination of *o*-(phenylacetylen)aniline **1** in the presence of $PtCl_2$ (0.5 mol %)[2] proceeds with the same initial reaction rate, final yield, and selectivity to product **2** regardless of the reaction mixture being filtered after 3 min (conversion 2%) or not, despite most of the solid precious salt remaining undissolved at the bottom of the flask. This effect also occurs for other precious metal chlorides ($PdCl_2$, AuCl, and $PtCl_4$), other solvents (dichloromethane and 1,4-dioxane), and other hydroaddition reactions to alkynes and alkenes (hydroalkoxylation of alkynes, cycloisomerization of

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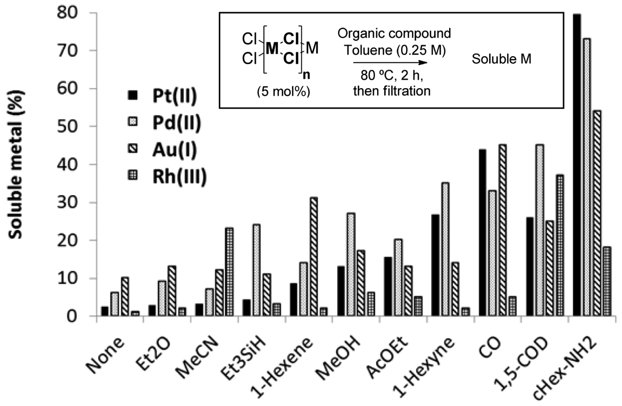

Figure 1. Percentage of precious metal dissolved from $PtCl_2$, $PdCl_2$, AuCl, or $RhCl_3{\cdot}nH_2O$ (5 mol %) in 0.25 M toluene solutions, calculated in two ways: (1) by inductively coupled plasma atomic emission spectroscopy (ICP-AES) of the filtered solution and (2) by differential gravimetry of the MCl_n solid. The results by both methods agree well within an estimated error of ±2% after an average of two experiments. In most of the cases, the amount of metal dissolved in toluene after 3 min was nearly the same after 2 h.

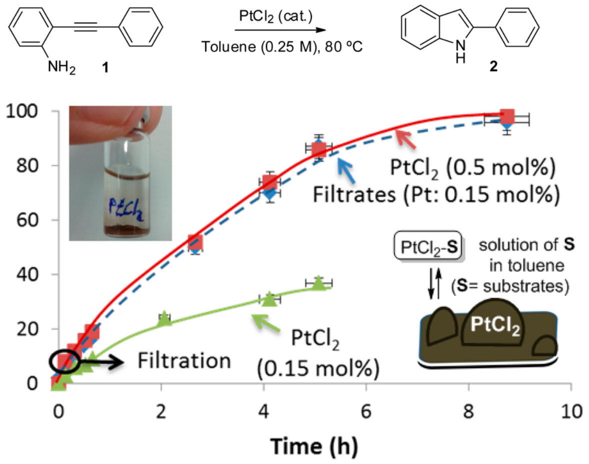

Figure 2. Yield−time plot for the hydroamination of *o*-(phenylacetylen)aniline **1** catalyzed by $PtCl_2$ under the indicated reaction conditions. Each point is an average of three different measurements, and bars represent an estimated error of 5%. The top left inset shows a photograph of the $PtCl_2$ remaining, and the bottom right inset illustrates the equilibrium-controlled dissolution of $PtCl_2$ with the substrates.

propargyl acetates, and cycloisomerization of 1,6-dienes, see Supporting Information Figures S1−S10). Notice that the small amounts of $PtCl_2$ or $PdCl_2$ that can dissolve in neat toluene (∼3% for Pt according to ICP-AES and the gravimetric test) are catalytically competent for the hydroamination of **1** (Figure S3).

