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Dehalogenation and Hydrogenation of Aromatic Compounds Catalyzed by Nanoparticles Generated from Rhodium Bis(imino)pyridine Complexes[§]

María L. Buil,[†] Miguel A. Esteruelas,*[,†] Sandra Niembro,[‡] Montserrat Oliván,[†] Lars Orzechowski,[†] Cristina Pelayo,[†] and Adelina Vallribera[‡]

[†]*Departamento de Química Inorgánica-Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain, and* [‡]*Departamento de Química, Universitat Autònoma de Barcelona, Cerdanyola del Vallès, 08193 Barcelona, Spain*

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Chloro[2,6-bis{1-(phenyl)iminoethyl}pyridine]rhodium(I) complexes (RhCl(N,N,N); **1**−**11**) have been prepared by reaction of the dimer $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$ with the corresponding nitrogen donor ligand. These complexes afford nanoparticles with a mean diameter of 1.5 ± 0.2 nm stabilized by the partially hydrogenated ligand, under 1 atm of hydrogen, in 2-propanol as solvent, at 60 °C, and in the presence of K^{t}BuO. Under a constant atmospheric pressure of hydrogen, the nanoparticles catalyze the dehalogenation of the chlorobenzene 1,2-, 1,3-, and 1,4-dichlorobenzene, 1,2,4-trichloro benzene, fluorobenzene, 2-, 3-, and 4-chlorobiphenyl, and 4,4′- and 3,5-dichlorobiphenyl and the hydrogenation of benzene, toluene, *p*-xylene, styrene, α-methylstyrene, biphenyl, aniline, phenol, and pyridine. A Hg(0) poisoning test reveals that homogeneous and heterogeneous catalysis coexist during the dehalogenation reactions, whereas the hydrogenation processes are heterogeneous. The nanoparticles can be also generated in the presence of basic aluminum oxide of 150 mesh, which at the same time acts as a support. When they are deposited on the alumina, the nanoparticles do not significantly modify their catalytic activity.

Introduction

The hydrogenolysis of C−Cl bonds of aromatic compounds is a reaction of great interest from both environmental and chemical points of view.[1] The accumulation of chloroarenes in the environment, in particular polychlorobiphenyls (PCBs),[2] is a serious health hazard, and their dehalogenation must be therefore a high-priority target. Hydrogenolysis of a C−Cl bond with deuterium has been employed for selectively labeling the corresponding position of the ring with this isotope.[3] The use of chlorine as a protecting group offers the opportunity to alter the orientation rules of aromatic electrophilic substitution.[4] Catalytic hydrodechlorination is usually mediated by transition metals, mainly Ru, Rh, Ni, Pd, and Pt, and performed with molecular hydrogen,[5] silanes,[6] alcohols,[7] cyclic amines,[8] dimethylformamide,[9] metal hydrides,[10] metal alkoxides,[11] sodium borohydride,[12] alkyl Grignard reagents,[13] and formic acid and its salts.[14]

The hydrodechlorination of chloroarenes is sometimes followed by hydrodearomatization of the dehalogenated aromatic compound.[15] The hydrogenation of benzene and

[§] Dedicated to Prof. Carmen Nájera on the occasion of her 60th birthday.

*To whom correspondence should be addressed. E-mail: maester@unizar.es.

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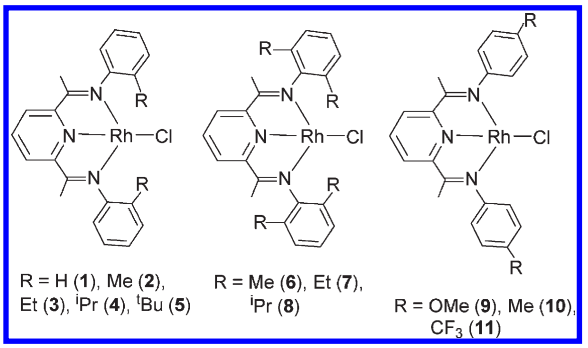
substituted aromatic compounds to the corresponding cyclohexyl derivatives is a goal of notable industrial interest.[16] Arene hydrogenation has also generated environmental interest[17] due to the demand for cleaner-burning low-aromatic-content diesel fuel, which has been stimulated in part by the discovery that diesel exhaust particles contain powerful carcinogens, and in relation to the hydrogen storage.[18] The greater number of arene hydrogenation catalysts are based on platinum-group metals.[19] While the majority are heterogeneous, it is conceivable that all of the so-called homogeneous catalysts are actually precursors to heterogeneous catalysts. Typical heterogeneous catalysts comprise metals supported on fixed beds, generally operated under harsh conditions,[20] or metal colloids or nanoparticles, which can be used under mild conditions.[21] A number of molecular compounds have been reported to be homogeneous catalysts. However, many have since been shown to be precursors to heterogeneous systems.[22]

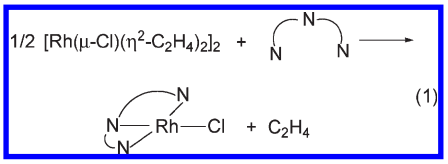
Chart 1



For a number of years we have been interested in developing new methods for the dehalogenation of both polychlorinated arenes and cycloalkanes.[23] During the course of these investigations we have found that rhodium complexes bearing bis(imino)pyridine ligands generate rhodium nanoparticles, which catalyze the dehalogenation of aromatic compounds, including PCBs, and the hydrogenation of benzene and functionalized aromatic compounds. Related rhodium complexes have previously proven to be catalyst precursors for the homologation of aromatic aldehydes with (trimethylsilyl)diazomethane[24] and for hydrosilylation, Mukaiyama aldol, and cyclopropanation reactions.[25]

Results and Discussion

1. Preparation of the Rhodium Catalyst Precursors. Treatment at room temperature of toluene solutions of the dimer $[Rh(\mu\text{-}Cl)(\eta^2\text{-}C_2H_4)_2]_2$ with 2.0 equiv of the corresponding 2,6-bis{1-(phenyl)iminoethyl}pyridine[26] ligand (N,N,N) for 6 h leads to the rhodium(I) derivatives RhCl(N,N,N) (**1**−**11**), according to eq 1.



