

Solid catalysts on the basis of supported ionic liquids and their use in hydroamination reactions

Stefan Breitenlechner, Martin Fleck, Thomas E. Müller*, Andreas Suppan

Institut für Technische Chemie II, Technische Universität München, Lichtenbergstraße 4, 85747 Garching, Germany

Received 31 July 2003; accepted 10 December 2003

Abstract

The scope for the immobilization of homogeneous catalysts in supported ionic liquids was explored. Here, a solution of cationic transition metal complexes in the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethanesulfonate was supported on diatomic earth. The catalysts were then tested in the direct addition of 4-isopropylaniline to phenylacetylene (hydroamination). Supported Rh(I), Pd(II) and Zn(II) complexes combined a higher intrinsic catalytic activity relative to the corresponding homogeneous catalysts with a high selectivity.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Supported catalysts; Addition; Amines; Two-phase catalysis; Ionic liquid

1. Introduction

New C–N bond forming processes are highly interesting for both organic syntheses and industrial processes due to the importance of nitrogen containing molecules as building blocks and in industrial applications. Commercially valuable products include amines, amides, ammonium and alkyl-ammonium salts, ureas, carbamates, isocyanates and amino acids [1]. Especially the direct addition of amines to alkenes and alkynes (hydroamination) gains rapidly increasing interest as an atom economic and direct route to amines, enamines and imines [2]. Several different types of homogeneous catalysts have been reported for hydroamination reactions [3]. However, there are only few examples for heterogeneously catalysed hydroamination reactions. Zeolites in the protonic form are currently used in industry in the addition of ammonia to 2-methylpropene. Ion exchanged zeolites [4,5] and tethered palladium complexes [6,7] were shown in laboratory experiments to be promising catalysts for the addition of amines to alkynes.

Especially homogeneous catalysts based on the late transition metals [8,9] seemed interesting candidates for the development of corresponding heterogeneous catalysts. This class of hydroamination catalysts has in common

that most are cationic complexes. A high catalytic activity in model reactions was observed for complexes of Rh(I), Pd(II), Cu(I) and Zn(II) [5,10–14]. In this study we focused on the complexes [Rh(DPPF)(NOR)]ClO₄ (DPPF: 1,1'-bis-(diphenylphosphino)-ferrocene, NOR: 2,5-norbornadiene), [Pd(DPPF)](CF₃SO₃)₂, [Cu₂(C₆H₅CH₃)](CF₃SO₃)₂ and Zn(CF₃SO₃)₂. In the preparation of heterogeneous catalysts the complexes were first dissolved in the ionic liquid [15] 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (IL). The solution was then supported on a porous material [16–19]. Here diatomic earth was used. The resulting solid catalyst was tested in the addition of 4-isopropylaniline to phenylacetylene (Fig. 1).

2. Experimental

2.1. Materials and methods

All reactions involving air- and/or water-sensitive compounds were performed using standard Schlenk techniques. Dry solvents were obtained from Aldrich; (4-isopropylphenyl)-(1-phenyl-ethylidene)-amine was synthesised according to reference [20]; 1-ethyl-3-methylimidazolium trifluoromethanesulfonate was prepared from *N*-methylimidazole (99%, Aldrich) and ethyl-trifluoromethanesulfonate (99%, Aldrich) as described in [21]. According to the ¹H NMR spectrum, the purity of the ionic liquid was >96.7%

* Corresponding author. Tel.: +49-89-289-13538; fax: +49-89-289-13544.

E-mail address: thomas.mueller@ch.tum.de (T.E. Müller).

