Contents lists available at SciVerse ScienceDirect

## **Catalysis** Today



journal homepage: www.elsevier.com/locate/cattod

# Rhodium nanoparticles stabilized with phosphine functionalized imidazolium ionic liquids as recyclable arene hydrogenation catalysts

### Samantha A. Stratton, Kylie L. Luska, Audrey Moores\*

Department of Chemistry, McGill University, Otto Maass Chemistry Building, 801 Sherbrooke Street West, Montreal, Quebec, Canada H3A 2K6

#### ARTICLE INFO

Article history: Received 3 July 2011 Received in revised form 14 September 2011 Accepted 14 September 2011 Available online 7 October 2011

Keywords: Rhodium Nanoparticles Biphasic catalysis Hydrogenation Functionalized ionic liquids Arene

#### ABSTRACT

Rhodium nanoparticles (Rh NPs) stabilized by phosphine functionalized ionic liquids (FILs) were prepared in [BDMI]NTf<sub>2</sub> (BDMI = 1-butyl-2,3-dimethylimidazolium, NTf<sub>2</sub> = bis(trifluoromethanesulfonyl)imide) using H<sub>2</sub>(g) (4 bar) as a reducer. Rh(allyl)<sub>3</sub> was used as a "salt-free" Rh NP precursor and allowed to enhance the stability of the Rh NPs compared to the usual RhCl<sub>3</sub> precursor. The synthesized FIL stabilized Rh NPs proved to be active biphasic catalysts for the hydrogenation of toluene, styrene and xylenes under mild conditions (75 °C, 40 bar H<sub>2</sub>(g), 3 h). The impact on activity of the length of the spacer between the phosphine function and the ionic liquid moiety in the FIL was studied. The Rh NPs stabilized by FILs showed higher catalytic activity and recyclability than NPs synthesized in the absence of a stabilizer and more stable than the system employing triphenylphosphine (PPh<sub>3</sub>) as a stabilizer. The size of the stabilized Rh NPs was measured to be around 2 nm by TEM, while those produced in the absence of a FIL stabilizer formed only aggregates.

© 2011 Elsevier B.V. All rights reserved.

#### 1. Introduction

Transition metal nanoparticles (NPs) have gained increasing interest in recent years due to their applications in such areas as catalysis, sensing and nanoelectronics [1]. These chemical species feature properties specific to their nanometric dimension and thus considerable research effort was dedicated to their stabilization in order to extend their lifetime [2]. In the context of catalysis, this additional stabilization influences the activity and the recyclability of the particles as well as the selectivity of the products. This stabilization can be provided by traditional organic ligands (i.e. phosphines or pyridines) [3–5], polymers [6–8] or solid supports [9–11].

Ionic liquids (ILs) have come into the spotlight as interesting systems for NP stabilization as they act as both solvent and ligand. DLVO theory has been used as a first approximation to explain the colloidal stabilization provided by the cationic head group and counter anion of the IL [12–14]. In addition, imidazolium ILs are known to feature hydrophobic and hydrophilic domains throughout the liquid [12,13,15], which help control growth during NP synthesis [15,16]. Numerous transition metal NPs have been synthesized in imidazolium ILs and they exhibit high catalytic activity. These biphasic systems allow the products to be extracted from the IL phase containing the catalytic particles and permits easy recoverability of the catalyst [17,18]. Recently, several groups have looked into the impact of alterations of the IL parameters (i.e. Nalkyl chain length, counter anion volume) and have shown them to influence the properties of the resulting NPs [19-22]. However, under catalytic conditions, these IL stabilized NPs have been observed to aggregate [21,23-26] as the displacement of the IL from the particle surface can occur facilely [27–29]. Several groups [22,30,31] have been developing functionalized ionic liquids (FILs) to increase the stabilization of catalytically active NPs in ILs to produce more robust recyclable catalysts. FILs offer electrostatic stabilization to NPs in a similar fashion to traditional ILs, while also providing covalent stabilization through an additional chemical moiety able to bind to the NP surface (i.e. bipyridine [22,28], phosphine [32], thiol [33]). For instance, the groups of Dyson and Roucoux have developed bipyridine ligands functionalized with an imidazolium head group to stabilize Rh NPs used as arene hydrogenation catalysts [22,28]. The group of Dyson studied the effect of the spacer between the bipyridine group and the imidazolium cation and found that a longer chain spacer had a beneficial effect on catalysis. Recently, our group synthesized phosphine FILs based on an imidazolium head group, varied in the N-alkyl chain length and the nature of the counter anion, as stabilizers for Pd NPs. The catalytic activity of these Pd NPs was also dependent on the N-alkyl chain length and the counter anion;



