JOC The Journal of Organic Chemistry

Article

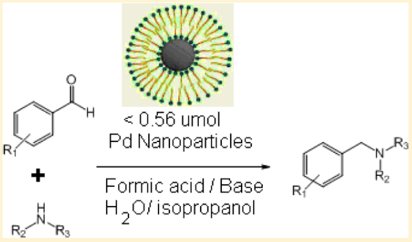
pubs.acs.org/joc

Zwitterionic-Surfactant-Stabilized Palladium Nanoparticles as Catalysts in the Hydrogen Transfer Reductive Amination of Benzaldehydes

Emma E. Drinkel, Roberta R. Campedelli, Alex M. Manfredi, Haidi D. Fiedler, and Faruk Nome*

Departamento de Química, Universidade Federal de Santa Catarina, INCT-Catalysis, Florianópolis, Santa Catarina 88040-900, Brazil

Supporting Information



ABSTRACT: Palladium nanoparticles (NPs) stabilized by a zwitterionic surfactant are revealed here to be good catalysts for the reductive amination of benzaldehydes using formate salts as hydrogen donors in aqueous isopropanol. In terms of environmental impact and economy, metallic NPs offer several advantages over homogeneous and traditional heterogeneous catalysts. NPs usually display greater activity due to the increased metal surface area and sometimes exhibit enhanced selectivity. Thus, it is possible to use very low loadings of expensive metal. The methodology eliminates the use of a hydrogen gas atmosphere or toxic or expensive reagents. A range of aromatic aldehydes were converted to benzylamines when reacted with primary and secondary amines in the presence of the Pd NPs, which also displayed good activity when supported on alumina. In every case, the Pd NPs could be easily recovered and reused up to three more times, and at the end of the process, the product was metal-free.

INTRODUCTION

The formation of C−N bonds is an important transformation, as amines are often found in naturally occurring molecules and have a wide range of application in pharmaceuticals and agrochemicals. Other methods of synthesizing amines include the alkylation of ammonia, reduction of other nitrogen-containing functional groups, and Buchwald−Hartwig coupling.[1] Reductive amination is a particularly useful method.[2] It is very adaptable because of the availability of a great range of amines and aldehydes, usually requires only mild conditions, and can be carried out in one pot without the need to isolate the intermediate imine (Figure 1). Previous reports on this reaction have focused on the use of metal hydrides,[3] cyanoborohydride[4] and other borohydride compounds,[5] and organosilanes[6] as the initiating species. These reagents are often used in stoichiometric quantities, thus increasing the yields of sometimes toxic side products and making the reaction less environmentally sound.

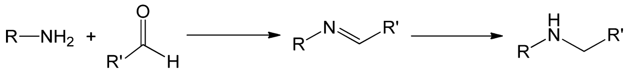


Figure 1. Reductive amination.

Other reports have demonstrated the use of metallic catalysts in combination with a hydrogen atmosphere.[7] The use of a hydrogen atmosphere also poses safety risks due to the use of high pressures of a flammable gas. Therefore, the use of hydrogen transfer agents such as formic acid or isopropanol is preferred. The side products (carbon dioxide or acetone, respectively) are nontoxic and easily removed, and high pressures of gas are not required. Transfer hydrogenation with metal catalysts and nontoxic hydrogen transfer agents has previously been reported to bring about reductive amination.[8]

With increasing concern for the environment, chemists are constantly looking for ways to reduce the impact of chemical processes. One way in which this can be achieved, in addition to controlling the side products produced, is by eliminating the use of organic solvents and instead carrying out reactions in environmentally benign solvents such as water. Another approach is to reduce the amount of metal required in catalytic processes, cutting the quantity of heavy metal waste at the end of reactions. Metallic nanoparticles have a much greater surface area of metal available compared with other heterogeneous catalysts and thus are potentially more active and require less metal to be used in catalysis. As with other heterogeneous catalysts, they also offer the advantage of being usable in more than one catalytic cycle. The use of palladium nanoparticles in reductive amination is known, but to the best of our knowledge only under an atmosphere of hydrogen.[9] Transfer hydrogenation reductive amination has been carried out using Pd/C[10] and nickel nanoparticles[8b,c] as the catalytic species, but in neither case was the catalyst reused for further cycles.