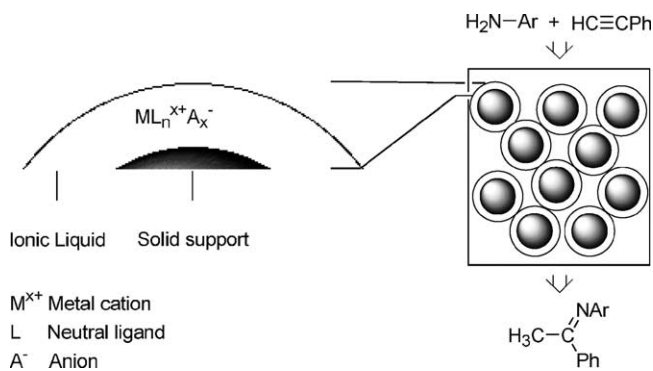


Fig. 1. Concept for the preparation of supported hydroamination catalysts.

with traces of water (1.2%) and *N*-methylimidazole (2.1%). This level of impurity was observed after outgassing the IL overnight at 50 °C in oil pump vacuum and might lead to modified catalyst properties. In this respect it is known that water has little effect on the rate of reaction whereas basic conditions can lead to a reduced catalytic activity of late transition metal catalysts in the hydroamination of alkynes [27]. Catalysts and other chemicals not described in the experimental section were obtained from Aldrich and used as purchased. The diatomic earth (Chromosorb P, 60–80 mesh, acid washed, silylated with Me_2SiCl_2) was obtained from Resteck.

2.2. Physical and analytical methods

1H , $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AM 400 instrument and referenced in ppm relative to tetramethylsilane using the solvent shift as internal standard [22] or a double walled NMR tube with $CDCl_3$ as external standard. IR spectra were obtained on a Perkin-Elmer FT-IR 2000 spectrometer as KBr pellets. Mass spectroscopic analyses were performed on a Finnigan MAT 311 A mass spectrometer by fast atom bombardment (FAB). GC analyses were performed on a Hewlett-Packard HP 5890 gas chromatograph equipped with a crosslinked 5% diphenyl–95% dimethyl–polysiloxane column (30 m, Restek GmbH, Rtx-5 Amine) and a flame ionization detector (temperature program: 5 min at 120 °C, 10 °C/min to 290 °C, 17 min at 290 °C). GC–MS analyses were performed on a Hewlett-Packard HP 5890 gas chromatograph equipped with an identical column and a mass selective detector HP 5971 A. Scanning electron microscopy images were obtained on a JSM-5900.

2.3. Synthesis and characterization of $[Pd(DPPF)(CF_3SO_3)_2]C_6H_{14}$

The complex $[Pd(DPPF)Cl_2]$ (5.0 g, 6.8 mmol) was dissolved in CH_2Cl_2 (100 cm^3). A solution of $AgCF_3SO_3$ in CH_3CN (20 cm^3) was added slowly, the mixture stirred for 30 min in the dark and the solid which had formed filtered off. The solvent was partially removed and the complex pre-

cipitated with Et_2O (100 cm^3). The precipitate was collected, dried in vacuum and recrystallised from CH_2Cl_2 /hexane.

Yield: 5.5 g, 92%.

Found: C, 54.8; H, 4.4; N, 0.0; Pd 10.3; S 6.0%. Calc. for $C_{42}H_{42}F_6FeO_6P_2PdS_2$: C, 48.3; H, 4.1; Pd, 10.2; S 6.1%.

1H NMR ($CDCl_3$): δ 7.9 (b, 6H, Ph), 7.5–7.4 (m, 12H, Ph), 6.9 (d, 2H, Ph), 5.3 (d, 3H, Cp), 4.6 (s, 2H, Cp), 4.5 (s, 3H, Cp), 2.3 (s, CH_3CN), 1.3 (b, CH_2), 0.9 (t, CH_3) ppm.

$^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 141.4 (s, Ph), 134.5 (t, Ph), 132.3 (s, Ph), 128.9 (t, Ph), 128.3 (s, Ph), 126.2 (s, Ph), 74.9 (s, Cp), 31.8 (s, CH_2), 21.3 (s, CH_2), 14.1 (s, CH_3) ppm.

$^{31}P\{^1H\}$ NMR ($CDCl_3$): δ -71.5 (s) ppm.