<sup>\*</sup> Corresponding author. Tel.: +1 514 398 4654; fax: +1 514 398 3797. *E-mail address:* audrey.moores@mcgill.ca (A. Moores).

<sup>0920-5861/\$ -</sup> see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.cattod.2011.09.016



Fig. 1. Synthesis of Rh NPs in [BDMI]NTf<sub>2</sub>.

although, the catalytic activity decreased as the N-alkyl chain length increased [32].

Herein, we report the employment of these phosphine FILs towards the synthesis of Rh NPs and their use as recyclable biphasic arene hydrogenation catalysts. These systems featured high activity under reasonably mild conditions for the hydrogenation of toluene, styrene and various xylenes. In our study we compared the influence of the chain length spacer on the activity and proved that FILs are superior stabilizers compared to using only the IL solvent in terms of activity and recyclability, respectively. We also demonstrated that PPh<sub>3</sub> is a good stabilizer, except that it leached out of the IL and contaminated the extracted product. We also selected two Rh precursors for this study: Rh(allyl)<sub>3</sub> and RhCl<sub>3</sub>. While RhCl<sub>3</sub> has been traditionally used to generate Rh NPs, Rh(allyl)<sub>3</sub> was introduced by Chaudret's group as a "salt-free" precursor. Under H<sub>2</sub> pressure, Rh(allyl)<sub>3</sub> decomposes into Rh<sup>0</sup> and volatiles, leaving no impurity at the NP surface [17].

#### 2. Experimental

#### 2.1. General

All syntheses were carried out under an inert atmosphere. Rh(allyl)<sub>3</sub> [34], [BDMI]NTf<sub>2</sub> [32], FIL **1** [35] and FIL **2** [32] were prepared following literature procedures. All substrates and solvents were purchased from commercial sources and used as received. Nuclear magnetic resonance (NMR) spectra were taken using a 200 MHz Varian Mercury spectrometer. The <sup>31</sup>P NMR spectra were calibrated using 85% H<sub>3</sub>PO<sub>4</sub>. Transmission electron microscopy (TEM) images were taken using a JEOL JEM-2100F microscope operating at 200 kV with a resolution of 0.1 nm. High-pressure experiments were performed using a 25 mL glass vessel in a Parr instruments 5000 Series Multiple Reactor System.

#### 2.2. Catalyst preparation

Rh NPs were synthesized by mixing Rh(allyl)<sub>3</sub> (0.05 mmol) with FIL **1**, **2** or PPh<sub>3</sub> (0.05 mmol) in [BDMI]NTf<sub>2</sub> (1 mL) to afford **1:Rh**, **2:Rh** and **PPh<sub>3</sub>:Rh** respectively. **1:Rh**\* was synthesized by mixing RhCl<sub>3</sub>·3H<sub>2</sub>O (0.05 mmol) with FIL **1** (0.05 mmol) in [BDMI]NTf<sub>2</sub> (1 mL). **none:Rh** was synthesized by mixing Rh(allyl)<sub>3</sub> (0.05 mmol) and [BDMI]NTf<sub>2</sub> (1 mL). All the above mentioned systems were stirred for 1 h under argon and then exposed to a constant pressure of H<sub>2</sub>(g) (4 bar) for 18 h at 50 °C (Fig. 1).

#### 2.3. Catalysis

The NP sample was prepared as outlined above and charged with the arene substrate (5.0 mmol, 100 equiv.). The reaction mixture was stirred under a constant pressure  $H_2(g)$  (40 bar) at 75 °C for 3 h (Fig. 3). The reactor was cooled to below room temperature and depressurized slowly. The catalysis products were extracted with pentane (3 mL × 8 mL) and analyzed by GC (Table 1). Each sample was dried for at least 1 h *in vacuo* between catalytic runs.