RESULTS AND DISCUSSION

Palladium nanoparticles stabilized by the zwitterionic surfactant molecules **ImS3-12** and **ImS3-14**[11] have previously been reported by our group as excellent catalysts for hydrogenation reactions[12] (Figure 2). Palladium nanoparticles stabilized by **ImS3-14** were made by the same method as previously

Received: January 8, 2014
Published: February 19, 2014

dx.doi.org/10.1021/jo5000362 | *J. Org. Chem.* 2014, 79, 2574−2579

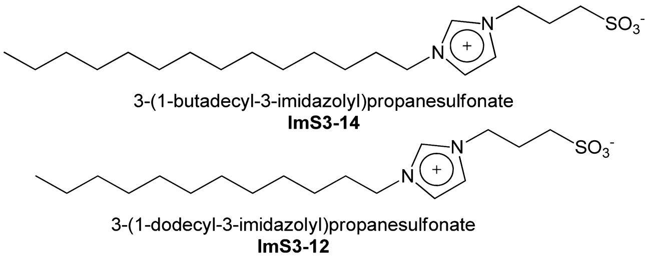


Figure 2. Zwitterionic surfactant molecules.

described for **ImS3-12**-stabilized nanoparticles.[12a] No presence of Pd black was detected by eye at the end of the synthesis, and the images obtained by transmission electron microscopy (TEM) confirmed the formation of palladium nanoparticles (Figure 3). The TEM images showed the nanoparticles to be well-dispersed with diameters of 3.4 ± 1.2 nm.

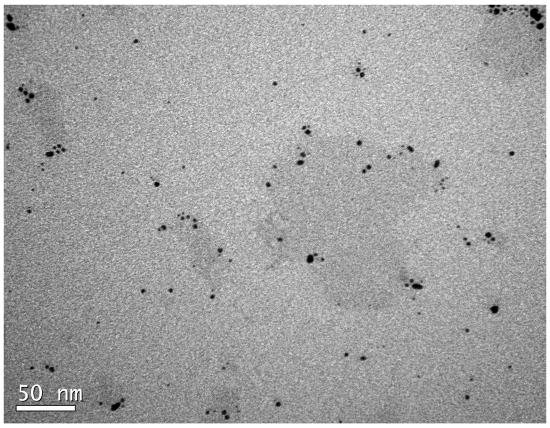


Figure 3. TEM image of **ImS3-14**-stabilized palladium nanoparticles.

To extend their utility, the **ImS3-14**-stabilized palladium nanoparticles were employed in the reductive amination of benzaldehydes (Scheme 1). In order to eliminate the use of flammable hydrogen gas as the reducing agent, the reaction was attempted using formate salts as the hydrogen donors. Table 1 shows the preliminary results obtained when the palladium nanoparticles were tested in the reaction shown in Scheme 1. Notably, the palladium loading was very low, with just 0.54 μmol used to catalyze the reactions of 1 mmol of reactants. In initial efforts, formic acid was used with an equal concentration of sodium hydroxide as the base (entry 1), but only traces of product were seen by GC−MS at the end of the reaction. It was subsequently found that using a large excess of formic acid relative to the base was beneficial to the reaction (entries 2 and 3). However, as entry 4 shows, the total absence of base resulted in no product. Interestingly, the nature of the base did not affect the yield greatly, and sodium formate was subsequently used as the preferred base. A 1:1 ratio of formic acid to sodium formate was found to be optimal (entry 5). The reaction was not tested in the absence of surfactant, since the palladium precipitated as a black solid.

Increasing the temperature to 70 °C increased the yield without causing decomposition of the nanoparticles (Table 1, entry 6). A reaction temperature of 90 °C, despite giving a good yield, caused decomposition of the nanoparticles, which could no longer be used in further catalytic cycles (entry 8). Comparison of entries 6 and 7 shows that the addition of 200 μL of isopropanol increased the yield by a further 11%, possibly by helping with phase transfer. Finally, the same palladium nanoparticles supported on alumina (entry 9) were less active than unsupported ones for this reaction.

