Ligand Design

DOI: 10.1002/anie.201001787

Recyclable Catalysts for Palladium-Catalyzed C−O Coupling Reactions, Buchwald–Hartwig Aminations, and Sonogashira Reactions**

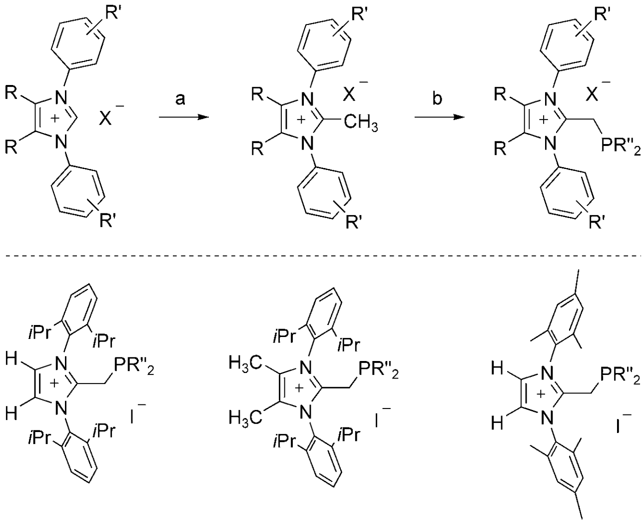
*Andreas Dumrath, Xiao-Feng Wu, Helfried Neumann, Anke Spannenberg, Ralf Jackstell, and Matthias Beller**

Dedicated to Professor Uwe Rosenthal on the occasion of his 60th birthday

Palladium-catalyzed coupling reactions have become an effective tool for advanced organic synthesis in both academic and industrial laboratories.[1,2] In particular, homogeneous palladium complexes allow for the reliable construction of all kinds of C−C and C−X bonds (X = O, N, S) from aryl and heteroaryl halides. Among the multitude of palladium complexes available for modern coupling reactions, bulky electron-rich phosphanes have become a privileged class of ligands,[3,4] which in addition to established coupling processes also enable more challenging reactions with water,[5] alcohols,[6] ammonia,[7] fluoride,[8] and synthesis gas.[9] The drawbacks of these sophisticated ligands are their multistep preparation and costs, which are often price determining for the respective catalyst system. Hence, recycling these ligands still constitutes a major challenge.

Common concepts for the recycling of palladium catalysts involved in coupling reactions include heterogenization of ligands on polymeric supports[10] and palladium-supported heterogeneous catalysts.[11] Recently, Jin and Lee also fixed homogeneous palladium catalysts onto nanoparticles to combine the advantages of homogeneous and heterogeneous catalysis.[12,13] On the basis of the development of liquid–liquid biphasic catalysis[14,15] and the immobilization of molecular catalysts on solid surfaces, elegant concepts for catalyst recycling have been realized in the last decade.[16] For example, Wasserscheid and co-workers[12] demonstrated the feasibility of supported ionic liquid phases as a catalyst support (SILP) in Fischer–Tropsch and hydrogenation reactions.[17]

Despite all these developments, to date there exist no examples of the recycling of ligands and palladium catalysts in difficult coupling reactions. In this respect, we describe a general and facile generation of novel sterically hindered, nucleophilic phosphane ligands, which allow for easy recycling and direct reuse in palladium-catalyzed C−O, C−N, and C−C bond-forming reactions.



1: R'' = Cy (54%)

2: R'' = Cy (80%)
3: R'' = *t*Bu (58%)
4: R'' = Ph (60%)

5: R'' = Cy (45%)

Scheme 1. Synthesis of imidazolium phosphanes **1**–**5**: a) 1. *n*BuLi, THF, −40 °C, 5 min; 2. MeI, THF, −40 °C, 20 min. b) 1. *n*BuLi, THF, −40 °C, 20 min; 2. Cl-PR''$_2$, THF, 30–50 °C.

As shown in Scheme 1, our ligand concept is based on 2-phosphanylmethyl-*N*,*N'*-biarylimidazolium salts. Ligands **1**–**5** are prepared in a straightforward manner in only two or three steps. The central *N*,*N'*-biaryl-1*H*-imidazolium unit is synthesized either by multicomponent condensation of the corresponding aniline with α-dicarbonyl compounds (glyoxal or 2,3-butadione) and paraformaldehyde or by sequential two-step reactions.[18] Both strategies allow for the preparation of imidazolium salts with different substituents in the 1-, 3-, 4-, and 5-positions. After selective deprotonation at the 2-position, the resulting carbene was methylated in situ. A second deprotonation occurred regioselectively at the methyl group at the 2-position. Final quenching with commercially available chlorodialkyl- or chlorordiarylphosphanes led, after work-up and recrystallization from H_2O/EtOH, to the desired phosphane ligands in good to excellent yields. The general