#### 2.4. CS<sub>2</sub> poisoning test

The NP sample was prepared as outlined above and charged with CS<sub>2</sub> (1.4  $\mu$ L, 0.5 equiv.) and toluene (5.0 mmol) [36]. The reaction mixture was stirred under a constant pressure H<sub>2</sub>(g) (40 bar) at 75 °C for 3 h (Fig. 3). The reactor was cooled to below room temperature and depressurized slowly. The catalysis products were extracted with pentane (3 mL × 8 mL).

#### 2.5. Catalyst characterization

The Rh NPs were characterized by TEM using a JEOL JEM-2100F microscope operating at 200 kV with a resolution of

#### Table 1

TEM characterization of Rh NPs before catalysis, after 1 catalytic cycle and after 10 catalytic cycles.

Entry	Rh NP	NP size (nm)					
		Before catalysis	After cycle 1	After cycle 10			
1	none:Rh	Clusters of small particles	$2.3\pm0.8$	Aggregates			
2	1:Rh	$2.4\pm0.6$	$2.3\pm0.5$	$1.5\pm0.4$			
3	2:Rh	$2.0\pm0.5$	$1.7\pm0.3$	$1.9 \pm 0.5$			
4	PPh3:Rh	$1.5\pm0.4$	Clusters of small particles	Aggregates			
5	1:Rh*	Very few particles	Aggregates	Aggregates			



Fig. 2. TEM images of Rh NPs: (A) none:Rh, (B) 1:Rh, and (C) PPh<sub>3</sub>:Rh.

0.1 nm. Sample preparation involved dissolving 2 drops of the Rh NP solution in  $\sim$ 1.5 mL of MeCN followed by the deposition of the NPs on a 400 mesh carbon-coated copper grid. Size distributions were calculated by measuring >100 particles per sample.

#### 3. Results and discussion

#### 3.1. Nanoparticle synthesis and characterization

The synthesis of Rh NPs **1:Rh** and **2:Rh** was achieved by reduction of the metal precursor Rh(allyl)<sub>3</sub> in the presence of one molar equivalent of FIL **1** or **2** in an IL solvent [BDMI]NTf<sub>2</sub>, under an atmosphere of 4 bar of H<sub>2</sub>(g) (Fig. 1). The mixture was heated at 50 °C for 1, 4, 10 or 18 h. Short reaction times provided clusters of ill-defined particles, while 18 h afforded well-dispersed Rh NPs. For comparison, Rh NPs were also synthesized in [BDMI]NTf<sub>2</sub>, in the absence of any additional stabilizer (**none:Rh**) or employing PPh<sub>3</sub> as stabilizer (**PPh<sub>3</sub>:Rh**). At last, we tested the influence of the rhodium precursor, by exposing RhCl<sub>3</sub>·3H<sub>2</sub>O to the same reaction conditions, in the presence of FIL **1** to afford **1:Rh**\*.

TEM analysis was employed to characterize the obtained NPs and determine their mean diameter (Table 1). In the absence of any stabilizer, the IL solvent alone [BDMI]NTf<sub>2</sub>, afforded clusters of small particles (Fig. 2A and Table 1, entry 1). These collections of particles did not allow the precise measurement of the size of individual particles. 1:Rh (Fig. 2B and Table 1, entry 2) and 2:Rh (Fig. S1C [37] and Table 1, entry 3) consisted of monodisperse small NPs of  $2.4 \pm 0.6$  nm and  $2.0 \pm 0.5$  nm respectively. When PPh<sub>3</sub> was used as a stabilizer (Table 1, entry 4) even smaller particles of  $1.5 \pm 0.4$  nm were obtained (Fig. 2C). The 1:Rh\* system also afforded much fewer particles than 1:Rh preventing us from measuring their size with precision (Fig. S1E [37] and Table 1, entry 5). We noticed during this synthesis that RhCl<sub>3</sub> was not as soluble as Rh(allyl)<sub>3</sub> in the IL, which may explain this observation. During TEM imaging, EDX measurements were conducted to confirm that the visible particles were composed of Rh metal (Fig S2 [37]).