The solubility effect is not restricted to Lewis-catalyzed reactions but also occurs for reactions following an oxidative-addition reductive-elimination mechanism[7] such as the hydrosilylation of alkynes and alkenes, which is perhaps the most important process in organic synthesis catalyzed by Pt salts.[4,8] The first Pt catalyst reported for the hydrosilylation of C−C multiple bonds was Speier's catalyst H_2PtCl_6, but the difficult handling and the low solubility of this highly hygroscopic salt lead to the rapid implementation in organic synthesis of Karstedt's catalyst [Pt_2(divinyltetramethyldisiloxane)$_3$ solution in *o*-xylene], despite the latter requiring additional synthetic steps and being more expensive than any Pt chloride. We wondered here if the treatment of $PtCl_2$ with the alkyne or the silane, just for a few minutes, could generate the active species in solution, as it occurs for the hydroamination, hydroalkoxylation, and cycloisomerization reactions, thus circumventing the use of Speier's or Karstedt's catalysts. Comparatively, $PtCl_2$ has been obviated as a catalyst for the hydrosilylation of alkynes although it is an easy-to-handle solid. The results showed that treatment of a 5 mol % of $PtCl_2$ with triethylsilane in toluene, for just 3 min, gives a solution that catalyzes the hydrosilylation of 1-dodecyne with better initial catalytic activity than the insoluble $PtCl_2$ or H_2PtCl_6 solids, without the typical induction time found in hydrosylilation reactions (Figure S8). Notice that this solution contains only 4% of the starting Pt (0.2 mol % of Pt respect to the reactants) according to ICP-AES and differential gravimetry. The same solubility effect was found for H_2PtCl_6 and when the reaction was carried out in other solvents (dichloromethane and tetrahydrofuran), when alkenes were used as substrates (Figure S9), and when $RhCl_3$ was used as the precious metal salt catalyst (Figure S10). These results suggest that the formation of catalytically active metal species in solution for the hydrosilylation reaction is general regardless of the substrate or metal used.

The amount of metal dissolved for the different hydroaddition reactions in toluene versus the amount of metal expected to be dissolved for the substrates (see Figure 1 and Figure S11) correlates well; thus, it seems that the solubility of the precious metal chloride ultimately controls the catalytic activity for each reaction. For instance, Pt analysis in solution during the hydroamination of **1** gives 30% of soluble Pt, which fits the 27% of $PtCl_2$ dissolved with 1-hexyne in toluene (see Figure 1).

The alkyne or alkene does not always exclusively control the metal solubility since the other coupling partner, or even the product, can play a major role in some cases. For instance, the cycloisomerization of a 1,6-diene proceeds with a clear induction time that corresponds, according to differential gravimetric measurements, to the time needed to dissolve the $PdCl_2$ catalyst (Figure S7). The sigmoidal curve comes from better dissolution of the metal in the presence of the cyclic product, probably by a preferred coordination with the 1,3-unsaturated ester. In accordance, the addition of increasing amounts of product progressively eliminates the induction time, and when so, the final filtration of the solid catalyst has no influence on the reaction outcome. Another remarkable example where the dissolution of the precious metal salt seems to not depend on the alkyne or alkene is the hydrosilylation reaction, since the solubility value of $PtCl_2$ with Et_3SiH (4%) matches the Pt dissolved during the $PtCl_2$-catalyzed hydrosilylation of alkynes (see Figure S11); if the $PtCl_2$ catalyst is treated with Et_3SiH in toluene for 3 min and filtered, and then the alkyne is added to the filtrate, the hydrosilylation reaction proceeds exactly with the same rate and selectivity. Thus, we can say that the silane and not the alkyne is the main species responsible for the formation of the catalytically active soluble Pt species, which is consistent with the redox nature of the reaction.

Increasing the Solubility of $PtCl_2$ with Carbon Monoxide. Since the catalytic effect is directly proportional to the metal dissolved, it should be possible to increase the conversion level by increasing the solubility of the metal during the reaction.

In principle, a simple way to increase the catalytic activity of the metal chloride would consist of the use of external agents that dissolve more metal without poisoning the catalyst. For instance, CO dissolves nearly double $PtCl_2$ as compared to the alkyne in toluene (~50%, see Figure 1); thus, a CO atmosphere may be beneficial for the hydroamination of alkynes. This is indeed what occurs,[2c] and Figure 3 (top left) shows that the catalytic activity is similar regardless of the presence or absence of the resting $PtCl_2$. Control experiments showed that the same Pt is extracted with CO in the presence or absence of the alkyne.