They were isolated as dark green solids in excellent yields (80−98%) and were characterized by elemental analysis, FAB mass spectrometry, and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. On the basis of the substituted positions on the phenyl groups of the bis(imino)pyridine ligands, they can be classified in three different categories (Chart 1): (i) substituted in one ortho position (complexes **2**−**5**), (ii) substituted

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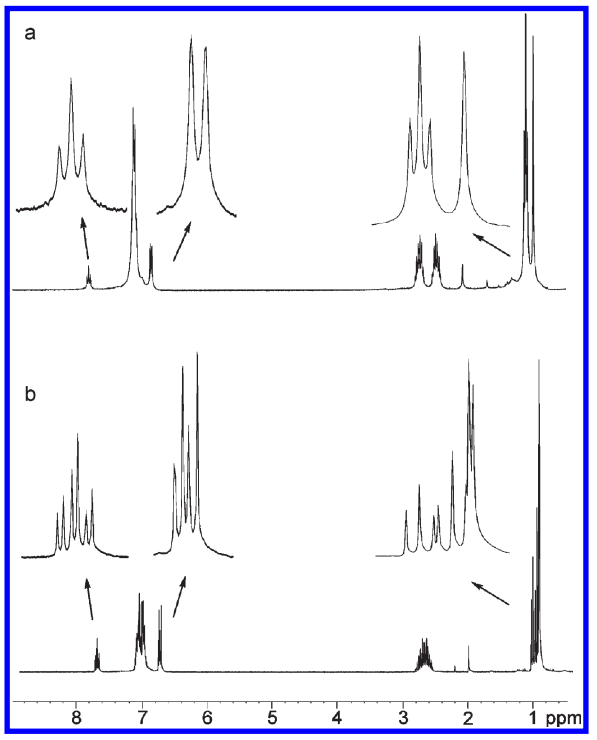
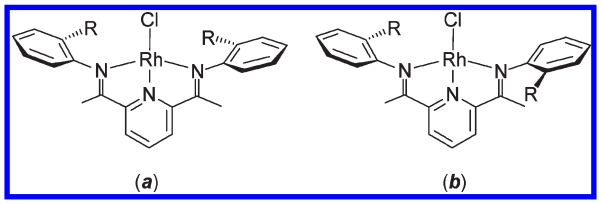


Figure 1. ^{1}H NMR spectra of complexes **7** (a) and **3** (b) in C_6D_6. The enlargements of the peaks of both aromatic and aliphatic regions of the spectra show the presence of two isomers for complex **3**.

Chart 2



in both ortho positions (complexes **6**−**8**), and (iii) substituted at the para position (complexes **9**−**11**). The ortho alkyl substituents seem to exercise a protective effect on the complex. Thus, while compounds **2**−**8** are moderately stable in air, complexes **1** and **9**−**11** are very air sensitive and need to be handled under rigorous exclusion of air.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of **1** and **6**−**11** are consistent with a square-planar C_{2v}-symmetrical ligand. Figure 1a shows the ^{1}H NMR spectrum of **7**. However, in the ^{1}H and ^{13}C{^{1}H} NMR spectra of complexes **2**−**5**, which derive from bis(imino)pyridine ligands with both phenyl groups substituted at one ortho position, two sets of peaks for each resonance are observed. Figure 1b shows the ^{1}H NMR spectrum of complex **3**.

The ^{1}H and ^{13}C{^{1}H} NMR spectra of the ortho-monosubstituted complexes **2**−**5** can be explained in terms of the existence in solution of the isomers ***a*** and ***b*** shown in Chart 2. Isomer ***a*** has C_s symmetry, and both substituents are situated in the same face of the plane defined by the pyridyl group, the rhodium atom, and the chlorine ligand, while in isomer ***b*** each substituent is situated on one face. In contrast to what is observed for other transition-metal complexes containing 2,6-bis{1-(phenyl)iminoethyl}pyridine ligands with asymmetrically substituted phenyl groups,[27] the isomer interconversion is slow on an NMR time scale, even at 80 °C, as is demonstrated by the ^{1}H NMR spectra performed at this temperature, which are the same as those at room temperature. Using a molecular model, it is possible to see how the rotation around the N−C_{ipso} bonds is blocked by steric hindrance between both phenyl groups and the chlorine ligand.

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Scheme 1

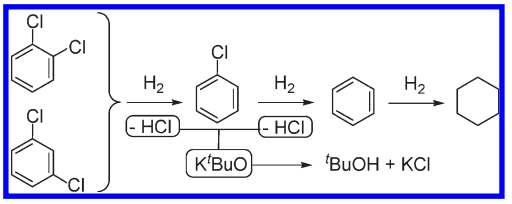


Table 1. Dehalogenation of Chloroarenes with K^{t}BuO/H_2 in the Presence of RhCl(N,N,N)[a]

Run	Catalyst precursor	substrate	Time (min)	Products		
						
1	**1** (*p*-H)		30	-	50	-
2	**2** (o-Me)		30	-	86	-
3	**3** (*o*-Et)		30	-	60	-
4	**4** (*o*-^{i}Pr)		30	-	71	-
5	**5** (*o*-^{t}Bu)		15	-	90	-
6	**9** (*p*-OMe)		30	-	65	
7	**10** (*p*-CH_3)		30	-	95	-
8	**11** (*p*-CF_3)		15	-	100	-
			200	-	45	55
9	**3** (*o*-Et)		30	13	47	-
			200	-	89	11
10	**4** (*o*-^{i}Pr)		30	19	36	-
			200	-	81	19
11	**5** (*o*-^{t}Bu)		30	13	87	-
			200	-	75	25
12	**11** (*p*-CF_3)		30	-	100	-
13	**2** (*o*-Me)		30	6	94	-
14	**4** (*o*-^{i}Pr)		30	40	20	-
			200	-	79	21
15	**11** (*p*-CF_3)		30	-	100	-

[a] Conditions: 60 °C; 0.024 mmol of catalyst precursor, 1.2 mmol of chlorinated arene; 1.2*x* mmol of K^{t}BuO (*x* being the number of chlorine atoms of the halogenated substrate), 5 mL of 2-propanol, 1 atm of H_2. Yields were determined by GC analyses.

2. Dehalogenation of Aromatic Compounds. Complexes **1**−**5** and **9**−**11** are efficient catalyst precursors for the hydrogenolysis of the C−Cl bonds of chlorobenzene, 1,2-dichlorobenzene, and 1,3-dichlorobenzene. The reactions were carried out under a constant atmospheric pressure of hydrogen, in 2-propanol as solvent, at 60 °C, using 2% mol of catalyst precursor, and in the presence of the stoichiometric amount of K^{t}BuO in order to neutralize the HCl

generated during the hydrogenolysis (Scheme 1). Under these conditions, benzene is formed in high yield after short reaction times (Table 1). Once the dehalogenation has taken place, the reduction of benzene to cylohexane is observed at rates significantly slower than those for the hydrogenolysis (Table 1, runs 8−11 and 14), in agreement with other tandem processes of this type.[15a−d,f−h]

The best catalyst precursor is complex **11** (runs 8, 12, and 15), containing a *p*-CF_3 substituent at the phenyl groups of the 2,6-bis{1-(phenyl)iminoethyl}pyridine ligand. With this complex, the quantitative dehalogenation of chlorobenzene occurs after 15 min (run 8), whereas those of 1,2- and 1,3-dichlorobenzene take place after 30 min (runs 12 and 15). The catalyst precursor keeps whole its activity for at least four loads of substrate.