3.2. Toluene hydrogenation and catalyst stability under catalysic conditions

Toluene was chosen as a model substrate [28] to test the activity of the various synthesized Rh NPs (Fig. 3). The reaction conditions chosen are relatively mild and on par with reported studies for this difficult reaction: 40 bar of  $H_2(g)$  for 3 h at 75 °C [22,28,38]. After each run, the product was extracted with pentane and the IL containing the NPs could be reused after being dried for at least 1 h *in vacuo*.

As can be seen in Table 2, the overall catalytic activity of the tested NPs differed dramatically depending on the nature of the stabilizing species. none:Rh (Table 2, entry 1) initially showed high yields for the conversion of toluene to methylcyclohexane. After run 2, the activity became inconsistent varying randomly between 40% and 90% in any given run. 1:Rh and 2:Rh (entries 2 and 3) had to go through an induction period of 3-4 cycles, after which both showed excellent activity, reaching complete conversion by the third or fourth cycle. **1:Rh** showed slightly better activity than 2:Rh with quantitative conversion very consistently after cycle 4. These results are comparable to the activities reported by the Dyson group [22] with bipyridine FILs under similar conditions, proving that phosphine FILs are good stabilizers in this context. In their studies on the effect of the spacer chain length between the bipyridine and the imidazolium moieties on catalytic activity, they reported a much higher activity for the longer chain FIL compared to the shorter chain FIL because of electronic and steric effects. We previously showed in our group the opposite effect on phosphine FIL stabilized Pd NPs on styrene hydrogenation catalysis [32]. In this system, both FIL 1 and 2 feature a very similar activity, with a slightly better reproducibility for 1 after run 4. This

Table 1	2
---------	---

Toluene hydrogenation catalyzed by Rh NPs.<sup>a</sup>

Entry	Catalyst	% Toluene conversion <sup>b</sup>									
		Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5	Cycle 6	Cycle 7	Cycle 8	Cycle 9	Cycle 10
1	None:Rh	91	95	63	90	86	40	59	50	53	74
2	1:Rh	72	93	96	100	100	100	100	100	95	100
3	2:Rh	32	98	100	100	89	95	94	93	100	100
4	PPh₃:Rh	9	68	94	97	100	100	100	89	99	93
5	1:Rh*	0	0	19	56	42	64	65	49	70	52

<sup>a</sup> Reaction conditions: Rh precursor (0.05 mmol), ligand (0.05 mmol), lL (1 mL), toluene (5.0 mmol, 100 equiv.), p[H<sub>2</sub>(g)] = 40 bar, T = 75 °C, t = 3 h. <sup>b</sup> Determined by GC analysis.



Fig. 4. TEM images of Rh NPs after 1 catalytic cycle: (A) none:Rh, (B) 1:Rh, and (C) PPh3:Rh.

effect is smaller but consistent with what we observed with Pd [32]. As can be seen, we do observe some induction period lasting for 2-4 cycles depending on the sample. This conditioning phase could result from: (1) an incomplete reduction of the Rh precursor during NP synthesis, which allowed the continued formation of NPs during the initial hydrogenation cycles; or (2) a restructuring of the NP surface under catalytic conditions, which produces more active catalytic sites. Janiak and co-workers have reported on using various transition metal NPs stabilized by ILs as hydrogenation catalysts in which a conditioning phase was also observed [36]. In order to test these hypotheses, we performed the synthesis of **1:Rh** under a higher temperature  $(75 \circ C)$  to favor the reduction of the precursor. The induction period was shortened to 1 catalytic cycle but was not completely eliminated, suggesting that the first hypothesis is more likely occurring in this system. In order to understand if the particles were undergoing major size or shape alteration under catalytic conditions, we analyzed them again by TEM after cycle 1 and 10 (Table 1, entries 2 and 3). We observed a subtle decrease in size for 1:Rh and no measurable change for 2:Rh. The unstabilized NPs, **none:Rh**, behaved very differently. Before catalysis all visible particles were small and collected into large clusters (Fig. 2A). The high activity in the initial runs was attributed to these small particles, which may be better dispersed in solution than what is visible on the TEM grid. The image after 1 cycle (Fig. 4A) clearly evidenced that some of these clusters tend to fuse into larger, ill-defined particles. After extended recycling runs, complete aggregation was observed by TEM and also plating of metal on the reaction vessel demonstrating the instability of the system over time. This correlates with irregularities observed for the long-term activity of none:Rh. Many reports evidenced that only small sized Rh NPs feature catalytic activity towards hydrogenation, which supports our observations [39]. The better and more consistent results of the FIL systems evidence the important role that stabilization plays for the long-term catalytic efficiency of Rh NPs in ILs [22].