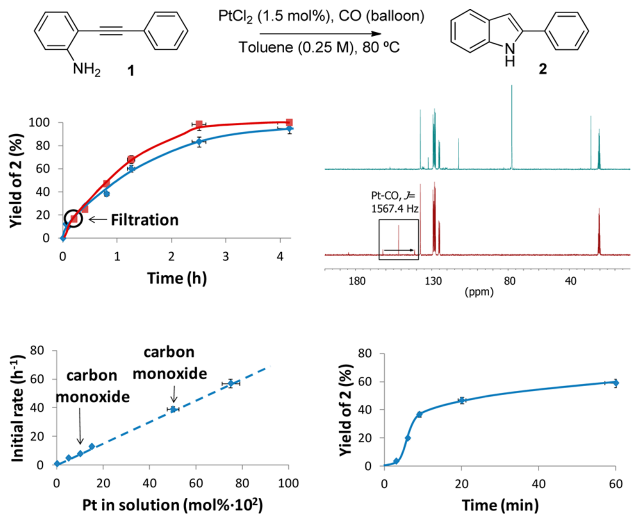

Figure 3. Top left: Yield−time plot for the hydroamination of *o*-(phenylacetylen)aniline **1** catalyzed by $PtCl_2$ (1.5 mol %) under an atmosphere of carbon monoxide. Top right: ^{13}C NMR of the extracts with an atmosphere of isotopically labeled ^{13}CO in toluene-d_8, before (down) and after (up) adding isotopically labeled **2**-^{13}C-phenylacetyene. Bottom left: Increasing of the initial rate with the amount of soluble Pt, in the presence or absence of a carbon monoxide atmosphere. Bottom right: Yield−time plot after extracting $PtCl_2$ in toluene with an atmosphere of carbon monoxide during 30 min, filtering, and then adding the alkyne. Bars in all graphics represent an estimated error of 5%.

^{13}C NMR measurements of the toluene extracts with an isotopically labeled ^{13}CO atmosphere confirm the formation of CO−Pt complexes (~150 ppm, 33% active ^{195}Pt, J = 1567.4 Hz) and that the CO molecules coordinated to Pt are rapidly displaced by the alkyne (disappearance of the CO−Pt signal, new ^{13}C signal corresponding to the alkyne at ~80 ppm, see Figure 3 top right). With these results in hand, we can suggest that the enhanced rate observed under an atmosphere of CO for some $PtCl_2$-catalyzed reactions (see Table S1) might be explained by the enhanced solubility of Pt beyond any electronic considerations. This proposal is supported by the good correlation found during the hydroamination of **1** between catalytic activity versus solubility of Pt in solution, regardless of a CO atmosphere being set or not, and also by the fact that the reaction proceeds well with the Pt extracted under an atmosphere of carbon monoxide before adding the alkyne (see bottom Figure 3).

Analysis of Pt in solution for different amounts of starting $PtCl_2$ shows that the amount of Pt dissolved is systematically $^1/_4$ of the originally added, and accordingly, the initial rate is linearly proportional (Figure S12). For instance, when 26.5 ± 0.5 mg of $PtCl_2$ is added as a catalyst (5 mol %), the ICP-AES analysis shows 27% of the starting Pt in solution, and the gravimetric method gives 5.9 ± 0.5 mg of a brown solid residue for the filtrates and 20.9 ± 0.5 mg for the resting $PtCl_2$ solid, after exhaustive drying. At the end of the reaction (conversion >95%), the recovered $PtCl_2$ solid still accounts for ~75 wt % of that initially added, so the dissolved Pt remains in solution even when no more **1** is present, which could be due to coordination with the indole product. Indeed, 22% of Pt is dissolved after treating a dispersion of $PtCl_2$ in toluene with indole **2**. These results together suggest that Pt is in equilibrium with the alkyne and/or the indole, as shown in Figure 2. Accordingly, Figure 4 shows that the amount of solid $PtCl_2$ recovered after 4 successive hydroamination reactions and, also, the initial rates systematically decrease ~$^1/_4$ with each use (see also Figures S12 and S13), which confirms that the hydroamination of **1** follows an equilibrium with 20−30% of Pt dissolved along the reaction.

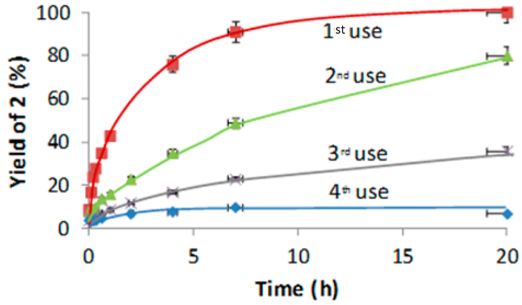

Figure 4. Yield−time plots for successive runs of the hydroamination of *o*-(phenylacetylen)aniline **1** catalyzed by the recovered $PtCl_2$ (0.5 mol %) under the reaction conditions indicated in Figure 2. Bars represent an estimated error of 5%.