The optimized conditions were then used to investigate the scope of the reaction catalyzed by the **ImS3-14**-stabilized nanoparticles (Table 2). Benzaldehydes with electron-donating groups gave considerably better yields than those with electron-withdrawing groups, as demonstrated by the poor yields for 4-nitrobenzaldehyde and 2-chlorobenzaldehyde (0 and 35%, respectively; entries 3 and 5). Furthermore, comparison of entries 2 and 7 reveals that the position of the electron-donating group is also important. The *ortho*-substituted anisaldehyde resulted in a yield 14% lower than the *para*-substituted analogue. It is possible that the mechanism of the reaction passes through a positively charged intermediate that is stabilized by electron donation from the aryl groups.

At the end of the reaction there was no visible evidence of decomposition of the palladium nanoparticles, and the aqueous solution in which they were present was therefore separated from the organic phase in order to test their recyclability. As is clear from Table 3, the Pd/**ImS3-14** nanoparticles could be successfully used four times in the reaction shown in Table 2, entry 2 without considerable loss in activity. Even after the fourth use, no Pd black was observed in the reaction tube. This shows that the catalyst was stable, with no or minimal leaching of Pd into the product (see below). The first and second uses of the nanoparticles gave about the same amount of product. However, in further uses, they gradually became less active. This is probably because the nanoparticles aggregated with continued use, therefore decreasing the surface area and reducing their efficiency.

Following the results with aniline, other amines were tested using the conditions described previously with Pd/**ImS3-14**. However, little or no product was usually obtained. Moreover, decomposition of the catalyst was usually observed at the end of the reaction time. It was hoped that Pd/**ImS3-14** nanoparticles supported on alumina, which have already been reported as excellent catalysts in the selective hydrogenation of biodiesel,[12b] would be more stable and able to overcome these problems. Initial tests using the same conditions as in entry 9 of Table 1 resulted in poor yields of product. However changing the base to NEt$_3$, eliminating the excess of formic acid, and using isopropanol as the solvent (the conditions shown in Scheme 2) drastically improved the outcome. With these new

Scheme 1. Palladium-Nanoparticle-Catalyzed Reductive Amination of Benzaldehyde with Aniline at 70°C

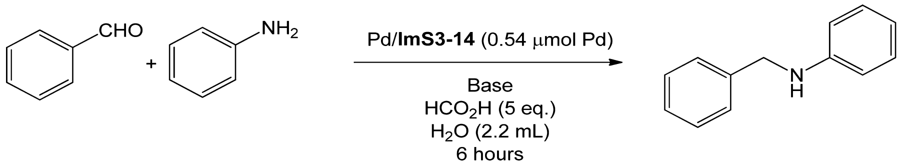
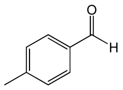
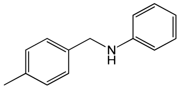
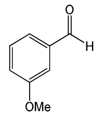
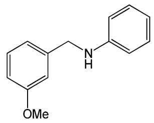
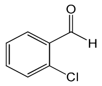
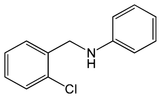
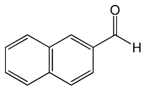
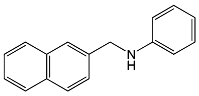
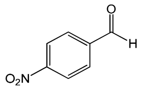
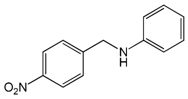
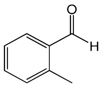
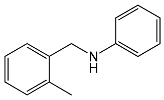
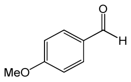
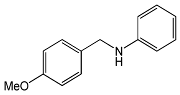


Table 1. Preliminary Tests of **ImS3-14**-Stabilized Palladium Nanoparticles in the Reductive Amination Reaction Shown in Scheme 1