In order to better understand the role of the phosphine ligand in NP stabilization and activity, we studied PPh<sub>3</sub> stabilized NPs, PPh3:Rh (Table 2, entry 4). Their catalytic activity was also excellent after a steep induction period. The activity of this system, which is comparable to the FIL systems, can be attributed to the presence of small particles collected into clusters (Fig. 2C). This confirms that phosphine ligands are providing excellent stabilization to the Rh NPs; however, the <sup>31</sup>P NMR analysis of the product supernatant after cycle 1 revealed that PPh<sub>3</sub> had leached into the organic layer during the extraction of the product. This observation is consistent with the poor solubility of PPh<sub>3</sub> in [BDMI]NTf<sub>2</sub>. While we did not observe any statically relevant decrease of catalytic activity during 10 cycles (Table 2, entry 4), this leaching may cause destabilization of the system in the long-term and may affect the activity or recyclability of the system. On the contrary, FILs 1 and 2 are immobilized within [BDMI]NTf<sub>2</sub> and provide sufficient stabilization to avoid aggregation of the NPs while allowing for a high catalytic activity (Fig. 4B).

We then underwent a study of the effect of the Rh precursor on NP synthesis and performance, specifically to compare Rh(allyl)<sub>3</sub> with a more traditionally used precursor, RhCl<sub>3</sub>. Based on the performance of 1:Rh, we selected 1 to form NPs employing RhCl<sub>3</sub>·3H<sub>2</sub>O, **1:Rh**\*. The activity for this sample was considerably lower than that of 1:Rh (Table 2, entry 5). TEM analysis revealed the presence of very few particles after synthesis, but only aggregates were visible after cycle 1 and cycle 10 (Fig. S1F [37], Table 1, entry 5). These results are explained by the much lower solubility of RhCl<sub>3</sub> in the IL solvent compared to the allyl precursor, resulting in much fewer active small NPs. The catalytic activity of 1:Rh\* increased in later hydrogenation cycles, which could result from the dissolution of a small quantity of precursor by toluene into the IL. Like for none:Rh, aggregates are associated with lower activity and irregular results. Rh(allyl)<sub>3</sub> was introduced by Chaudret's group as a clean NP precursor, that decomposes easily under H<sub>2</sub> pressure [17], and in our hands it proves a more efficient precursor than RhCl<sub>3</sub>.

One further study was conducted in the optimization of the catalytic conditions and involved a low temperature hydrogenation of toluene. A catalytic run of the **1:Rh** system was carried out at 35 °C, 40 bar  $H_2(g)$ , for 24 h and resulted in 27% conversion of toluene to methylcyclohexane and thus the NPs are even active at low temperatures.

A CS<sub>2</sub> poisoning test was also carried out on the **1:Rh** sample to determine whether a homogeneous mechanism was involved in the hydrogenation of toluene [36]. The addition of 0.5 equiv. of CS<sub>2</sub> to the IL phase after NP synthesis rendered the NP catalyst completely inactive in the hydrogenation of toluene. This result



**Fig. 5.** Hydrogenation of other arene substrates. Reaction conditions: Rh precursor (0.05 mmol), ligand (0.05 mmol), IL (1 mL), toluene (5.0 mmol, 100 equiv.),  $p[H_2(g)] = 40$  bar,  $T = 75 \circ C$ , t = 3 h. Determined by GC analysis.

supports a heterogeneous mechanism for the hydrogenation of arenes employing these Rh NP catalysts and removes the possibility of an active homogeneous species in the system.