Determination of the Soluble Species in the $PtCl_2$-Catalyzed Hydroamination of Alkynes. In order to determine the soluble Pt active species for the hydroamination of **1** (5 mol % $PtCl_2$), electrospray ionization high-resolution mass spectrum (ESI-HRMS) of the filtrates at 7% conversion time were carried out (Figure S14). The results unequivocally showed that the single Pt species present in solution is the $PtCl_2(\mathbf{1})_2$ complex, according to the isotopic pattern and the expected fragmentations. Treatment of this complex in solution with a stoichiometric amount of the bis-alkene COD gave the $PtCl_2(COD)$ complex after ligand displacement (Figure S15), and a gravimetric test of the filtered solution with $AgNO_3$ confirmed the presence of two chloride atoms per Pt atom. These results indicate that **1** dislodges monomeric $PtCl_2$ units from the insoluble chloride during reaction and that these species are catalytically competent for the hydroamination reaction.

$PtCl_4$ is also considered an active and selective catalyst for the Lewis-catalyzed intramolecular hydroamination of alkynes under homogeneous reaction conditions,[1] since the high catalytic efficiency of Pt for this reaction is ascribed to its high alkynophilicity, which stemmed from relativistic effects,[1f] together with the expected high Lewis acidity of Pt^{4+}. When $PtCl_4$ (0.5 mol %) is used as a catalyst instead of $PtCl_2$ under the reaction conditions indicated in Figure 2, and the solution is filtered after 3 min of reaction, the kinetic profile is similar to that when the insoluble $PtCl_4$ is still present in the reaction medium. However, in contrast to $PtCl_2$, an induction time of 15 min is found (Figure S4). If the amount of $PtCl_4$ is decreased 3 times, the induction time lengthens to 4 h, and then the hydroamination starts with an initial reaction rate 3 times lower. Ultraviolet−visible spectroscopy (UV−vis) of the filtrates of the $PtCl_4$-catalyzed reaction does not show any bands during the induction time, but a new band appears when the reaction starts and proceeds, a band that corresponds to $PtCl_2$ in solution. These results, although not conclusive, strongly suggest that the induction time found with $PtCl_4$ corresponds to the formation of $PtCl_2$ in solution, so the same soluble monatomic $PtCl_2$−alkyne complex found for $PtCl_2$ seems to be the one catalyzing the reaction when starting with $PtCl_4$ which catalyzes the reaction.

With these data in hand, it seems that the key issue to catalyze the hydroamination of **1** is just having discrete Pt(II) species; however, the absence of catalytic activity for soluble monatomic Pt chloride complexes, such as, for instance, $PtCl_2(COD)$ or $PtCl_2(NH_3)_2$ (conversion <5% under the conditions in Figure 2, 9 h reaction time), indicates that the limitation for the ligand-promoted complete solubility of Pt(II) in toluene is the lack of catalytic activity for the hydroamination of **1**, at least for complexes having stronger ligands than **1**, that avoid ligand exchange in the Pt coordination sphere.[9]

Solid Catalysts with Isolated Pt(II) Based on a Zeolite.

Since the Pt catalyst for the hydroamination of **1** consists of isolated Pt(II) atoms attached to weak ligands, we thought of zeolite Y to introduce Pt(II).[10] In principle this solid has some properties that can help to achieve a relatively large amount of catalytically active Pt(II) species on its surface: (1) Zeolite Y has a very large surface area (~800 m^2 g^{-1}) and exchange capacity that enable high dispersion of the Pt(II) atoms.[11] (2) The oxygen atoms (the counteranions) on the zeolite walls act as weak ligands. (3) The Lewis acidity of Pt(II) can be modulated by varying the electronic density of the crystalline framework. (4) Incorporation of Pt(II) by cationic exchange is easy and nearly quantitative. (5) Potential generation of mesopores in the zeolite may allow the reaction of relatively large molecules.[12,13] Thus, Pt(II)−NaY (~1 wt % Pt according to ICP−AES) was prepared by cationic exchange with an aqueous solution of $Pt(NH_3)_4(NO_2)_2$ followed by aerobic thermal elimination of the NH_3 ligands at 100−400 °C (see preparation and characterization details in Figures S16−S21), preserving the microstructure and total surface area of the zeolite.