MS (FAB) m/z 829 ($M^+ - CF_3SO_3 + HF$), 659 ($M^+ - 2CF_3SO_3 - H$), 582 ($M^+ - 2CF_3SO_3 - Ph - H$).

2.4. Preparation of the supported catalysts

Saturated solutions of the catalysts $[Rh(DPPF)(NOR)]ClO_4$, $[Pd(DPPF)](CF_3SO_3)_2$, $[Cu_2(C_6H_5CH_3)](CF_3SO_3)_2$ and $Zn(CF_3SO_3)_2$ in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (2.2 cm^3) were prepared at room temperature and carefully filtered. The solution was diluted with 20 cm^3 CH_2Cl_2 (in case of $[Rh(DPPF)(NOR)]ClO_4$ and $[Pd(DPPF)](CF_3SO_3)_2$) or acetone (in case of $[Cu_2(C_6H_5CH_3)](CF_3SO_3)_2$ and $Zn(CF_3SO_3)_2$). Diatomic earth (abbreviated T, 10 g) was added and the suspension shaken for 5 min. The suspension was then rapidly cooled to liquid nitrogen temperature and freeze-dried to give a well flowing orange powder. For comparison reasons, a further sample (IL/T) was prepared in the same way, but without addition of a metal catalyst. The analytic data of the supported catalysts (abbreviated Rh/IL/T, Pd/IL/T, Cu/IL/T and Zn/IL/T, respectively) are summarized in Table 1.

Supported $[Pd(DPPF)](CF_3SO_3)_2$ (Pd/IL/T): $^{31}P\{^1H\}$ NMR (no solvent): δ 51 (b) ppm.

Supported $Zn(CF_3SO_3)_2$ (Zn/IL/T): 1H NMR (no solvent): δ 7.57 (s, 1H, Im), 7.32 (s, 1H, Im), 6.25 (s, 1H, Im), 3.93 (s, 3H, NCH_3), 3.32 (s, 1H, CH_aH_b), 3.17 (s, 1H, CH_aH_b), 2.54 (s, 2H, $CH_aH_bH_c$), 2.50 (s, 1H, $CH_aH_bH_c$) ppm.

2.5. Catalytic experiments

The catalysts (amount corresponding to 1.5×10^{-3} mmol M^{n+}) were weighed into flasks as follows: Rh/IL/T 1.75 g, Pd/IL/T 1.56 g, Cu/IL/T 0.95 g, Zn/IL/T 0.10 g, $[Pd(DPPF)](CF_3SO_3)_2$ 14.4×10^{-3} g, $[Cu_2(C_6H_5CH_3)](CF_3SO_3)_2$ 7.8×10^{-3} g, $Zn(CF_3SO_3)_2$ 5.5×10^{-3} g. For comparison reasons catalytic experiments were also performed with a solution of $[Cu_2(C_6H_5CH_3)](CF_3SO_3)_2$ 7.8×10^{-3} g in 0.5 cm^3 IL and a solution of $Zn(CF_3SO_3)_2$ 5.5×10^{-3} g in 0.5 cm^3 IL. Dry heptane (11.6 cm^3) was added to each of these samples, the mixtures heated to reflux temperature (98 °C) and the catalytic reaction started by addition of 4-isopropylaniline (0.21 cm^3 , 1.5 mmol) and phenylacetylene (0.16 cm^3 , 1.5 mmol). During the reaction,

Table 1
Analytic data of the catalysts used in this study

Sample	Elemental analysis			AAS Metal (wt.%)	Calculated	
	C (wt.%)	H (wt.%)	N (wt.%)		IL (wt.%)	Cat (wt.%)
T	0.10	0.16	–	–	–	–
IL/T	8.02	1.27	2.68	–	24.9	–
Zn/IL/T	3.80	0.74	1.02	1.03	9.5	5.7
Cu/IL/T	2.29	0.39	0.63	0.10	5.9	0.8
Pd/IL/T	6.71	1.04	2.02	0.10	18.8	0.9
Rh/IL/T	7.91	1.22	2.60	0.09	24.1	0.7

samples were taken for GC-analysis referencing the peak areas to undecane as internal standard. Samples containing heterogeneous catalysts were centrifuged for 10 min at 14 000 rpm and decanted before analysis. No catalytic activity was observed in reference experiments with diatomic earth (0.76 g) or IL/T (1.08 g).