In order to understand the scope of the reaction, our best catalyst, **1:Rh**, was employed in the reduction of more demanding arene substrates (Fig. 5). The first substrate investigated was styrene, which was reduced to ethylcyclohexane in high yields, reaching 100% after 6 cycles under the conditions described above (Fig. 4). Xylene substrates were also investigated and were reduced to the corresponding dimethylcyclohexane in high yields, reaching up to 70% conversion. *tert*-Butylbenzene [40] was also used as a substrate in this study; although, the conversion proved more modest than what had been seen for the previous substrates.

#### 4. Conclusion

Phosphine FILs are effective stabilizers in the formation of biphasic Rh NP catalysts. This new class of ligands increased both the catalytic activity and lifetime of the Rh NP catalysts beyond those stabilized by an unfunctionalized IL solvent or a traditional organic stabilizer for the hydrogenation of toluene to methylcyclohexane. This observation was rationalized by the size and shape analysis of the NPs before and after catalysis. The heterogeneous nature of catalysis was also demonstrated. Furthermore, the FIL stabilized Rh NPs were also active catalysts in the reduction of more challenging substrates including styrene and xylenes. This study proves the catalytic activity of Rh NPs stabilized by phosphine FILs and also introduces Rh(allyl)<sub>3</sub> as an efficient Rh NP precursor in ILs.

#### Acknowledgements

We thank the Natural Science and Engineering Research Council of Canada (NSERC), the Canada Foundation for Innovation (CFI), the Canada Research Chairs (CRC), the Fonds de Recherche sur la Nature et les Technologies (FQRNT), Hydro-Québec Master Fellowship, the Center for Green Chemistry and Catalysis (CGCC) and McGill University for their financial support. We also thank Dr. Jean-Philippe Masse (École Polytechnique de Montréal) for TEM measurements, as well as Dr. Tom Baker for his help.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.cattod.2011.09.016.

#### References

- [1] H. Bonnemann, R.M. Richards, Eur. J. Inorg. Chem. (2001) 2455-2480.
- [2] L. Ott, R. Finke, Coord. Chem. Rev. 251 (2007) 1075-1100.