The amount of NH_3-free Pt(II) sites was determined by the loss of NH_3 in temperature-programmed infrared spectroscopy and by the ratio of Pt(II) to Pt(0) atoms with X-ray photoelectron spectroscopy (XPS), the results being double-checked by low-temperature IR experiments with carbon monoxide as a probe. It was found that the amount of Pt(II) remaining after activation depends very much on the decomposition conditions of the cationic amino complex. A maximum number of NH_3-free Pt(II) sites (77%, Table S2) are obtained at a calcination temperature of 200 °C over 48 h, which is in good agreement with the decomposition temperature of the Pt(II) ammonia complex precursor (~250 °C, see thermogravimetric analysis in Figure S22). Larger calcination times and/or higher temperatures decrease the amount of NH_3-free Pt(II) sites since further reduction to Pt(0) occurs, as observed by dark-field scanning transmission electron microscopy (DF STEM) and diffuse reflectance ultraviolet−visible spectroscopy (DR-UV−vis, Pt plasmon bands as a broad downhill band covering from 230 to 700 nm, Figures S23 and S24).

Figure 5 shows that the catalytic activity of Pt(II)−NaY for the hydroamination of **1** (1 mol % Pt) correlates linearly with the number of NH_3-free Pt(II) sites (see also Figure S25), with a calculated TOF_0 per NH_3-free Pt(II) atom of 273 h^{-1}. Notice that the TOF_0 with $PtCl_2$ under the same reaction conditions is 66 h^{-1} (~200 h^{-1} per dissolved Pt atom). This result indicates that the supported Pt(II) atoms on NaY are intrinsically some more active than dissolved $PtCl_2$ monomers, in accordance with the weaker electron donation of the NaY framework compared to chloride anions.

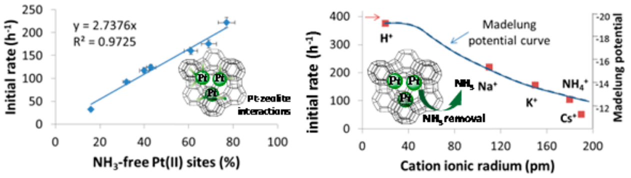

Figure 5. Initial conversion rates for the hydroamination of **1**, at 110 °C, catalyzed by different Pt(II)−Y zeolites (1 mol %) where the number of NH_3-free Pt(II) sites for NaY (right) or charge compensating cation ionic radius (samples calcined at 200 °C for 48 h, left) has been varied. Error bars account for 5% uncertainty. The electronic density of the zeolite framework is represented as the Madelung potential curve; notice that the initial rate for the electron rich CsY zeolite is lower than expected because significant reduction of Pt(II) to Pt(0) occurs after calcination.

It should be remarked that the Pt(II)−NaY samples calcined at temperatures ≤200 °C do not show any Pt nanoparticles before or after use, according to ultramicotome-cut DF STEM and HR-TEM (up to the limit of detection of the 400 keV instrument, ~1 nm) and RD-UV−vis spectroscopy (since only the band of Pt(II) oxide at ~215 nm is detected, see Figures S17 and S24). On the other hand, the samples calcined at temperatures ≥300 °C lose their higher initial catalytic activity during reaction due to further Pt aggregation under reaction conditions, as confirmed by the increase of the number and average diameter size of Pt nanoparticles formed during calcination, from ~3 nm in the fresh sample to ~6 nm after reaction, as also confirmed by the increase of the Pt(0) plasmon band intensity in the sample after reaction (see Figures S23−S25). Thus, we can conclude that the Pt(II) zeolite must be prepared by calcining the exchanged zeolite at a temperature and time sufficient to eliminate ammonia from the Pt complex without reducing and agglomerating Pt. In our case, the optimal catalytic activity for the hydroamination of **1** in toluene at 110 °C corresponds to a Pt(II)−NaY sample calcined at 200 °C for 48 h.