---

[*] A. Dumrath, X.-F. Wu, Dr. H. Neumann, Dr. A. Spannenberg, Dr. R. Jackstell, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse an der Universität Rostock e. V.
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
E-mail: matthias.beller@catalysis.de
Homepage: www.catalysis.de

[**] This work was funded by the State of Mecklenburg-Western Pomerania, the BMBF, and the DFG (Leibniz Prize). We thank Dr. W. Baumann, Dr. C. Fischer, and S. Buchholz (all LIKAT) for their analytical support.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201001787.

synthesis sequence is easily carried out on a multigram scale and no chromatographic purification is involved. Notably, despite their cationic character, all of the imidazolium salts behaved as nucleophilic donor ligands. Single-crystal X-ray measurements on **4** demonstrate the steric bulk of the imidazolium part of the ligand (Figure 1).

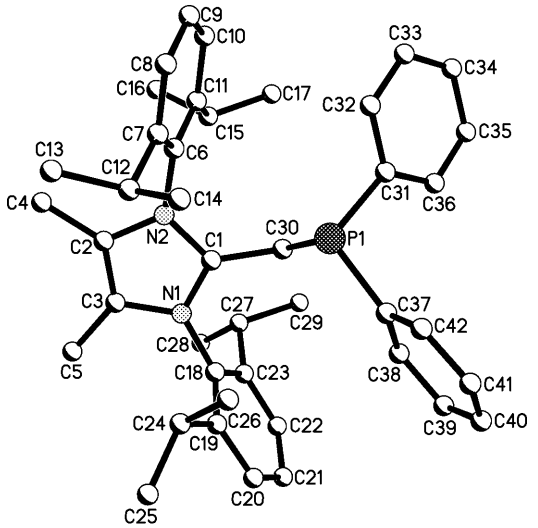
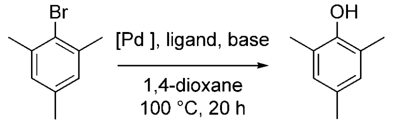
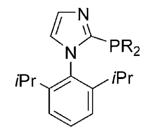
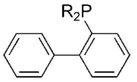


Figure 1. Structure of ligand **4**. Included solvent (one molecule of ethanol), the I^- counterion, and H atoms are omitted for clarity. Selected bond lengths [pm] and angles [°]: C1–N1 134, C1–N2 134.4, C30–P1 187.5, C31–P1 183.7; C1-C30-P1 118.8, C31-P1-C37 102.5.

Table 1: Hydroxylation of 2-bromomesitylene in the presence of different ligands.[a]



Entry	Ligand	R	Yield[b] [%]
1	**1**		96
2	**2**		57
3	**3**		31
4	**4**		66
5	**5**		79
6		Cy	0
7		Ad	95
8		Ph	0
9	PR_3	Cy	0
10		Ph	0
11		*o*-tolyl	0
12		*t*Bu	7

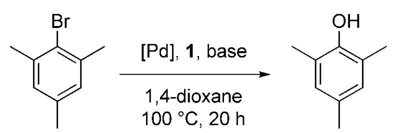
[a] Reaction conditions: 2-Bromomesitylene (1.0 mmol) $[\{Pd(cinnamyl)Cl\}_2]$ (1.0 mol%), ligand (4.0 mol%), $CsOH\cdot H_2O$ (3.0 equiv), hexadecane as internal standard (0.2 mmol), 1,4-dioxane (1.2 mL), 100°C, 20 h. [b] Determined by gas chromatography.

To compare the catalytic performance of the new ligands **1**–**5** with standard electron-rich phosphanes, the palladium-catalyzed hydroxylation of aryl bromides with 1,4-dioxane was studied as a benchmark reaction. Apart from recent examples where copper catalysts were used,[19] only highly electron-rich, biaryl ligands, and to a lesser extent $P\mathit{t}Bu_3$, in combination with palladium allow for this transformation.[5]