Entry	Catalyst	Base	*T* (°C)	Yield (%)[a]	TON[e]
1	Pd/**ImS3-14**	NaOH (5 equiv)[b]	60	trace	–
2	Pd/**ImS3-14**	NaOH (0.1 equiv)	60	37	685
3	Pd/**ImS3-14**	($NaHCO_3$ 0.1 equiv)	60	35	648
4	Pd/**ImS3-14**	–	60	–	–
5	Pd/**ImS3-14**	$NaCO_2H$ (5 equiv)	60	54	1000
6	Pd/**ImS3-14**	$NaCO_2H$ (5 equiv)	70	66	1222
7[c]	Pd/**ImS3-14**	$NaCO_2H$ (5 equiv)	70	77	1426
8[c,d]	Pd/**ImS3-14**	$NaCO_2H$ (5 equiv)	90	93	1722
9[c]	Pd/**ImS3-14**@Al_2O_3	$NaCO_2H$ (5 equiv)	70	52	963
10	Pd/C	$NaCO_2H$ (5 equiv)	70	39	722

Reaction conditions: 1 mmol of benzaldehyde, 2 mmol of aniline, 0.54 μmol of Pd, 5 mmol of formic acid, 2 mL of H_2O, 6 h. [a]Isolated yields by column chromatography. [b]Amounts are equivalents with respect to benzaldehyde. [c]200 μL of ^{i}PrOH was added. [d]Pd black was observed at the end of the reaction. [e]Turnover number (mol of product/mol of Pd).

Table 2. Reductive Amination with Pd/**ImS3-14**

Entry	Aldehyde	Product	Yield %[a]	TON[b]
1			88	1629 (4654)
2			74	1370 (3914)
3			35	648 (1851)
4			87	1611 (4602)
5			0	0
6			85	1574 (4497)
7			88	1629 (4654)

Reaction conditions: 1 mmol of aldehyde, 2 mmol of aniline, 0.54 μmol of Pd, 5 mmol of formic acid, 5 mmol of sodium formate, 200 μL of ^{i}PrOH, 2 mL of H_2O, 6 h, 70 °C. [a]Isolated yields by column chromatography. [b]Turnover number (mol of product/mol of Pd). Values in parentheses are corrected turnover numbers (by means of the magic-number approach) considering only the exposed atoms on the nanoparticle surface (35%).

Table 3. Reuse of Pd/**ImS3-14** in the Reductive Amination of *p*-Tolualdehyde with Aniline

Use	1	2	3	4
Yield (%)[a]	88	87	75	63

Reaction conditions for reuse: 1 mmol of 4-tolualdehyde, 1 mmol of aniline, 1 mmol of formic acid, 200 μL of ^{i}PrOH, 6 h, 70 °C. [a]Isolated yields by column chromatography.

conditions, Pd/**ImS3-14**@Al_2O_3 could successfully catalyze the reductive amination of *p*-tolualdehyde with cyclic secondary amines (Table 4). Excellent yields of over 90% were obtained with piperazine and piperidine (entries 1 and 2). Although slightly lower, the yield of product recovered from the reaction with morpholine was still very good (entry 3). In these reactions, the loading of palladium required to achieve these results was again very low (0.56 μmol), and no Pd black was observed at the end of the reaction.

In the case of Pd/**ImS3-14**@Al_2O_3, it was seen that the catalyst gave better results with respect to recyclability when the temperature of the reaction was lowered to 50 °C. Table 5 shows the yields obtained over four uses of Pd/**ImS3-14**@Al_2O_3 in the reductive amination of *p*-tolualdehyde with piperidine. As can be seen, the first three uses of Pd/**ImS3-14**@Al_2O_3 resulted in essentially the same amount of product when the reaction was carried out at 50 °C. The fourth cycle led to a decrease in yield by about 10%, but no decomposition of the

Scheme 2. Reductive Amination of *p*-Tolualdehyde with Cyclic Amines Catalyzed by Supported Palladium Nanoparticles

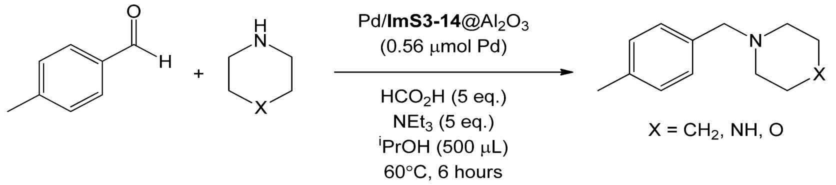
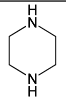
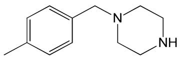
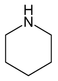
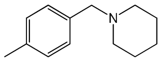
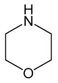
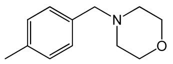