The possible leaching of catalytically active Pt species into solution was evaluated for Pt(II)-NaY by the hot filtration test, showing that the liquid phase accounts for 11% of the catalytic activity after filtration of the solid catalyst at ~35% conversion, which is within the range of the noncatalyzed thermal cyclization (blank experiment, 8% conversion, Figure S26). ICP-AES analyses showed that <0.01% of Pt was present in the liquid phase, and elemental analysis of the recovered Pt(II)-NaY solid confirmed that Pt remains on the zeolite. These results are in accordance with previous reports on the low level of leaching in zeolite-supported containing noble metals when toluene is the solvent.[14] For the sake of comparison, we also supported by impregnation the soluble $PtCl_2$−alkyne species dislodged from $PtCl_2$ on zeolite NaY, and we found a complete leaching of the active Pt catalyst to the solution during the hydroamination reaction. These results illustrate the stability of the Pt(II) species supported on Pt(II)–NaY during reaction, without losses of precious metal.

Other Pt-supported catalysts including Pt on carbon and Pt supported on alumina or silica–alumina gave TOF values <10 h^{-1}.

Influence of the Zeolite. The Lewis acidity of the Pt(II) atoms bound to the oxygen atoms of the zeolite walls is controlled by the electronic density of the zeolite network;[15] thus, in principle we could increase the Lewis acidity of the Pt(II) sites in electronically deficient zeolite frameworks.[12] Figure 6 shows a slight shift of the peaks corresponding to the Pt(II) Lewis sites to higher wavenumber values (more acidic) in the different Pt(II)-zeolites, in the order HY > NaY > KY, using pyridine as a probe molecule together with infrared spectroscopy measurements (for detailed temperature-programmed spectra see Figure S27), with a relatively similar number of total Pt(II) Lewis sites. Thus, it seems that the acid strength of the NH_3-free Pt(II) sites increases after decreasing the electron density of the zeolite by changing the charge-compensating cation (from K^+ to H^+). Notice that Brønsted sites are significant only in Pt(II)–HY (see Figure S27).

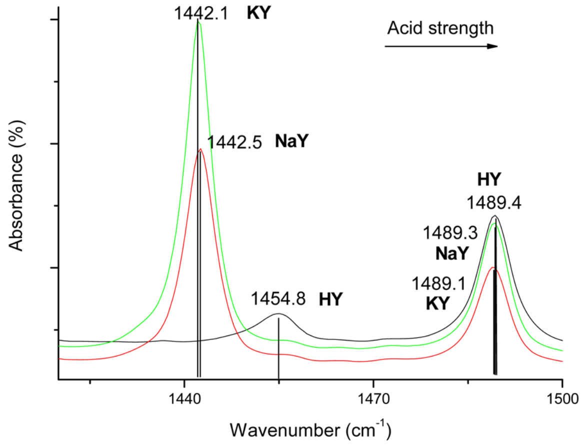

Figure 6. Comparison of the acidity of Pt(II)–HY, Pt(II)–NaY, and Pt(II)–KY by pyridine-desorption IR spectroscopy at 150 °C, under vacuum, for samples previously calcined at 200 °C.

If the energy of the lower unoccupied molecular orbital (LUMO) of Pt(II) is decreased by modifying the average Madelung electronegativity of the zeolite,[16] the catalytic activity of Pt(II) in an orbital-controlled reaction such as the Lewis-catalyzed hydroamination of alkynes should improve. Figure 5 shows that, indeed, the catalytic activity increases for electronically deficient zeolites, with the maximum catalytic activity found for zeolite Pt(II)–HY (TOF = 375 h^{-1}). Blank experiments showed that the zeolite HY without Pt is inactive toward the hydroamination reaction.

Scope of Pt(II)– and Pd(II)–Zeolite Y in Hydroaddition Reactions. Considering the hydroamination of **1** catalyzed by Pt(II)–Y zeolite as a proof of concept for other hydroaddition reactions, it could be expected that Pt(II)–Y would be a good catalyst not only for other alkynes but also for other nucleophiles, alkenes, and metals. Figure 7 shows the scope for some Lewis-acid-catalyzed hydroadditions to alkenes and alkynes, and indeed, different aromatic aminoalkynes (products **3–6**, **9–12**, and **14**), amidoalkynes (**7–8** and **13**), alkynols (**15–16**), and one diene (**17**) cyclize well in excellent isolated yields with a TON and TOF_0 up to 10 000 and 32 700 h^{-1}, respectively, the highest reported as far as we know for these hydroaddition reactions.[3] Particularly relevant are indoles **9–12**, which are key intermediates during the synthesis of the widely used drug indomethacin and analogues (see Figure S28 for the complete syntheses). The Pt(II)–NaY can be recycled up to 10 times with high yields after 24 h reaction time (Figure S29 for kinetics). After each use, the zeolite was extracted with dichloromethane under microsoxhlet conditions to give ~5 wt % of retained product, giving a mass balance >95%.