- [3] E. Ramirez, S. Jansat, K. Philippot, P. Lecante, M. Gomez, A.M. Masdeu-Bultó, B. Chaudret, J. Organomet. Chem. 689 (2004) 4601–4610.
- [4] S. Son, Y. Jang, K. Yoon, E. Kang, T. Hyeon, Nano Lett. 4 (2004) 1147–1151.
- [5] B. Léger, A. Denicourt-Nowicki, H. Olivier-Bourbigou, A. Roucoux, Inorg. Chem. 47 (2008) 9090–9096.
- [6] C.W. Chen, T. Serizawa, M. Akashi, Chem. Mater. 11 (1999) 1381-1389.
- [7] J.L. Pellegatta, C. Blandy, V. Colliere, R. Choukroun, B. Chaudret, P. Cheng, K. Philippot, J. Mol. Catal. A: Chem. 178 (2002) 55-61.
- [8] A.B. Lowe, B.S. Sumerlin, M.S. Donovan, C.L. McCormick, J. Am. Chem. Soc. 124 (2002) 11562–11563.
- [9] B. Panella, A. Vargas, A. Baiker, J. Catal. 261 (2009) 88-93.
- [10] T. Maegawa, A. Akashi, K. Yaguchi, Y. Iwasaki, M. Shigetsura, Y. Monguchi, H. Sajiki, Chem. Eur. J. 15 (2009) 6953–6963.
- [11] L.M. Rossi, I.M. Nangoi, N.J.S. Costa, Inorg. Chem. 48 (2009) 4640–4642.
- [12] H. Bonnemann, W. Brijoux, R. Brinkmann, E. Dinjus, T. Joussen, B. Korall, Angew. Chem. Int. Ed. 30 (1991) 1312–1314.
- [13] H. Bonnemann, R. Brinkmann, P. Neiteler, Appl. Organomet. Chem. 8 (1994) 361–378.
- [14] A. Roucoux, J. Schulz, H. Patin, Chem. Rev. 102 (2002) 3757-3778.
- [15] J. Dupont, J.D. Scholten, Chem. Soc. Rev. 39 (2010) 1780–1804.
- [16] T. Gutel, C.C. Santini, K. Philippot, A. Padua, K. Pelzer, B. Chaudret, Y. Chauvin, J.M. Basset, J. Mater. Chem. 19 (2009) 3624–3631.
- [17] M.R. Axet, S. Castillon, C. Claver, K. Philippot, P. Lecante, B. Chaudret, Eur. J. Inorg. Chem. (2008) 3460–3466.
- [18] A. Bosmann, G. Francio, E. Janssen, M. Solinas, W. Leitner, P. Wasserscheid, Angew. Chem. Int. Ed. 40 (2001) 2697–2699.
- [19] E. Redel, R. Thomann, C. Janiak, Chem. Commun. (2008) 1789-1791.
- [20] E. Redel, R. Thomann, C. Janiak, Inorg. Chem. 47 (2008) 14–16.
- [21] E. Redel, J. Kramer, R. Thomann, C. Janiak, J. Organomet. Chem. 694 (2009) 1069-1075.
- [22] R.R. Dykeman, N. Yan, R. Scopelliti, P.J. Dyson, Inorg. Chem. 50 (2011) 717–719.
- [23] M.H.G. Prechtl, P.S. Campbell, J.D. Scholten, G.B. Fraser, G. Machado, C.C. Santini, J. Dupont, Y. Chauvin, Nanoscale 2 (2010) 2601–2606.
- [24] E.T. Silveira, A.P. Umpierre, L.M. Rossi, G. Machado, J. Morais, G.V. Soares, I.L.R. Baumvol, S.R. Teixeira, P.F.P. Fichtner, J. Dupont, Chem. Eur. J. 10 (2004) 3734–3740.
- [25] D. Raut, K. Wankhede, V. Vaidya, S. Bhilare, N. Darwatkar, A. Deorukhkar, G. Trivedi, M. Salunkhe, Catal. Commun. 10 (2009) 1240–1243.
- [26] Y. Zhao, G.R. Cui, J.J. Wang, M.H. Fan, Inorg. Chem. 48 (2009) 10435–10441.
- [27] A. Umpierre, G. Machado, G. Fecher, J. Morais, J. Dupont, Adv. Synth. Catal. 347 (2005) 1404–1412.
- [28] B. Léger, A. Denicourt-Nowicki, H. Olivier-Bourbigou, A. Roucoux, Tetrahedron Lett. 50 (2009) 6531–6533.
- [29] M.A. Gelesky, S.S.X. Chiaro, F.A. Pavan, J.H.Z. dos Santos, J. Dupont, Dalton Trans. (2007) 5549–5553.
- [30] D.B. Zhao, Z.F. Fei, T.J. Geldbach, R. Scopelliti, P.J. Dyson, J. Am. Chem. Soc. 126 (2004) 15876-15882.
- [31] Y. Hu, Y.Y. Yu, Z.S. Hou, H. Li, X.G. Zhao, B. Feng, Adv. Synth. Catal. 350 (2008) 2077–2085.
- [32] K.L. Luska, A. Moores, Adv. Synth. Catal (2011), doi:10.1002/adsc.201100551.
- [33] K.L. Luska, A. Moores, Can. J. Chem., in press.
- [34] K.D. John, K.V. Salazar, B.L. Scott, R.T. Baker, A.P. Sattelberger, Organometallics 20 (2001) 296–304.
- [35] C.S. Consorti, G.L.P. Aydos, G. Ebeling, J. Dupont, Org. Lett. 10 (2008) 237–240.
- [36] C. Vollmer, E. Redel, K. Abu-Shandi, R. Thomann, H. Manyar, C. Hardacre, C. Janiak, Chem. Eur. J. 16 (2010) 3849–3858.
- [37] Available in the supplementary content.
- [38] B. Leger, A. Denicourt-Nowicki, H. Olivier-Bourbigou, A. Roucoux, Chemsuschem 1 (2008) 984–987.
- [39] J.A. Widegren, R.G. Finke, J. Mol. Catal. A: Chem. 191 (2003) 187-207.
- [40] J. Schulz, A. Roucoux, H. Patin, Chem. Euro. J. 6 (2000) 618–624.