The formation of a dark precipitate is observed during the reactions. This, along with the hydrogenation of benzene to cyclohexane, does not seem to be consistent with a homogeneous catalytic process. Therefore, in order to distinguish homogeneous catalysis from heterogeneous catalysis, we performed a Hg(0) poisoning test[19a] by adding 1 mL of Hg(0) (2820 equiv/equiv of Rh) to a well-stirred solution. Figure 2 shows the course of the dehalogenation−hydrogenation of chlorobenzene in the presence of complex **11**, both in the absence of mercury (a) and with mercury in the medium (b). As can be observed, the addition of Hg(0) produces a decrease of the initial hydrogenolysis rate, which falls to zero

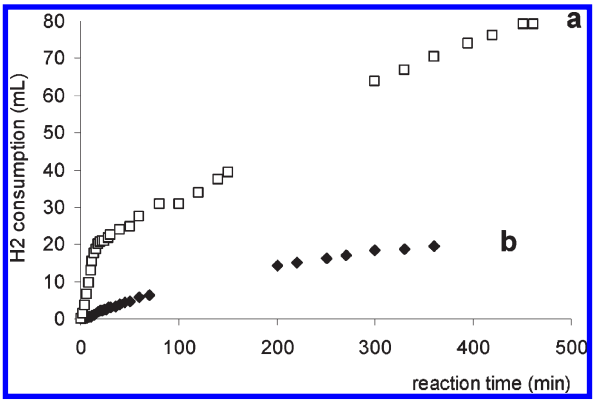


Figure 2. Hydrogen consumption (mL) vs time (min) in the catalytic dehalogenation−hydrogenation of chlorobenzene (1.2 mmol) with catalyst precursor **11** (0.024 mmol) and K^{t}BuO (1.2 mmol) in 2-propanol (5 mL) at 60 °C and 1 atm of H_2: (a) in the absence of Hg; (b) in the presence of added Hg.

when about 60% of the substrate has been dehalogenated, and inhibits the hydrogenation of benzene to cyclohexane. This suggests the coexistence of homogeneous and heterogeneous catalysis during the dehalogenation reaction while, as expected, the benzene hydrogenation appears to be a heterogeneous process.[19a,22] During the dehalogenation process, the reduction of **11** takes place. Both the reduced metal, in a heterogeneous manner, and the molecular complex or/and the molecular intermediate species of the reduction process, in a homogeneous manner, appear to catalyze the halogen abstraction. According to Figure 2, the amount of substrate dehalogenated in an homogeneous manner in the absence of Hg(0) should not be higher than 15%.

In an effort to gain insight into the nature of the true catalyst, complex **11** was stirred under catalytic conditions in the absence of substrate. After 7 h, the formed suspension was filtered off. The catalytic inactivity of the resulting solution was verified, and the solid was characterized by transmission electron microscopy (TEM). The technique revealed the presence of small and homogeneously dispersed nanoparticles (Figure 3) showing a quite narrow size distribution around a mean diameter of 1.5 ± 0.2 nm. We note that some rhodium organometallic precatalysts under the TEM beam are shown to form nanoclusters.[22d,e] However, typically those colloids are not as well dispersed as the nanoparticles seen herein. The nanoparticles are partially soluble in chloroform-*d*. Their ^{1}H NMR spectrum at room temperature shows aromatic resonances between 7.6 and 6.3 ppm and aliphatic signals between 2.3 and 0.5 ppm, whereas the $^{19}F\{^1H\}$ NMR spectrum contains a singlet at −61.1 ppm, characteristic of a CF_3 group. These spectra suggest that the presence of a partially hydrogenated bis(imino)pyridine ligand stabilizes the nanoparticles. Rhodium nanoparticles stabilized by 2,2′-, 3,3′-, and 4,4′-bipyridines have been shown to be efficient for arene catalytic hydrogenation in ionic liquids.[22f,g]

Table 2 collects the results obtained for the dehalogenation of other halogenated aromatic compounds, using complex **11** as a catalyst precursor. Under the same conditions as those used for the dehalogenation of chlorobenzene and 1,2- and 1,3-dichlorobenzene, the dehalogenation of 1,4-dichlorobenzene and 1,2,4-trichlorobenzene also takes place. The dehalogenation of 1,4-dichlorobenzene is slower than that of the 1,2- and 1,3-isomers. Thus, after 45 min 19% of chlorobenzene still remains in the catalytic solution (run 1). After 400 min, the chlorine abstraction is quantitative and 14% of benzene is reduced to cyclohexane. The dehalogenation of 1,2,4-trichlorobenzene (run 2) occurs at a rate similar to that

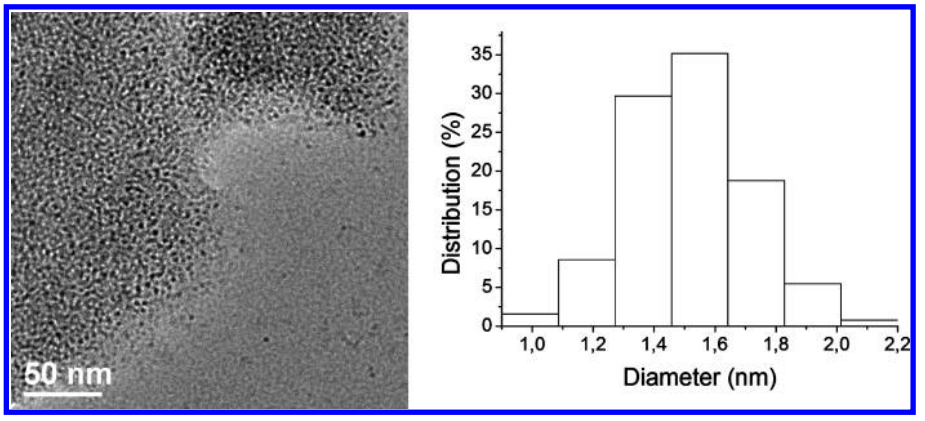
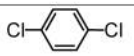
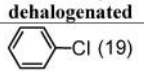
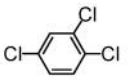
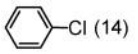
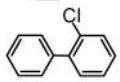
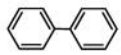
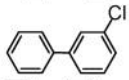
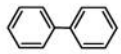
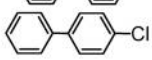
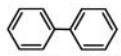
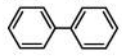
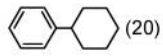
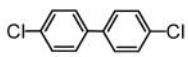
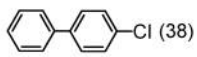
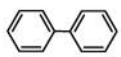
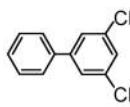
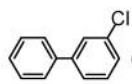
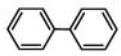


Figure 3. TEM image (left) and particle size distribution histogram (right) of the nanoparticles generated from complex **11**.