Exploratory studies demonstrated that the reaction proceeded with CsOH in 1,4-dioxane (Table 1). Catalysts prepared with all the new imidazolium-based ligands **1**–**5** revealed significant activity in the hydroxylation of 2-bromomesitylene, and gave moderate to excellent yield (31–96%) of the corresponding phenol (Table 1, entries 1–5). The previously published "state-of-the-art" ligand bisadamantylphosphanylimidazol gave 95% of the corresponding product (Table 1, entry 7). To our delight, the combination of $[\{Pd(cinnamyl)Cl\}_2]$ and **1** gave a similar yield (96%). Cyclohexyl-substituted ligands, for example, **5**, performed better than the *tert*-butyl- and phenyl-substituted phosphanes. Nevertheless, the performance of the phenyl-substituted imidazolium salt **4** is remarkable. This is the first time that a non-alkyl phosphane has shown significant activity in hydroxylation reactions. In contrast, the cyclohexyl- and phenyl-substituted imidazol-based ligands gave no product at all (Table 1, entries 6 and 8). Moreover, commercially available monodentate and bidentate ligands led to no product or a low yield, which demonstrates the challenging nature of this coupling reaction (Table 1, entries 9–12). It is noteworthy that the hydroxylation reaction can be easily scaled up to 20 mmol of substrate and the reaction time can be decreased to 30 minutes by using a microwave.

Next, we tested the potential recycling of our cationic catalysts. For this purpose, we took advantage of the solubility behavior of ligand **1** in 1,4-dioxane.[20] While the ligand itself is not soluble at room temperature, under the reaction conditions it forms a soluble palladium complex, which can easily be separated from the corresponding precipitated phenolate. As shown in Table 2 the hydroxylation of 2-bromomesitylene was performed eight times without adding any new ligand or palladium. This procedure led to a catalyst productivity of nearly 700 being realized, which is the highest turnover number achieved so far in catalytic hydroxylations of aryl halides. Phosphorus NMR studies of the reaction solution of the recycling experiments showed that the ligand endured the reaction without significant oxidation (<5%). However, the concentration of the base decreased slightly with each run. Indeed, a strong influence of additional water on the catalyst productivity was observed. As shown in Table 3, the yield rapidly dropped when water was added. Interestingly, the ligand itself is stable in water and can be stored for several months under water without significant decomposition (<5%, see the Supporting Information). The viability of our catalyst recycling was further demonstrated in four consecutive hydroxylations of 1-bromo-3,5-dimethylbenzene on a 10 mmol scale. Again, no significant decrease in the product yield occurred (90–95% yield).

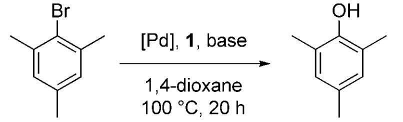
Table 2: Recycling of catalysts in the hydroxylation of 2-bromomesitylene.[a]



Run	Yield [%][b]	TON
1	95	95
2	96	191
3	94	285
4	92	377
5	90	467
6	87	554
7	79	633
8	61	694

[a] Reaction conditions: 2-Bromomesitylene (1.0 mmol) [{Pd(cinnamyl)Cl}$_2$] (1.0 mol%), ligand **1** (4.0 mol%), CsOH·H$_2$O (3.0 equiv), hexadecane as internal standard (0.2 mmol), 1,4-dioxane (1.2 mL), 100°C, 20 h. [b] Determined by gas chromatography, all reactions were carried out twice.

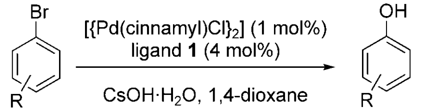
Table 3: Influence of water on the hydroxylation of 2-bromomesitylene.[a]

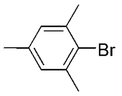
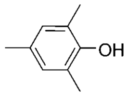
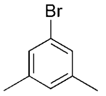
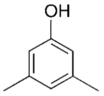
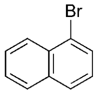
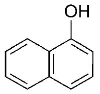
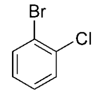
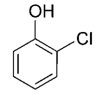
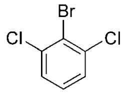
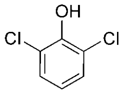
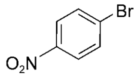
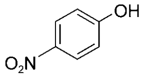
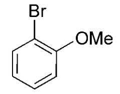
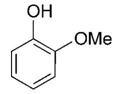


Entry	Water [mL]	Yield [%][b]
1	0.0	96
2	0.5	17
3	1.0	3

[a] Reaction conditions: 2-Bromomesitylene (1.0 mmol), [{Pd(cinnamyl)Cl}$_2$] (1.0 mol%), ligand **1** (4.0 mol%), CsOH·H$_2$O (3.0 equiv), hexadecane as internal standard (0.2 mmol), 1,4-dioxane (1.2 mL), 100°C, 20 h. [b] Determined by gas chromatography, all reactions were carried out twice.