3. Results and discussion

The following procedure was adopted for the immobilisation of homogeneous catalysts (Fig. 2). The metal complexes $[\text{Rh}(\text{DPPF})(\text{NOR})]\text{ClO}_4$, $[\text{Pd}(\text{DPPF})](\text{CF}_3\text{SO}_3)_2$, $[\text{Cu}_2(\text{C}_6\text{H}_5\text{CH}_3)](\text{CF}_3\text{SO}_3)_2$ and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ were dissolved in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate so that the solution was saturated at room temperature. The solution was filtered carefully and diluted with CH_2Cl_2 ($[\text{Rh}(\text{DPPF})(\text{NOR})]\text{ClO}_4$ and $[\text{Pd}(\text{DPPF})](\text{CF}_3\text{SO}_3)_2$) or acetone ($[\text{Cu}_2(\text{C}_6\text{H}_5\text{CH}_3)](\text{CF}_3\text{SO}_3)_2$ and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$). These solvents were chosen in such a way that both complex and ionic liquid would dissolve well. After addition of diatomic earth to the solution, the mixture was shock frozen and freeze dried to ensure an even distribution of the ionic liquid as thin layer on the support.

After freeze drying a well flowing powder was obtained. An electron micrograph of the material with the supported IL on the particles is shown in Fig. 3. The diatomic earth forms particles of 180–250 μm diameter with pores of approxi-



Fig. 3. SEM-picture of the zinc catalyst used in the experiments.

mately 1 μm diameter. The ionic liquid spreads as an even layer with approximately 20 nm thickness on the surface of the particles. The effect of the supported IL on the pore size distribution was analysed with mercury porosimetry. Two maxima in mercury uptake can be distinguished which correspond to the interparticle voids with 86 μm mean diameter and the intraparticle voids with 0.9 μm mean diameter. After the IL had been supported, the volume of the interparticle voids of 1.18 cm^3/g had decreased by 10–20%. The volume of the intraparticle voids of 0.80 cm^3/g had decreased by 20–50% (Table 2). In parallel, the surface area (10.3 m^2/g for

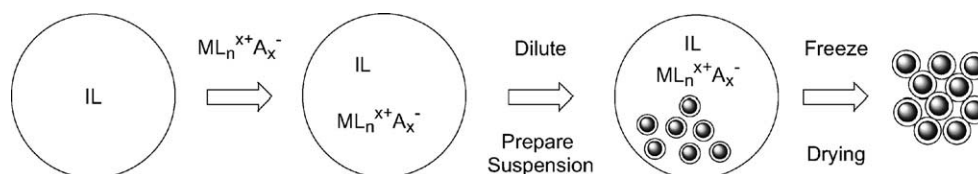


Fig. 2. Experimental procedure for the preparation of the supported catalysts.

Table 2
Pore volume measured by mercury porosimetry

Sample	Interparticle volume (cm^3/g)	Pore volume (cm^3/g)	Total pore volume (cm^3/g)	Surface area (cm^2/g)
T	1.18	0.80	1.96	10.33
IL/T	0.88	0.45	1.33	4.63
Zn/IL/T	0.94	0.47	1.41	4.85
Cu/IL/T	1.07	0.64	1.71	3.24
Pd/IL/T	0.93	0.47	1.40	3.24
Rh/IL/T	1.05	0.38	1.43	3.04