Table 2. Dehalogenation of Polychloroarenes and Fluorobenzene with K^{t}BuO/H_2 in the Presence of Catalyst Precursor 11[a]

Run	Substrate	Time (min)	Products (%) Partially dehalogenated	Dehalogenated	Hydrogenated
1		45	 (19)	 (81)	-
		200	-	 (86)	 (14)
2		45	 (14)	 (86)	-
		400	-	 (73)	 (27)
3		50	-	 (100)	-
4		100	-	 (100)	-
5		115	-	 (100)	-
6		55	-	 (100)	-
		400	-	 (80)	 (20)
7		300	 (38)	 (30)	-
8		300	 (35)	 (23)	-

[a] Conditions: 60 °C, 0.024 mmol of catalyst precursor, 1.2 mmol of chlorinated arene, 1.2x mmol of K^{t}BuO (x being the number of chlorine atoms of the halogenated substrate), 5 mL of 2-propanol, 1 atm of H_2. Yields were determined by GC analyses.

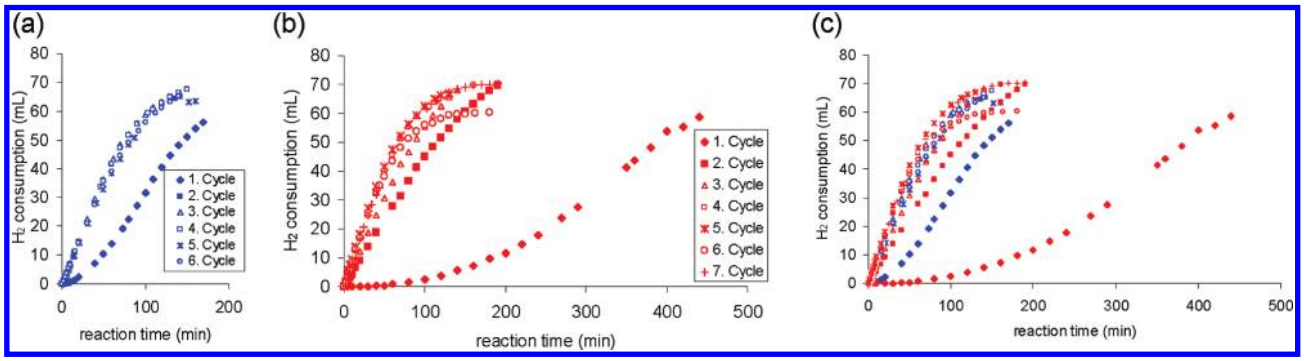


Figure 4. (a) Plots of the hydrogen consumption (mL) vs time (min) during six runs of hydrogenation of benzene to cyclohexane (1 atm of H_2, 2-propanol, 60 °C) catalyzed by 2 mol % of catalyst precursor **11** and K^{t}BuO (10% mol). (b) Plots of the hydrogen consumption (mL) vs time (min) during seven runs of hydrogenation of benzene to cyclohexane (1 atm of H_2, 2-propanol, 60 °C) catalyzed by 2 mol % of catalyst precursor **11** and Al_2O_3. (c) Comparison of the catalytic performance of the systems formed by catalyst precursor **11**/K^{t}BuO (blue) and **11**/Al_2O_3 (red).

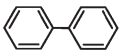
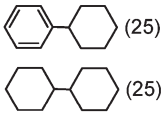
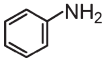
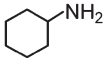
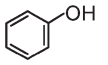
of the dehalogenation of 1,4-dichlorobenzene. Fluorobenzene is also efficiently dehalogenated (run 3). Carbon−fluorine bonds are stronger than carbon−chlorine bonds.[28] In agreement with this, the hydrogenolysis of fluorobenzene is slightly slower than that of chlorobenzene. The quantitative formation of benzene from fluorobenzene requires 50 min.

Complex **11** is also an efficient catalyst precursor for the dehalogenation of 2-, 3-, and 4-chlorobiphenyl and 4,4′- and 3,5-dichlorobiphenyl. The monochlorinated substrates are transformed into biphenyl in quantitative yield after 100 (run 4), 115 (run 5), and 55 min (run 6). After 400 min, 20% of biphenyl is reduced to cyclohexylbenzene and dicyclohexyl is also formed after longer reaction times. The dehalogenation of the dichlorobiphenyls occurs by stages via the corresponding chlorobiphenyl (runs 7 and 8). Thus, after 300 min between 58% and 68% of the substrates were dehalogenated to chlorobiphenyl (35−38%) and biphenyl (23−30%).

3. Hydrogenation of Aromatic Compounds. Figure 4a summarizes the course of the hydrogenation of benzene to cyclohexane at a constant atmospheric pressure of hydrogen, at 60 °C, in the presence of a 2 mol % mixture of complex **11** and K^{t}BuO in a 1:5 molar ratio, and using 2-propanol as solvent. In agreement with a heterogeneous process, the reaction shows an induction period corresponding to the formation of the small nanoparticles, which act as a solid catalyst. The transformation of the molecular complex into nanoparticles is quantitative when the first load of substrate

(28) Smart, B. E. In *The Chemistry of Functional Groups*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1983; Suppl. D, Chapter 14.

Table 3. Hydrogenation of Aromatic Substrates with Catalyst Precursor 11/K^{t}BuO[a]

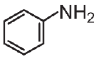
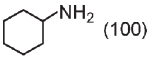
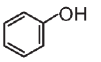
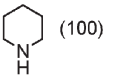
Run	Substrate	Time (min)	Product (%)	TOF[b]
1		200	 (100)	45
2		400	 (93)	21
3		400	 (31)	7
4		2	 (100)	1500
		380	 (67)	21
5		5	 (100)	600
		455	 (53)	14
6		580	 (25) (25)	
7		270	 (100)	33
8		300	 (100)	30
9		65	 (100)	138

[a] Reaction conditions: 0.024 mmol of RhCl{N,N,N-*p*-$(CF_3)_2$}, 0.12 mmol of K^{t}BuO, 5 mL of 2-propanol, 1 h of preactivation under a H_2 atmosphere (1 atm), 60 °C. The aromatic substrate (1.2 mmol) was then added, and the hydrogen consumption was measured. [b] Turnover frequency defined as mol of H_2/((mol of rhodium) h).

has been reduced. Thus, the reduction process is faster during the second load and the activity that is reached is entirely kept at least during the following five loads.