Table 4: Palladium-catalyzed hydroxylation of aryl bromides.[a]



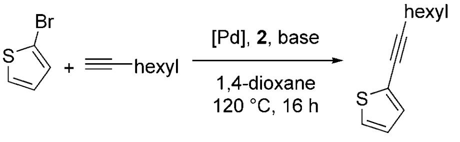
Entry	Aryl halide	Product	Yield[b] [%]
1			96
2			95
3			90[e]
4			97
5			76[d]
6			92
7			70[c]

[a] Reaction conditions: Aryl bromide (1.0 mmol), [{Pd(cinnamyl)Cl}$_2$] (1.0 mol%), ligand **1** (4.0 mol%), CsOH·H$_2$O (3.0 equiv), hexadecane as internal standard (0.2 mmol), 1,4-dioxane (1.2 mL), 100°C, 20 h. [b] Determined by gas chromatography. [c] 120°C, 30 h. [d] 100°C, 30 h. [e] 120°C, 15 h.

Next, we applied the optimized reaction conditions to the hydroxylation of various aryl bromides (Table 4). Both sterically hindered and unhindered substrates reacted well (Table 4, entries 1 and 2). Activated 4-bromonitrobenzene and also deactivated 2-bromoanisole were successfully hydroxylated in 92% and 70% yield, respectively (Table 4, entries 6 and 7). In particular, the hydroxylation of different bromochlorobenzenes proceeded with high chemoselectivity to the corresponding chlorophenols in 76–97% yield.

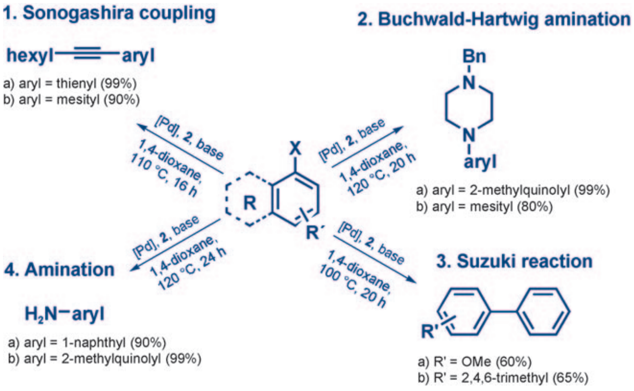
To demonstrate the general synthetic usefulness of the ionic ligands we also investigated other important palladium-catalyzed cross-coupling reactions. As shown in Scheme 2, the new catalyst system successfully promoted the Buchwald–Hartwig amination of 4-chloro-2-methylquinoline and 2-bromomesitylene with 1-benzylpiperazine, as well as the direct amination of 1-chloronaphthalene and 4-chloro-2-methylquinoline with ammonia. Here, the corresponding anilines were obtained in 80 and 99% yield, respectively. Moreover, the catalyst was re-isolated without problems in the case of the amination of 1-chloronaphthalene. Furthermore, Sonogashira and Suzuki coupling reactions of aryl and heteroaryl bromides proceeded smoothly to 3-(oct-1-ynyl)-thiophene, 2-(oct-1-ynyl)-mesitylene, 2,4,6-trimethylbiphenyl, and 4-methoxybiphenyl in good to excellent yields (60–99%). Finally, we demonstrated the generality of the recycling concept in a copper-free Sonogashira coupling. As

Table 5: Catalyst recycling in copper-free Sonogashira reactions.[a]



Run	Yield [%][b]	TON
1	96	96
2	99	195
3	98	293
4	95	388

[a] Reaction conditions: Aryl bromide (1.0 mmol), Pd(OAc)$_2$ (1.0 mol%), ligand **2** (3.0 mol%), Na$_2$CO$_3$ (4.0 equiv), hexadecane as internal standard (0.2 mmol), 1,4-dioxane (2.0 mL), 120°C, 16 h (reaction time not optimized). [b] Determined by gas chromatography, all reactions were carried out twice.



Scheme 2. Applications of imidazolium phosphane ligands in palladium-catalyzed cross-coupling reactions. Reaction conditions: 1.0 mol% Pd(OAc)$_2$, 2.0 mL 1,4-dioxane, hexadecane as internal standard. 1 a) 3.0 mol% **2**, 4.0 equiv Na$_2$CO$_3$, 1.0 mmol 3-bromothiophene, 2.0 mmol 1-octyne. 1 b) 1.0 mmol 2-bromomesitylene. 2 a) 2.0 equiv NaO*t*Bu, 2.0 mol% **2**, 1.0 mmol 4-chloro-2-methylquinoline, 1.2 mmol 1-benzylpiperazine. 2 b) 1.0 mmol 2-bromomesitylene. 3 a) 2.0 mol% **2**, 1.0 mmol phenylboronic acid, 1.0 mmol 4-chloroanisole. 3 b) 1.0 mmol 2-bromomesitylene. 4 a) 1.0 mol% Pd(OAc)$_2$, 4.0 mol% **2**, 2.0 mL NH$_3$ (0.5 M in 1,4-dioxane), 0.2 mmol 1-chloronaphthalene, 10 bar N$_2$. 4 b) 0.5 mol% Pd(OAc)$_2$, 2 mol% **2**, 0.2 mmol 4-chloro-2-methylquinoline. Yields were determined by gas chromatography, all reactions were carried out twice.

shown in Table 5, the reaction was realized four times in very good yields without the addition of new catalyst.