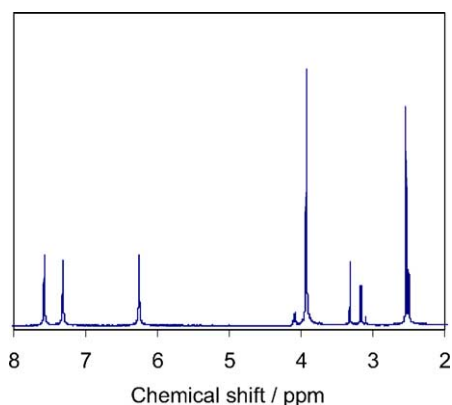


Fig. 4. ^1H NMR spectrum of the supported zinc catalyst.

the parent material) had decreased by two-thirds to $4.9\text{ m}^2/\text{g}$ for the supported zinc catalyst and $3.0\text{ m}^2/\text{g}$ for the supported rhodium catalyst.

Although a solid material, a high resolution ^1H NMR spectrum could be obtained of the supported zinc catalyst (Fig. 4). The line width was similar to that observed for the spectrum of the ionic liquid dissolved in CDCl_3 . This indicates that the supported layer resembles a liquid with highly mobile molecules. Closer inspection of the NMR spectrum showed that the resonances due to the aromatic protons in 1-ethyl-3-methylimidazolium trifluoromethanesulfonate (in CDCl_3 at 9.23, 7.32 and 7.28 ppm) had shifted considerably to 7.57, 7.32 and 6.25 ppm. The signal of the

methylene protons was split into two resonances at 3.32 and 3.16 ppm and the methyl protons of the ethyl group into two resonances at 2.54 and 2.50 ppm in a two to one ratio. This indicates that the free rotation around the $\text{N}-\text{C}_{\text{Ethyl}}$ bond is hindered in the supported ionic liquid. Probably, the nitrogen atom strongly interacts with the surface of the support. The zinc cations cannot be responsible for this effect as the molar ratio of zinc salt to ionic liquid is 1:13. The methyl group directly attached to the second nitrogen atom showed a single resonance at 3.93 ppm in the NMR spectrum indicating that the free rotation around the $\text{N}-\text{C}_{\text{Methyl}}$ bond is retained in the supported ionic liquid.

The supported complexes were then tested for the catalytic activity in the addition of 4-isopropylaniline to phenylacetylene. The reaction yields the enamine (4-isopropyl-phenyl)-(1-phenyl-vinyl)-amine which isomerises in situ to the corresponding imine (4-isopropyl-phenyl)-(1-phenyl-ethylidene)-amine (Eq. (1)). The product was formed according to approximate second order kinetics. The initial rate of reaction (Table 3) was highest for the supported palladium catalyst ($4.30\text{ mol}(\text{mol}_{\text{cat}}\text{ h})^{-1}$). For the supported $[\text{Rh}(\text{DPPF})(\text{NOR})]\text{ClO}_4$, $[\text{Pd}(\text{DPPF})](\text{CF}_3\text{SO}_3)_2$ and $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ catalysts the rate of reaction was significantly higher than in the corresponding homogeneous catalysis. In contrast, for $[\text{Cu}_2(\text{C}_6\text{H}_5\text{CH}_3)](\text{CF}_3\text{SO}_3)_2$ the catalytic activity was higher for the homogeneous catalyst. Latter can be readily explained by the IL which competes with coordination of the substrate.

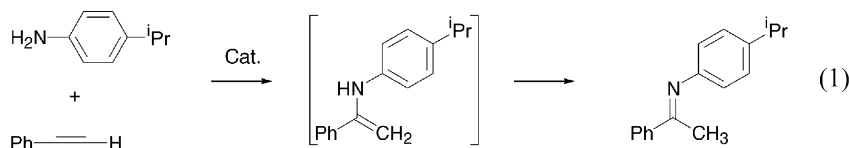


Table 3

Initial catalytic activity of the supported catalysts in the addition of 4-isopropylaniline to phenylacetylene (at 98°C), conversion after 22h reaction time and selectivity to (4-isopropyl-phenyl)-(1-phenyl-ethylidene)-amine at the end of the experiment (conversion stated in brackets)