Table 4. Reductive Amination with Pd/ImS3-14@Al_2O_3

Entry	Amine	Product	Yield %[a]	TON[b]
1			94	1678 (4794)
2			96	1714 (4897)
3			80	1428 (4080)

Reaction conditions: 1 mmol of *p*-tolualdehyde, 1 mmol of amine, 5 mmol of triethylamine, 5 mmol of formic acid, 0.56 μmol of Pd, 500 μL of ^{i}PrOH, 6 h, 60 °C. [a]Isolated yields by column chromatography. [b]Turnover numbers (mol of product/mol of Pd). Values in parentheses are the corrected turnover numbers (by means of the magic-number approach) considering only the exposed atoms on the nanoparticle surface (35%).

Table 5. Reuse of Pd/ImS3-14@Al_2O_3 in the Reductive Amination of *p*-Tolualdehyde with Piperidine

Use	1	2	3	4
Yield (%)[a]	87	86	87	77

Reaction conditions for reuse: 1 mmol of *p*-tolualdehyde, 1 mmol of amine, 1 mmol of triethylamine, 1 mmol of formic acid, 200 μL of ^{i}PrOH, 6 h, 50 °C. [a]Isolated yields by column chromatography.

nanoparticles was observed postreaction. As suggested above, the nanoparticles probably lose activity as they begin to aggregate over more uses.

After the good outcome of the recyclability tests, another experiment was conducted to ensure that Pd did not leach into the organic phase during the course of the reaction. The reaction between benzaldehyde and aniline was set up as usual using the optimized conditions from Table 1 in two separate reaction tubes. After 1 h, the aqueous phase containing the nanoparticles was removed from one of the reactions and replaced by an equal volume of an aqueous solution containing all of the reagents except the nanoparticles. Both reactions were monitored by GC−MS, and the results are shown in Figure 4. As can be seen, when the catalyst was removed after 1 h, the reaction did not continue. This proves that the nanoparticles do not leach into the product, confirming that the **ImS3-14**-stabilized nanoparticles can be quantitatively recovered and reused.

Finally, the determination of Pd was carried out by direct analysis of the organic phase using energy-dispersive X-ray fluorescence (EDXRF), following the Pd Kα1 signal. With this method, the detection limit (DL) for Pd is 0.6 μg/mL.[13] The analysis of the organic phase (products) showed that Pd could not be detected, indicating that the Pd concentration was lower than the detection limit of the equipment and that the final product was metal-free.

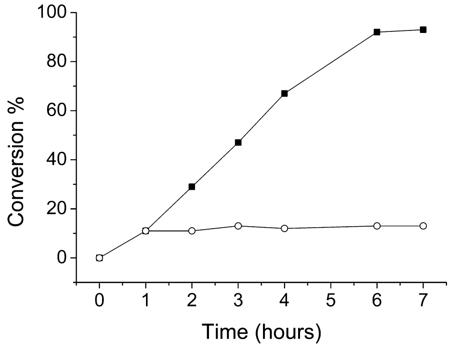


Figure 4. Graph showing the progress of the reductive amination reactions of benzaldehyde with aniline: (■) with Pd nanoparticles throughout; (○) with Pd nanoparticles removed after 1 h of reaction.

■ CONCLUSIONS

We have shown that zwitterionic-surfactant-stabilized palladium nanoparticles, which have previously proven to be excellent catalysts in hydrogenation reactions, are also good catalysts for transfer hydrogenation reductive amination. Yields of up to 88% could be achieved using the unsupported nanoparticles in water, and yields of up to 96% were obtained using the supported nanoparticles in the reductive amination of *p*-tolualdehyde with secondary amines. In both cases, the nanoparticles could be used up to four times without critical loss of activity, and no observable precipitation of Pd black was seen. Notably, the loading of Pd required to catalyze the reaction is extremely low compared with standard homogeneous and heterogeneous catalysts: only 0.54−0.56 μmol was required to obtain the results shown.