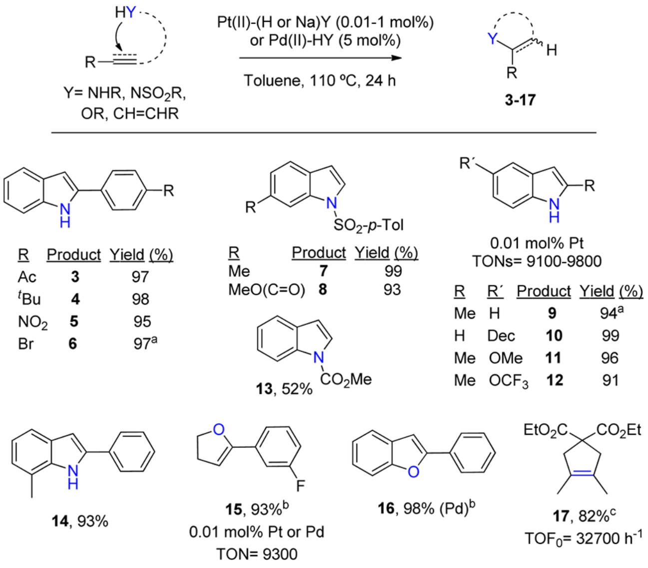

Figure 7. Hydroadditions to alkynes catalyzed by Pt(II)–NaY. Isolated yields, 1 mol% of Pt otherwise indicated. [a] Indicates Pt(II)–NaY reused 3 times. [b] Indicates Pt(II)–HY used as a catalyst. [c] Indicates Pd(II)–HY reused 8 times, TOF_0 for the first use.

Notice that Pt–HY was not used as a general catalyst for the hydroamination of alkynes since the Brønsted-catalyzed hydration to form the ketone occurs at some extent, and this problem could not be alleviated by further drying the zeolite since, then, reduction of Pt(II) occurs. In the case of 1,6-dienes, Pd–HY was prepared in the same way that Pt–HY was, characterized (Figure S30) and used as a catalyst to give a good yield of **17** after 8 reuses (Figure S31). In this case, the expected primary asymmetric cyclized product[17] gradually isomerizes to the symmetric cycle by the action of the Brønsted sites of the zeolite. This result demonstrates that the synthesis of dispersed noble metal cations in zeolites for hydroaddition reactions can be applied to other metals rather than Pt.

■ CONCLUSIONS

Finely dispersed Pt(II) or Pd(II) within zeolite Y circumvents the low efficiency of precious metal chlorides in a variety of hydroaddition reactions. Electrophilic alkyne activation has enormous potential in the synthesis of heterocycles, and given the importance of those in agrochemistry and pharma, the results shown here should greatly help to make this versatile chemistry more practical and bring it closer to applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07304.

General information, experimental procedures, characterization of starting materials and products with NMR spectra, and additional Figures S1−S31 with comments (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Selected reviews: (a) Müller, T. E.; Beller, M. *Chem. Rev.* **1998**, *98*, 675. (b) Pohlki, F.; Doye, S. *Chem. Soc. Rev.* **2003**, *32*, 104. (c) Fürstner, A.; Davies, P. W. *Angew. Chem., Int. Ed.* **2007**, *46*, 3410. (d) Chianese, A. R.; Lee, S. J.; Gagné, M. R. *Angew. Chem., Int. Ed.* **2007**, *46*, 4042. (e) Wu, X.−F.; Anbarasan, P.; Neumann, H.; Beller, M. *Angew. Chem., Int. Ed.* **2010**, *49*, 9047. (f) Leyva-Pérez, A.; Corma, A. *Angew. Chem., Int. Ed.* **2012**, *51*, 614. (g) Fürstner, A. *Acc. Chem. Res.* **2014**, *47*, 925.