The rhodium nanoparticles can be also generated in the absence of an aromatic substrate, by means of the preactivation for 1 h of the catalytic mixture under constant atmospheric hydrogen pressure at 60 °C. The suspension generated in this way catalyzes the reduction of benzene, substituted benzenes, functionalized benzenes such as aniline and phenol, and pyridine (Table 3). Benzene is reduced to cyclohexane in quantitative yield after 200 min (run 1), whereas toluene (run 2) and *p*-xylene (run 3) give the corresponding cycloalkanes in 93% and 31% yields, respectively, after 400 min. The exocyclic carbon−carbon double bonds of styrene (run 4) and α-methylstyrene (run 5) are hydrogenated more quickly than the aromatic rings. Ethylbenzene and cumene are formed in quantitative yield after 2 and 5 min, while ethylcyclohexane and isopropylcyclohexane are generated in 67% and 53% yields after 380 and 480 min, respectively. Biphenyl is hydrogenated to cyclohexylbenzene and dicyclohexyl, both in 25% yield, after 580 min (run 6). These results show that the steric demand of the substituents of benzene prevents the reduction of the aromatic ring, probably as a result of the hindrance experienced by the substituents of the aromatic ring and the nanoparticle stabilizer. Aniline is reduced to cyclohexylamine in quantitative yield after 270 min (run 7). Phenol gives cyclohexen-1-ol as result of the hydrogenation of two carbon−carbon double bonds of the aromatic ring. In the basic reaction medium, the enol tautomerizes and cyclohexanone is formed in quantitative yield after 300 min (run 8). The reduction of pyridine is faster than those of aniline and phenol. Thus, after 65 min piperidine is obtained in quantitative yield (run 9).

Table 4. Hydrogenation of Aromatic Substrates with Catalyst Precursor 11/Al_2O_3[a]

Run	Substrate	Time (min)	Product (%)	TOF[b]
1		400	 (100)	23
2		420	 (51)	11
3		420	 (13)	3
4		3	 (100)	1000
		260	 (14)	6
5		14	 (100)	214
		300	 (20)	8
6		350	 (100)	26
7		300	 (98)	29
8		120	 (100)	75

[a] Reaction conditions: 0.024 mmol of RhCl{N,N,N-*p*-$(CF_3)_2$}, 122.4 mg of Al_2O_3, 5 mL of 2-propanol, 1 h of preactivation under a H_2 atmosphere (1 atm), 60 °C. The aromatic substrate (1.2 mmol) was then added, and the hydrogen consumption was measured. [b] Turnover frequency defined as mol of H_2/((mol of rhodium) h).

The versatility of this catalytic system prompted us to deposit the nanoparticles on a support. We selected basic aluminum oxide of 150 mesh (Al_2O_3), since it is a Brønsted base as K^{t}BuO, is easily accessible, is cheap, and is the usual support in heterogeneous catalysis. Figure 4b summarizes the course of the hydrogenation of benzene to cyclohexane at a constant atmospheric pressure of hydrogen, at 60 °C, in the presence of a 2 mol % mixture of complex **11** and Al_2O_3 in a 1:8.7 weight ratio, and using 2-propanol as solvent. As in the presence of K^{t}BuO, the reduction shows an induction period corresponding to the generation of the nanoparticles, which are deposited on the alumina. After the reduction of the first load of substrate, the deposition process is finished. Thus, the reduction of the second load of substrate is faster than the first one and, in a manner similar to the reduction in the presence of K^{t}BuO, the reached catalytic activity is entirely kept at least during the following five loads. Interestingly, although the hydrogenation of the first load of substrate in the presence of Al_2O_3 is slower than in the presence of K^{t}BuO, the reached activity from the second to the seventh load is the same in both cases (Figure 4c).

Table 4 collects the results obtained for the reductions of benzene, substituted benzenes, functionalized benzenes, and pyridine catalyzed by the suspension generated in the absence of the substrates by means of the preactivation for 1 h of a mixture of complex **11** and Al_2O_3 in a 1:8.7 weight ratio, under a constant atmospheric pressure of hydrogen at 60 °C. Although the hydrogenations are slightly slower than those shown in Table 3, in agreement with a longer activation

period of the catalytic system, these results demonstrate that (i) the nanoparticles can also be generated with Al_2O_3 instead of K^{t}BuO and (ii) the nanoparticles supported on Al_2O_3, in addition to being more handy, do not significantly modify their catalytic activity.

Concluding Remarks

This study has revealed that the complex [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ reacts with 2,6-bis{1-(phenyl)iminoethyl}pyridines to give rhodium(I) derivatives, which afford small nanoparticles with a mean diameter of 1.5 ± 0.2 nm under a hydrogen atmosphere and in the presence of a Brønsted base. These nanoparticles, which are stabilized by the partially hydrogenated bis(imino)pyridine ligand, catalyze the dehalogenation and hydrogenation of aromatic compounds under mild conditions, at a atmospheric pressure of hydrogen, and at 60 °C. The nanoparticles can be deposited on alumina. Under these conditions, they do not significantly modify their catalytic activity.

Experimental Section

All reactions were done either in a drybox or under argon using standard Schlenk techniques. Solvents were dried by known procedures and distilled under argon prior to use. C, H, and N analyses were measured on a Perkin-Elmer 2400 CHNS/O analyzer. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Varian Gemini 2000, Bruker ARX 300, or Bruker Avance 400 spectrometer. Chemical shifts are referenced to residual solvent peaks or external $CFCl_3$ (^{19}F). Coupling constants are given in hertz. All peaks in the ^{13}C{^{1}H} NMR spectra are singlets, unless otherwise stated. Mass spectral analyses were performed with a VG Auto Spec instrument. [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$,[29] **6**,[30] **8**,[31] **9**,[32] and the bis(imino)pyridine ligands[33] were prepared as previously reported.

Physical Measurements. The catalytic reactions were followed, at constant pressure, by measuring the hydrogen consumption as a function of time on a gas buret (Afora 516256) connected to a hydrogen gas reservoir. The analyses of the products of the catalytic reactions were carried out on a HP5890 II series gas chromatograph with a flame ionization detector, using a 100% cross-linked methylsilicone gum column (25 m × 0.32 mm, with 0.17 μm film thickness) and *n*-octane as internal standard. The oven conditions used are as follows: 50 °C (hold 4 min) to 250 at 25 °C/min (hold 3 min). The reaction products were identified by comparison of their retention times with those observed for pure samples and by GC-MS experiments run on an Agilent 5973 mass selective detector interfaced to an Agilent 6890 series gas chromatograph system. Samples were injected into a 30 m × 250 μm HP-5MS 5% phenylmethylsiloxane column with a film thickness of 0.17 μm (Agilent). The GC oven temperature was programmed as follows: 35 °C for 6 min, 35−280 °C at 25 °C/min, 280 °C for 4 min. The carrier gas was helium at a flow of 1 mL/min.