The use of nanoparticles such as these to catalyze reactions is of great interest for green chemistry, not only because they can be employed in exceptionally low loadings but also because they are in a different phase than the product and thus can be easily separated for reuse without contamination of the product. Furthermore, reactions can be employed using more environmentally sound solvents such as water or alcohol. Work continues in our laboratory to further extend the utility of these zwitterionic-surfactant-stabilized palladium nanoparticles in other green catalytic processes.

■ EXPERIMENTAL SECTION

General. Sodium hydride, imidazole, 1-bromododecane, isopropanol, K_2PdCl_4, and $NaBH_4$ were of analytical grade and were used without further purification. Organic solvents were carefully dried using molecular sieves (type 3A or 4A), and synthetic reactions were carried out under strictly anhydrous conditions under argon. Chemicals and inorganic salts were of the highest purity available and were used as purchased. ^{1}H NMR spectra were recorded on a 400 or 200 MHz NMR spectrometer with sodium 3-(trimethylsilyl)-propionate (TSP) as an internal reference. Chemical shifts (δ) are reported in parts per million.

Synthesis of 3-(1-Tetradecyl-3-imidazolyl)propanesulfonate (ImS3-14). The surfactant 3-(1-tetradecyl-3-imidazolyl)-propanesulfonate (**ImS3-14**) was described previously.[11] The synthesis involved *N*-alkylation of imidazole followed by reaction with 1,3-propanesultone. The zwitterionic **ImS3-14** surfactant was characterized by ^{1}H NMR (400 MHz) in $CDCl_3$ (δ relative to TMS): 10.26 (s, 1H), 8.03 (s, 1H), 7.68 (s, 1H), 4.87 (t, 2H), 4.53 (t, 2H), 3.04 (t, 2H), 2.55 (t, 2H), 1.99 (m, 2H), 1.33 (22H, m), 0.94 (t, 3H). The signals are fully consistent with those reported previously.[11]

Synthesis of Palladium Nanoparticles. The nanoparticles were synthesized as described previously.[12] To a solution of **ImS3-14** (1.75 mmol, 676.5 mg), K_2PdCl_4 (0.52 mmol, 171.4 mg), and NaCl (14 mmol, 818.3 mg) in doubly distilled water (175 mL) was added 17.5 mL of a freshly prepared 0.3 M aqueous solution of $NaBH_4$ with vigorous stirring. The solution became black immediately and was stirred for an additional 24 h at room temperature. The nanoparticles were stable and could be kept for more than a year without any Pd black precipitate being observed.

Synthesis of Palladium/ImS3-14@Al_2O_3.[12b] Basic aluminum oxide (2.58 g) was stirred with 50 mL of the palladium nanoparticle solution prepared as described above. The uptake of the nanoparticles was monitored by UV–vis spectroscopy of the supernatant, and after 7 days the nanoparticles were quantitatively adsorbed. The Pd/**ImS3-14**@Al_2O_3 nanoparticles were centrifuged at 4000 rpm, washed twice with 20 mL of doubly distilled water, and allowed to dry in air at 60 °C to give a pale-gray powder. The theoretical palladium content based on total adsorption of the nanoparticles on the aluminum oxide support was 0.56 mol %. A 10 mg sample of the prepared Pd/**ImS3-14**@Al_2O_3 nanoparticles was mixed with aqua regia, and this solution was diluted and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES). This gave a value of 0.57 ± 0.02 mol % for the Pd content, which is in excellent agreement with the value calculated assuming 100% adsorption.