Metal complex	Initial activity		Conversion %	Selectivity %
	$10^{-3}\text{ mol}(\text{g}_{\text{cat}}\text{ h})^{-1}$	$\text{mol}(\text{mol}_{\text{cat}}\text{ h})^{-1}$		
Homogeneous catalysis				
$\text{Zn}(\text{CF}_3\text{SO}_3)_2$	0.27	0.10	2.7	90.7 (37)
$[\text{Pd}(\text{DPPF})](\text{CF}_3\text{SO}_3)_2$	2.19	2.10	23.3	84.2 (23)
$[\text{Cu}_2(\text{C}_6\text{H}_5\text{CH}_3)](\text{CF}_3\text{SO}_3)_2$	32.8	17.0	79.3	97.0 (80)
$[\text{Rh}(\text{DPPF})(\text{NOR})]\text{ClO}_4$	0.40	0.34	–	77.7 (27)
Catalysis with supported complexes				
$\text{Zn}(\text{CF}_3\text{SO}_3)_2$	1.59	0.58	31.2	100 (86)
$[\text{Pd}(\text{DPPF})](\text{CF}_3\text{SO}_3)_2$	4.48	4.30	45.4	100 (65)
$[\text{Cu}_2(\text{C}_6\text{H}_5\text{CH}_3)](\text{CF}_3\text{SO}_3)_2$	1.60	0.83	19.7	99.4 (40)
$[\text{Rh}(\text{DPPF})(\text{NOR})]\text{ClO}_4$	0.85	0.72	14.6	84.7 (34)
Two phase catalysis				
$\text{Zn}(\text{CF}_3\text{SO}_3)_2$	1.99	0.72	8.6	100 (41)
$[\text{Cu}_2(\text{C}_6\text{H}_5\text{CH}_3)](\text{CF}_3\text{SO}_3)_2$	3.47	1.79	34.4	98.1 (87)

In case of the homogeneous catalysis the most pronounced side reaction was the oligomerisation of phenylacetylene. It is especially noteworthy that, for all four metal complexes, the selectivity to (4-isopropyl-phenyl)-(1-phenyl-ethylidene)-amine was increased for the supported catalyst (see Table 3).

Already 5 min after the start of the reaction the concentration of the starting material had decreased from 0.13 mol/l to 0.10 and 0.08 mol/l for phenylacetylene and 4-isopropylaniline, respectively (Pd/IL/T). At longer reaction times, the concentration of the starting material decreased further although more slowly and in parallel to the formation of the product. This indicates that a considerable amount of the starting material had rapidly dissolved in the ionic liquid as had been observed before [20]. The product is hardly soluble in the ionic liquid, which favours desorption of the product from the supported liquid layer. Thus, catalysis with these supported complexes is very similar to the corresponding two-phase catalysis [19,23]. Under similar reaction conditions, the performance of the two-phase system was intermediate between the catalysis using homogeneous and supported catalysts (Table 3).

4. Conclusions

The scope of immobilising cationic homogeneous complexes as supported ionic liquids was explored. By this strategy a high surface area between two liquid phases can be stabilised allowing for a rapid mass transfer across the phase boundary. The choice of the ionic liquid enables to tune the phase equilibria in such a way that the reactants are readily adsorbed in the liquid layer whereas the products are not soluble and are desorbed fast. In this respect the tunability of the properties of ionic liquids as designer solvents is especially beneficial [24–26]. By choosing the relative solubility of reactants and products in this way, it should be possible to accelerate catalytic reactions where the catalyst is preferentially dissolved in the ionic liquid phase. Here, this effect was utilized to enhance the catalysis of the hydroamination reactions choosing 1-ethyl-3-methylimidazolium trifluoromethanesulfonate as the ionic liquid.