Transmission electron microscopy (TEM) analyses were performed at the Servei de Microscòpia of the Universitat Autònoma de Barcelona, using a JEOL JEM-2010 model at 200 kV. The TEM measurements were made by sonication of the nanoparticulated material in ethanol for several minutes; then, one drop of the finely divided suspension was placed on a specially produced structureless carbon support film having a thickness of 4−6 nm and dried before observation.

Preparation of RhCl[2,6-bis-{1-(phenyl)iminoethyl}pyridine] (1). 2,6-Bis{1-(phenyl)iminoethyl}pyridine (241 mg, 0.77 mmol) was added to a solution of [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ (150 mg, 0.38 mmol) in toluene, giving a dark green suspension. After the mixture was stirred for 6 h, the solvent was removed, and pentane was added to afford a dark green solid, which was washed repeatedly with pentane and dried in vacuo. Yield: 314 mg (90%). Anal. Calcd for $C_{21}H_{19}ClN_3Rh$: C, 55.83; H, 4.24; N, 9.30. Found: C, 55.55; H, 4.12; N, 9.18. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.75 (t, J_{H-H} = 7.9, 1H, 4-py), 7.42 (d, J_{H-H} = 7.3, 4H, *o*-Ph), 7.18 (t, J_{H-H} = 7.3, 4H, *m*-Ph), 7.05 (t, J_{H-H} = 7.3, 2H, *p*-Ph), 6.76 (d, J_{H-H} = 7.9, 2H, 3,5-py), 0.99 (s, 6H, N=CCH_3). The ^{13}C{^{1}H} NMR spectrum could not be recorded due to the low solubility of the complex in C_6D_6. MS (FAB$^+$): *m*/*z* 416 (M$^+$ − Cl).

Preparation of RhCl[2,6-bis-{1-(2-methylphenyl)iminoethyl}-pyridine] (2). This complex was prepared analogously to complex **1**, starting from 2,6-bis{1-(2-methylphenyl)iminoethyl}-pyridine (263 mg, 0.77 mmol) and [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ (150 mg, 0.38 mmol). Yield: 340 mg (92%). Anal. Calcd for $C_{23}H_{23}ClN_3Rh$: C, 57.57; H, 4.83; N, 8.76. Found: C, 57.18; H, 4.68; N, 8.58. ^{1}H and ^{13}C{^{1}H} NMR spectroscopy revealed the presence of two isomers (ratio 1:1). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.80 and 7.75 (both t, J_{H-H} = 7.9, 1H, 4-py), 7.19−6.98 (m, 8H, Ph), 6.85 and 6.83 (both d, J_{H-H} = 7.9, 2H, 3,5-py), 2.25 and 2.23 (s, 6H, $-CH_3$), 0.97 (s, 6H, N=CCH_3). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz): δ 166.6, 166.5 (C=N), 156.4 and 156.3 (2,6-py), 150.7, 131.0, 130.9, 130.8, 129.3, 126.2, 126.1, 125.6, 124.5, 122.9, 121.9 (Ph and py), 19.1 and 18.9 ($-CH_3$), 17.0 (N=CCH_3). MS (FAB$^+$): *m*/*z* 444 (M$^+$ − Cl).

Preparation of RhCl[2,6-bis{1-(2-ethylphenyl)iminoethyl}pyridine] (3). This complex was prepared analogously to complex **1**, starting from 2,6-bis{1-(2-ethylphenyl)iminoethyl}pyridine (284 mg, 0.77 mmol) and [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ (150 mg, 0.38 mmol). Yield: 372 mg (95%). Anal. Calcd for $C_{25}H_{27}ClN_3Rh$: C, 59.12; H, 5.36; N, 8.27. Found: C, 59.31; H, 5.08; N, 8.16. ^{1}H and ^{13}C{^{1}H} NMR spectroscopy revealed the presence of two isomers (ratio 1:0.9). Major isomer: ^{1}H NMR (C_6D_6, 300 MHz): δ 7.85 (t, J_{H-H} = 7.9, 1H, 4-py), 7.20−7.06 (m, 8H, Ph), 6.91 (d, J_{H-H} = 7.9, 2H, 3,5-py), 2.86−2.70 (m, 4H, $-CH_2-$), 1.05 (s, 6H, N=CCH_3), 1.04 (t, J_{H-H} = 7.5, 6H, $-CH_3$). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz): δ 166.8 (d, J_{Rh-C} = 2, C=N), 156.4 (2,6-py), 149.9, 137.0, 128.8, 126.3, 126.0, 124.8, 123.0, 122.4 (Ph and py), 25.3 ($-CH_2-$), 17.4 (N=CCH_3), 14.1 ($-CH_3$). Minor isomer: ^{1}H NMR (C_6D_6, 300 MHz): δ 7.86 (t, J_{H-H} = 7.9, 1H, 4-py), 7.20−7.06 (m, 8H, Ph), 6.94 (d, J_{H-H} = 7.9, 2H, 3,5-py), 2.86−2.70 (m, 4H, $-CH_2-$), 1.11 (t, J_{H-H} = 7.5, 6H, $-CH_3$), 1.05 (s, 6H, N=CCH_3). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz): δ 166.7 (d, J_{Rh-C} = 2, C=N), 156.2 (2,6-py), 149.9, 136.8, 128.8, 126.3, 126.1, 124.8, 123.0, 122.4 (Ph and py), 25.2 ($-CH_2-$), 17.4 (N=CCH_3), 14.2 ($-CH_3$). MS (FAB$^+$): *m*/*z* 472 (M$^+$ − Cl).

Preparation of RhCl[2,6-bis{1-(2-isopropylphenyl)iminoethyl}-pyridine] (4). This complex was prepared analogously to complex **1**, starting from 2,6-bis{1-(2-isopropylphenyl)iminoethyl}-pyridine (305 mg, 0.77 mmol) and [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ (150 mg, 0.38 mmol). Yield: 362 mg (88%). Anal. Calcd for $C_{27}H_{31}ClN_3Rh$: C, 60.51; H, 6.25; N, 7.84. Found: C, 60.05; H, 6.47; N, 8.04. ^{1}H and ^{13}C{^{1}H} NMR spectroscopy revealed the presence of two isomers (ratio 1:0.3). Major isomer: ^{1}H NMR (C_6D_6, 300 MHz): δ 7.87 (t, J_{H-H} = 7.5, 1H, 4-py), 7.40−7.09 (m, 8H, Ph), 6.95 (d, J_{H-H} = 7.5, 2H, 3,5-py), 3.59 (m, 2H, CH(CH$_3$)$_2$), 1.50 (d, J_{H-H} = 6.9, 6H, CH(CH_3)$_2$), 1.14 (s, 6H, N=CCH_3), 1.08 (d, J_{H-H} = 6.9, 6H, CH(CH_3)$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz): δ 166.5 (C=N), 156.4 (2,6-py), 149.0, 141.8, 126.7, 126.3, 125.9, 124.6, 122.9, 122.2 (Ph and py), 28.5 (CH, ^{i}Pr), 24.2, 23.0 (CH$_3$, ^{i}Pr), 17.4 (N=CCH_3).