General Procedure for the Reductive Amination of Benzaldehyde with Aniline. A reaction tube was charged with 2 mL of sodium formate aqueous solution (2.5 M), to which were added 200 μL of isopropanol, 189 μL of formic acid (5 equiv, 5 mmol), 101 μL of benzaldehyde (1 equiv, 1 mmol), and 182 μL of aniline (2 equiv, 2 mmol). Finally, 200 μL of Pd/**ImS3-14** aqueous solution (2.7 mM, 0.54 μmol of Pd) was added, and the reaction was sealed with a rubber septum and heated to 70 °C in an oil bath for 6 h. After this time, the reaction tube was removed from the oil bath and allowed to cool. Petroleum ether (1 mL) was added to the reaction mixture to extract the product. The Pd nanoparticles remained in a separate phase, and the organic layer could be decanted off carefully. This was repeated twice more to remove all of the product and remaining reactant. The product could be isolated by column chromatography using 4% ethyl acetate in petroleum ether as the eluent. The nanoparticles could then be used again to catalyze another cycle of the same reaction. To the recovered nanoparticles were added 38 μL of formic acid (1 equiv, 1 mmol), 200 μL of isopropanol, 101 μL of benzaldehyde, and 91 μL of aniline (1 equiv, 1 mmol), and the reaction tube was again heated to 70 °C and left for 6 h. After this time, the product was isolated as described before.

General Procedure for the Reductive Amination of *p*-Tolualdehyde with Other Amines. A reaction tube was charged with 695 μL of NEt_3 (5 equiv, 5 mmol), and 188 μL of formic acid (5 equiv, 5 mmol) was slowly added with stirring. Subsequently, 500 μL of isopropanol, 118 μL of *p*-tolualdehyde (1 equiv, 1 mmol), and 1 mmol of the appropriate amine were added. Finally, the Pd/**ImS3-14**@Al_2O_3 nanoparticles (10 mg, 0.56 μmol of Pd) were added, and the reaction tube was then sealed with a rubber septum and heated to the stated temperature for 6 h. After this time, the reaction tube was allowed to cool, and 1 mL of petroleum ether was added to the mixture to form two phases, with the products in the organic phase above and the nanoparticles in the lower phase. The organic phase was removed, and the addition of petroleum ether was repeated twice more to remove all of the product and remaining starting material. The product could be isolated by column chromatography using 4% ethyl acetate in petroleum ether as the eluent.

EDXRF Analysis. The EDXRF measurements were made in a temperature-controlled room (23 ± 1 °C). Before analysis, instrument calibration and a stability check were performed, and the detection limit (DL) for Pd was 0.6 μg/mL. Samples (5 mL) were placed in an X-Cell (with a diameter of 40 mm) and covered with a 5 μm thick polypropylene film, special for XRF analyses. The measurements were carried out using a Pd X-ray tube operated with Cu filter at 50 kV and 250 μm. The acquisition time was 150 s (measurement time per region using helium), and the X-rays to excite the sample were produced using a 50 W (50 kV, 2 mA) VF50 X-ray tube. The tube and generator are capable of operating at voltages ranging from 10 to 50 kV and currents from 1 to 2000 μA, providing that the maximum power of 50 W is not exceeded.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR data, chromatograms, and mass spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*Tel: +55 48 3721-6849. Fax: +55 48 3721-6850. E-mail: faruk.nome@ufsc.br.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We are grateful to INCT-Catálise, PRONEX, FAPESC, CNPq, and CAPES for financial support.

■ REFERENCES

(1) Schlummer, B.; Scholz, U. *Adv. Synth. Catal.* **2004**, *346*, 1599.

(2) (a) Margaretha, P. *Sci. Synth.* **2008**, *40*, 65. (b) Tripathi, R. P.; Verma, S. S.; Pandey, J.; Tiwari, V. K. *Curr. Org. Chem.* **2008**, *12*, 1093. (c) Nugent, T. C.; El-Shazly, M. *Adv. Synth. Catal.* **2010**, *352*, 753. (d) Gomez, S.; Peters, J. A.; Maschmeyer, T. *Adv. Synth. Catal.* **2002**, *344*, 1037.

(3) (a) Schellenberg, K. A. *J. Org. Chem.* **1963**, *28*, 3259. (b) Kim, S.; Oh, C. H.; Ko, J. S.; Ahn, K. H.; Kim, Y. J. *J. Org. Chem.* **1985**, *50*, 1927. (c) Ranu, B. C.; Majee, A.; Sarkar, A. *J. Org. Chem.* **1998**, *63*, 370.