The catalytic performance of the supported catalysts prepared in this study was tested in the direct addition of 4-isopropylaniline to phenylacetylene. For [Rh(DPPF)-(NOR)]ClO₄, [Pd(DPPF)](CF₃SO₃)₂ and Zn(CF₃SO₃)₂ the intrinsic catalytic activity of the supported complexes was higher than of the corresponding homogeneous catalysts. It is particularly noteworthy that the supported catalysts combined the enhanced catalytic activity with an improved selectivity. In summary, the immobilisation of homogeneous complexes in supported ionic liquids is a straightforward

method for bringing the advantages of homogeneous and heterogeneous catalysis together.

Acknowledgements

This study was performed within the scope of an undergraduate project and was supported by Dr. -Ing. Leonhard-Lorenz-Stiftung. The financial contribution is gratefully acknowledged.

References

- [1] D.M. Roundhill, Chem. Rev. 91 (1992) 1.
- [2] T.E. Müller, in: I.T. Horváth, Encyclopaedia of Catalysis, vol. 3, Wiley, Hoboken, NJ, 2003, pp. 492–515 and 518–539.
- [3] M. Nobis, B. Driessen-Hölscher, Angew. Chem. Int. Ed. 40 (2001) 3983.
- [4] R.S. Neale, L. Elek, R.E. Malz, J. Catal. 27 (1972) 432.
- [5] J. Penzien, C. Haeßner, A. Jentys, K. Köhler, T.E. Müller, J.A. Lercher, J. Catal. 221 (2004) 302.
- [6] M.K. Richmond, S.L. Scott, G.P.A. Yap, H. Alper, Organometallics 21 (2002) 3395.
- [7] M.K. Richmond, S.L. Scott, H. Alper, J. Am. Chem. Soc. 123 (2001) 10521.
- [8] H.M. Senn, P.E. Blöchl, A. Togni, J. Am. Chem. Soc. 122 (2000) 4098.
- [9] C. Hahn, P. Morvillo, A. Vitagliano, Eur. J. Inorg. Chem. (2001) 419.
- [10] M. Beller, O.R. Thiel, H. Trauthwein, C.G. Hartung, Chem. Eur. J. 6 (2000) 2513.
- [11] O. Löber, J.F. Hartwig, Kawatsura, J. Am. Chem. Soc. 123 (2001) 4366.
- [12] M. Kawatsura, J.F. Hartwig, Organometallics 20 (2001) 1960.
- [13] M. Kawatsura, J.F. Hartwig, J. Am. Chem. Soc. 122 (2000) 9546.
- [14] X. Cheng, K.K. Hii, Tetrahedron 57 (2001) 5445.
- [15] H. Olivier-Bourbigou, L.J. Magna, Mol. Catal. A: Chem. 3484 (2002) 1.
- [16] P. Panster, S. Wieland, in: B. Cornils, W.A. Hermann, Applied Homogeneous Catalysis with Organometallic Compounds: A Comprehensive Handbook, vol. 2, VCH, Weinheim, 1996, p. 618.
- [17] M.H. Valkenberg, C. deCastro, W.F. Hölderich, Green Chem. 4 (2002) 88.
- [18] S. Csihony, H. Mehdi, I.T. Horváth, Green Chem. 3 (2001) 307.
- [19] K. Bernardo-Gusmão, L.F.T. Queiroz, R.F. de Souza, F. Leca, C. Loup, R. Réau, J. Catal. 219 (2003) 59.
- [20] J. Bodis, T.E. Müller, J.A. Lercher, Green Chem. 5 (2003) 227.
- [21] P. Bonhote, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Inorg. Chem. 35 (1996) 1168.
- [22] H.E. Gottlieb, V. Kotlyar, A. Nudelman, J. Org. Chem. 62 (1997) 7512.
- [23] S. Cacchi, V. Carnicelli, F. Marinelli, J. Organomet. Chem. 475 (1994) 289.
- [24] T. Welton, Chem. Rev. 99 (1999) 2071.
- [25] R. Sheldon, Chem. Commun. (2001) 2399.
- [26] P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. Engl. 39 (2000) 3772.
- [27] T.E. Müller, M. Grosche, E. Herdtweck, A.-K. Pleier, E. Walter, Y.-K. Yan, Organometallics 19 (2000) 170.