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Minor isomer: ^{1}H NMR (C_6D_6, 300 MHz): δ 7.86 (t, J_{H-H} = 7.5, 1H, 4-py), 7.40−7.09 (m, 8H, Ph), 6.92 (d, J_{H-H} = 7.5, 2H, 3,5-py), 3.59 (m, 2H, C*H*(CH_3)$_2$), 1.40 (d, J_{H-H} = 6.9, 6H, CH(C*H*$_3$)$_2$), 1.14 (s, 6H, N=CC*H*$_3$), 1.04 (d, J_{H-H} = 6.9, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz): δ 166.7 (C=N), 156.4 (2,6-py), 149.1, 141.9, 126.6, 126.3, 125.8, 124.7, 123.1, 122.1 (Ph and py), 28.6 (CH, ^{i}Pr), 24.1, 23.0 (CH_3, ^{i}Pr), 17.6 (N=C*C*H$_3$). MS (FAB$^+$): *m*/*z* 535 (M$^+$), 500 (M$^+$ − Cl).

Preparation of RhCl[2,6-bis{1-(2-*tert*-butylphenyl)iminoethyll}-pyridine] (5). This complex was prepared analogously to complex **1**, starting from 2,6-bis{1-(2-*tert*-butylphenyl)iminoethyl}-pyridine (328 mg, 0.77 mmol) and [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ (150 mg, 0.38 mmol). Yield: 374 mg (86%). Anal. Calcd for $C_{29}H_{35}ClN_3Rh$: C, 61.76; H, 6.25; N, 7.45. Found: C, 61.46; H, 5.76; N, 7.44. ^{1}H and ^{13}C{^{1}H} NMR spectroscopy revealed the presence of two isomers (ratio 1:1). ^{1}H NMR (C_6D_6, 300 MHz): δ 7.77 and 7.79 (both t, J_{H-H} = 7.9, 1H, 4-py), 7.38−7.46 (m, 2H, Ph), 7.16−6.97 (m, 6H, Ph), 6.78 and 6.82 (both d, J_{H-H} = 7.9, 2H, 3,5-py), 1.40 and 1.43 (both s, 18H, −^{t}Bu), 1.03 and 1.04 (both s, 6H, N=CC*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz): δ 166.3, 166.2 (both d, J_{Rh-P} = 2.8, C=N), 156.2 and 156.1 (both d, J_{Rh-P} = 2.8, 2,6-py), 150.3, 150.1, 140.9, 129.3, 129.1, 128.6, 128.5, 126.3, 126.2 125.1, 124.8, 124.7, 121.4 (Ph and py), 19.1 and 18.9 (−CH_3), 36.6 (−*C*(CH_3)$_3$), 33.0 and 32.8 (−C(*C*H$_3$)$_3$), 18.4 and 18.3 (both s, N=C*C*H$_3$). MS (FAB$^+$): *m*/*z* 528 (M$^+$ − Cl).

Preparation of RhCl[2,6-bis{1-(2,6-diethylphenyl)iminoethyl}-pyridine] (7). This complex was prepared analogously to complex **1**, starting from 2,6-bis{1-(2,6-diethylphenyl)iminoethyl}-pyridine (328 mg, 0.77 mmol) and [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ (150 mg, 0.38 mmol). Yield: 426 mg (98%). Anal. Calcd for $C_{29}H_{35}ClN_3Rh$: C, 61.76; H, 6.25; N, 7.45. Found: C, 62.03; H, 6.46; N, 7.05. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.82 (t, J_{H-H} = 7.9, 1H, 4-py), 7.13−7.01 (m, 6H, Ph), 6.86 (d, J_{H-H} = 7.9, 2H, 3,5-py), 2.74 (dq, J_{H-H} = 7.5, J_{H-H} = 14.8, 4H, −CH_2−), 2.50 (dq, J_{H-H} = 7.5, J_{H-H} = 14.8, 4H, −CH_2−), 1.12 (t, J_{H-H} = 7.5, 12H, −CH_3), 1.01 (s, 6H, N=CC*H*$_3$). ^{13}C{^{1}H} NMR (C_6D_6, 75.4 MHz): δ 167.0 (d, J_{Rh-C} = 1.6, C=N), 156.3 (d, J_{Rh-C} = 2.6, *2*,6-py), 148.0, 135.6, 126.5, 126.1, 124.6, 122.0 (Ph and py), 25.1 (−CH_2−), 17.6 (N=C*C*H$_3$), 14.1 (−CH_3). MS (FAB$^+$): *m*/*z* 528 (M$^+$ − Cl).

Preparation of RhCl[2,6-bis{1-(4-methylphenyl)iminoethyl}-pyridine] (10). This complex was prepared analogously to complex **1**, starting from 2,6-bis{1-(4-methylphenyl)iminoethyl}-pyridine (263 mg, 0.77 mmol) and [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ (150 mg, 0.38 mmol). Yield: 332 mg (90%). Anal. Calcd for $C_{23}H_{23}ClN_3Rh$: C, 57.57; H, 4.83; N, 8.76. Found: C, 57.46; H, 4.46; N, 8.48. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.79 (t, J_{H-H} = 7.9, 1H, 4-py), 7.39 (d, J_{H-H} = 8, 4H, Ph), 7.00 (d, J_{H-H} = 8, 4H, Ph), 6.81 (d, J_{H-H} = 7.9, 2H, 3,5-py), 2.07 (s, 6H, −CH_3), 1.08 (s, 6H, N=CC*H*$_3$). The ^{13}C{^{1}H} NMR spectrum could not be recorded, due to the low solubility of the complex in C_6D_6. MS (FAB$^+$): *m*/*z* 444 (M$^+$ − Cl).