(2) Selected publications concerning $PtCl_2$-catalyzed reactions: (a) Chatani, N.; Furukawa, N.; Sakurai, H.; Murai, S. *Organometallics* **1996**, *15*, 901. (b) Fürstner, A.; Szillat, H.; Gabor, B.; Mynott, R. *J. Am. Chem. Soc.* **1998**, *120*, 8305. (c) Fürstner, A.; Davies, P. W. *J. Am. Chem. Soc.* **2005**, *127*, 15024. (d) For one of the most active molecular ligand modified $PtCl_2$-catalyzed systems, see: Carreras, J.; Patil, M.; Thiel, W.; Alcarazo, M. *J. Am. Chem. Soc.* **2012**, *134*, 16753.

(3) Müller, T. E.; Hultzsch, K. C.; Yus, M.; Foubelo, F.; Tada, M. *Chem. Rev.* **2008**, *108*, 3795.

(4) (a) Brook, M. A. *Silicon in Organic, Organometallic, and Polymer Chemistry*; Wiley Interscience: New York, 2000. (b) Marciniec, B. *Hydrosilylation: A Comprehensive Review on Recent Advances*; Springer Science: The Netherlands, 2008; Vol. *1*.

(5) Witham, C. A.; Huang, W.; Tsung, C.−K.; Kuhn, J. N.; Somorjai, G. A.; Toste, F. D. *Nat. Chem.* **2010**, *2*, 36.

(6) (a) Angelici, R. J. Reagents for transition metal complex and organometallic syntheses. In *Inorganic Synthesis*; John Wiley & Sons Inc.: New York, 1990; Vol. *28*, p 346. (b) Unger, D. Y. M.; Molt, O.; Schildknecht, C.; Münster, I.; Wagenblast, G.; Strassner, T.; Meyer, D. *Angew. Chem., Int. Ed.* **2010**, *49*, 10214.

(7) Harrod, J. F.; Chalk, A. J. *Nature* **1965**, *205*, 280.

(8) Speier, J. L.; Webster, J. A.; Barnes, G. H. *J. Am. Chem. Soc.* **1957**, *79*, 974.

(9) When we tried the intermolecular hydroamination between cyclohexylamine and 1-octyne catalyzed by $PtCl_2$, under the indicated reaction conditions in Figure 2, no coupling products were found, but only the transformation of the brown $PtCl_2$ solid into a white precipitate. This precipitate corresponds to the $PtCl_2(CyNH_2)_2$ complex (see Figure 1), and this result suggests that the formation of stable amino Pt(II) chlorides is the reason why the intermolecular hydroamination of alkynes does not proceed with $PtCl_2$.

(10) Corma, A. *J. Catal.* **2003**, *216*, 298.

(11) de Graaf, J.; van Dillen, A. J.; de Jong, K. P.; Koningsberger, D. C. *J. Catal.* **2001**, *203*, 307.

(12) Oudenhuijzen, M. K.; van Bokhoven, J. A.; Miller, J. T.; Ramaker, D. E.; Koningsberger, D. C. *J. Am. Chem. Soc.* **2005**, *127*, 1530.

(13) Cabrero-Antonino, J. R.; Leyva-Pérez, A.; Corma, A. *Angew. Chem., Int. Ed.* **2015**, *54*, 5658.

(14) (a) Dams, M.; Drijkoningen, L.; Pauwels, B.; Van Tendeloo, G.; De Vos, D. E.; Jacobs, P. A. *J. Catal.* **2002**, *209*, 225. (b) Corma, A.; Garcia, H.; Leyva, A. *Appl. Catal., A* **2002**, *236*, 179. (c) Corma, A.; Garcia, H.; Leyva, A.; Primo, A. *Appl. Catal., A* **2003**, *247*, 41. (d) Li, Y.; Liu, J. H.−C.; Witham, C. A.; Huang, W.; Marcus, M. A.; Fakra, S. C.; Alayoglu, P.; Zhu, Z.; Thompson, C. M.; Arjun, A.; Lee, K.; Gross, E.; Toste, F. D.; Somorjai, G. A. *J. Am. Chem. Soc.* **2011**, *133*, 13527.

(15) Corma, A.; Garcia, H.; Leyva, A. *J. Catal.* **2004**, *225*, 350.

(16) Dempsey, E. *J. Phys. Chem.* **1969**, *73*, 3660.

(17) Widenhoefer, R. A. *Acc. Chem. Res.* **2002**, *35*, 905.