(4) (a) Barney, C. L.; Huber, E. W.; McCarthy, J. R. *Tetrahedron Lett.* **1990**, *31*, 5547. (b) Ashweek, N. J.; Coldham, I.; Vennall, G. P. *Tetrahedron Lett.* **2000**, *41*, 2235. (c) Grenga, P. N.; Sumbler, B. L.; Beland, F.; Priefer, R. *Tetrahedron Lett.* **2009**, *50*, 6658.

(5) Ramachandran, P. V.; Gagare, P. D.; Sakavuyi, K.; Clark, P. *Tetrahedron Lett.* **2010**, *51*, 3167.

(6) (a) Prakash, G. K. S.; Do, C.; Mathew, T.; Olah, G. A. *Catal. Lett.* **2010**, *137*, 111. (b) Chen, B. C.; Sundeen, J. E.; Guo, P.; Bednarz, M. S.; Zhao, R. *Tetrahedron Lett.* **2001**, *42*, 1245. (c) Robichaud, A.; Ajjou, A. N. *Tetrahedron Lett.* **2006**, *47*, 3633. (d) Apodaca, R.; Xiao, W. *Org. Lett.* **2001**, *3*, 1745. (e) Patel, J. P.; Li, A. H.; Dong, H. Q.; Korlipara, V. L.; Mulvihill, M. J. *Tetrahedron Lett.* **2009**, *50*, 5975.

(7) (a) Bagal, D. B.; Watile, R. A.; Khedkar, M. V.; Dhake, K. P.; Bhanage, B. M. *Catal. Sci. Technol.* **2012**, *2*, 354. (b) Fleischer, S.; Zhou, S. L.; Junge, K.; Beller, M. *Chem.—Asian J.* **2011**, *6*, 2240. (c) Werkmeister, S.; Junge, K.; Beller, M. *Green Chem.* **2012**, *14*, 2371. (d) Bhor, M. D.; Bhanushali, M. J.; Nandurkar, N. S.; Bhanage, B. M. *Tetrahedron Lett.* **2008**, *49*, 965. (e) Imao, D.; Fujihara, S.; Yamamoto, T.; Ohta, T.; Ito, Y. *Tetrahedron* **2005**, *61*, 6988.

(8) (a) Zhang, M.; Yang, H. W.; Zhang, Y.; Zhu, C. J.; Li, W.; Cheng, Y. X.; Hu, H. W. *Chem. Commun.* **2011**, *47*, 6605. (b) Alonso, F.; Riente, P.; Yus, M. *Synlett* **2008**, 1289−1292. (c) Alonso, F.; Riente, P.; Yus, M. *Acc. Chem. Res.* **2011**, *44*, 379.

(9) (a) Erathodiyil, N.; Ooi, S.; Seayad, A. M.; Han, Y.; Lee, S. S.; Ying, J. Y. *Chem.—Eur. J.* **2008**, *14*, 3118. (b) Sreedhar, B.; Reddy, P. S.; Devi, D. K. *J. Org. Chem.* **2009**, *74*, 8806.

(10) Byun, E.; Hong, B.; De Castro, K. A.; Lim, M.; Rhee, H. *J. Org. Chem.* **2007**, *72*, 9815.

(11) Tondo, D. W.; Leopoldino, E. C.; Souza, B. S.; Micke, G. A.; Costa, A. C.; Fiedler, H. D.; Bunton, C. A.; Nome, F. *Langmuir* **2010**, *26*, 15754.

(12) (a) Souza, B. S.; Leopoldino, E. C.; Tondo, D. W.; Dupont, J.; Nome, F. *Langmuir* **2012**, *28*, 833. (b) Souza, B. S.; Pinho, D. M. M.; Leopoldino, E. C.; Suarez, P. A. Z.; Nome, F. *Appl. Catal., A* **2012**, *433*, 109.

(13) Fiedler, H. D.; Drinkel, E. E.; Orzechovicz, B.; Leopoldino, E. C.; Souza, F. D.; Almerindo, G. I.; Perdona, C.; Nome, F. *Anal. Chem.* **2013**, *85*, 10142.