Preparation of RhCl[2,6-bis{1-(4-trifluoromethylphenyl)iminoethyl}pyridine] (11). This complex was prepared analogously to complex **1**, starting from 2,6-bis{1-(4-(trifluoromethyl)phenyl)-iminoethyl}pyridine (346 mg, 0.77 mmol) and [Rh(μ-Cl)(η^2-C_2H_4)$_2$]$_2$ (150 mg, 0.38 mmol). Yield: 323 mg (71%). Anal. Calcd for $C_{23}H_{17}ClF_6N_3Rh$: C, 47.00; H, 2.91; N, 2.38. Found: C, 46.64; H, 3.08; N, 2.50. ^{1}H NMR (acetone-d_6, 300 MHz): δ 8.63 (t, J_{H-H} = 8, 1H, *p*-py), 8.02 (d, J_{H-H} = 8, 2H, *m*-py), 7.75 (d, J_{H-H} = 8.4, 4H, Ph), 7.58 (d, J_{H-H} = 8.4, 4H, Ph), 1.85 (s, 6H, N=CC*H*$_3$). ^{19}F NMR (acetone-d_6, 282.33 MHz): δ −57.8 ppm (s, −CF_3). The ^{13}C{^{1}H} NMR spectrum could not be recorded, due to the low solubility of the complex in acetone-d_6. MS (FAB$^+$): *m*/*z* 587 (M$^+$), 552 (M$^+$ − Cl).

Catalytic Reactions of Dehalogenation−Hydrogenation. In a typical procedure, the halogenated arene (1.2 mmol) was added, under a hydrogen atmosphere, to a solution of the catalyst precursor (0.024 mmol), K^{t}BuO (1.2*x* mmol, *x* being the number of chlorine atoms of the halogenated substrate), and *n*-octane (200 μL) in 2-propanol (5 mL) placed in a 25 mL flask attached to a gas buret, which was in turn connected to a Schlenk manifold that had been previously evacuated and refilled with hydrogen. The flask was then immersed in a 60 °C bath, and the mixture was vigorously shaken (500 rpm) during the run. The reaction was monitored by measuring the hydrogen consumption and by periodic GC analysis of samples removed via syringe.

Hg(0) Poisoning Test. Hg(0) (1 mL, 67.8 mmol) was added, under a hydrogen atmosphere, to a solution of chlorobenzene (1.2 mmol), complex **11** (0.024 mmol), K^{t}BuO (1.2 mmol), and *n*-octane (200 μL) in 2-propanol (5 mL) placed in a 25 mL flask attached to a gas buret, which was in turn connected to a Schlenk manifold that had been previously evacuated and refilled with hydrogen. The flask was then immersed in a 60 °C bath, and the mixture was vigorously shaken (500 rpm) during the run. The reaction was monitored by measuring the hydrogen consumption. The hydrogen consumption was compared to that of the same experiment performed in the absence of added mercury.

Preparation of the Nanoparticles. Complex **11** (28.2 mg, 0.048 mmol) and K^{t}BuO (27 mg, 0.24 mmol) were dissolved in 10 mL of 2-propanol and were transferred under a hydrogen atmosphere to a 25 mL reaction flask. The flask was connected to the hydrogen reservoir and then was immersed in a 60 °C bath, and the mixture was shaken (500 rpm) for 7 h. After this time the hydrogen atmosphere was replaced by an argon atmosphere; the black residue that formed was left to decant, and the solution was removed. 2-Propanol was added to wash the residue, which was then dried. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.57−6.37 (m, Ph), 2.2−0.5 (m, aliphatic protons). ^{19}F NMR ($CDCl_3$, 235.4 MHz): δ −61.1 ppm (s, −CF_3).

Hydrogenation Reactions in the Presence of K^{t}BuO. In a typical procedure, the catalyst precursor **11** (14.1 mg, 0.024 mmol) and K^{t}BuO (135 mg, 0.12 mmol) were dissolved in 5 mL of 2-propanol and the resulting solution was transferred under a hydrogen atmosphere to a 25 mL reaction flask. The flask was connected to the hydrogen reservoir and then was immersed in a 60 °C bath, and the mixture was shaken (500 rpm) for 1 h. After this time, the substrate (1.2 mmol) was added to the flask via syringe and hydrogen uptake was recorded. In the case of phenol it was dissolved in 2 mL of 2-propanol and added via syringe to a preactivated solution of 2-propanol (3 mL) containing the catalyst precursor and K^{t}BuO. The reactions were monitored by measuring the hydrogen consumption and by periodic GC analysis of samples removed via syringe.

Hydrogenation Reactions in the Presence of Al_2O_3. In a typical procedure, the catalyst precursor **11** (14.1 mg, 0.024 mmol) was dissolved in 5 mL of 2-propanol and was transferred under a hydrogen atmosphere to a 25 mL reaction flask containing basic Al_2O_3 (122.4 mg). The flask was connected to the hydrogen reservoir and then was immersed in a 60 °C bath, and the mixture was shaken (500 rpm) for 1 h. After this time, the substrate (1.2 mmol) was added to the flask via syringe and hydrogen uptake was recorded. In the case of phenol it was dissolved in 2 mL of 2-propanol and added via syringe to a preactivated mixture containing the catalyst precursor and aluminum oxide in 3 mL of 2-propanol. The reaction was monitored by measuring the hydrogen consumption and by periodic GC analysis of samples removed via syringe.

Cycles of Hydrogenation of Benzene in the Presence of K^{t}BuO. The catalyst precursor **11** (14.1 mg, 0.024 mmol) and K^{t}BuO (135 mg, 0.12 mmol) were dissolved in 5 mL of 2-propanol, the resulting solution was transferred under a hydrogen atmosphere to a 25 mL reaction flask connected to the hydrogen reservoir, and benzene (1.2 mmol) was added to the flask via syringe. The flask was then immersed in a 60 °C bath and shaken (500 rpm). The reaction was monitored by measuring the hydrogen consumption and by periodic GC analysis of samples removed via

syringe. After 160 min the first load of benzene was hydrogenated to cyclohexane. The system was refilled with hydrogen, and benzene (second load, 1.2 mmol) was added via syringe. The procedure was repeated up to six loads of benzene.

Cycles of Hydrogenation of Benzene in the Presence of Al_2O_3. The catalyst precursor **11** (14.1 mg, 0.024 mmol) was dissolved in 5 mL of 2-propanol and was transferred under a hydrogen atmosphere to a 25 mL reaction flask containing basic Al_2O_3 (122.4 mg). The flask was connected to the hydrogen reservoir, and benzene (1.2 mmol) was added to the flask via syringe. The flask was then immersed in a 60 °C bath and shaken (500 rpm). The reaction was monitored by measuring the hydrogen consumption and by periodic GC analysis of samples removed via syringe. After 460 min the first load of benzene was hydrogenated to cyclohexane. The system was refilled with hydrogen, and benzene (second load, 1.2 mmol) was added via syringe. The procedure was repeated up to seven loads of benzene.

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