In summary, a series of new cationic imidazolium-based phosphanes have been synthesized. These derivatives represent an interesting class of recyclable ligands because of their ionic nature. The novel phosphanes are extraordinary stable towards air as well as water, and have been successfully applied in various palladium-catalyzed hydroxylations, aminations, and Sonogashira coupling reactions of aryl bromides and chlorides. Notably, the catalysts can be recycled several times without significant loss of reactivity. It is clear that the new ligands offer further potential in modern recycling technologies such as SILP catalysis.

Received: March 26, 2010
Revised: August 23, 2010
Published online: October 15, 2010

Keywords: catalyst recycling · hydroxylation · palladium · phosphanes · Sonogashira reaction

---

[1] For recent reviews, see a) F. Alonso, I. P. Beletskaya, M. Yus, *Tetrahedron* **2008**, *64*, 3047–3101; b) I. P. Beletskaya, A. V. Cheprakov, *J. Organomet. Chem.* **2004**, *689*, 4055–4082; c) P. Rollet, W. Kleist, V. Dufaud, L. Djakovitch, *J. Mol. Catal. A* **2005**, *241*, 39–51; d) L. Djakovitch, P. Rollet, *Adv. Synth. Catal.* **2004**, *346*, 1782–1792; e) A. Brennführer, H. Neumann, M. Beller, *Angew. Chem.* **2009**, *121*, 4176–4196; *Angew. Chem. Int. Ed.* **2009**, *48*, 4114–4133; f) A. Brennführer, H. Neumann, M. Beller, *ChemCatChem* **2009**, *1*, 28–41; g) T. Schulz, C. Torborg, S. Enthaler, B. Schäffner, A. Dumrath, A. Spannenberg, H. Neumann, A. Börner, M. Beller, *Chem. Eur. J.* **2009**, *15*, 4528–4533.

[2] For industrial applications, see a) L. Djakovitch, K. Koehler, J. de Vries, *Nanoparticles and Catalysis*, Wiley-VCH, Weinheim, **2008**, pp. 303–348; b) A. Alimardanov, L. Schmieder-van de Vondervoort, A. H. M. de Vries, J. G. de Vries, *Adv. Synth. Catal.* **2004**, *346*, 1812–1817; c) M. T. Reetz, J. G. de Vries, *Chem. Commun.* **2004**, 1559–1563; d) A. H. M. de Vries, J. H. M. Mommers, H. J. W. Henderickx, J. G. de Vries, *Org. Lett.* **2003**, *5*, 3285–3288.

[3] For reviews, see a) C. A. Fleckenstein, H. Plenio, *Chem. Soc. Rev.* **2010**, *39*, 694–711; b) C. A. Fleckenstein, H. Plenio, *Chem. Eur. J.* **2007**, *13*, 2701–2716; c) D. S. Surry, S. L. Buchwald, *Angew. Chem.* **2008**, *120*, 6438–6461; *Angew. Chem. Int. Ed.* **2008**, *47*, 6338–6361; d) R. Martin, S. L. Buchwald, *Acc. Chem. Res.* **2008**, *41*, 1461–1473; e) T. E. Barder, S. D. Walker, J. R. Martinelli, S. L. Buchwald, *J. Am. Chem. Soc.* **2005**, *127*, 4685–4696; f) A. F. Littke, G. C. Fu, *Angew. Chem.* **2002**, *114*, 4350–4386; *Angew. Chem. Int. Ed.* **2002**, *41*, 4176–4211; g) K. C. Nicolaou, P. G. Bulger, D. D. Sarlah, *Angew. Chem.* **2005**, *117*, 4516–4563; *Angew. Chem. Int. Ed.* **2005**, *44*, 4442–4489; h) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem.* **2007**, *119*, 2824–2870; *Angew. Chem. Int. Ed.* **2007**, *46*, 2768–2813.

[4] For selected recent examples, see a) U. Christmann, R. Vilar, *Angew. Chem.* **2005**, *117*, 370–378; *Angew. Chem. Int. Ed.* **2005**, *44*, 366–374; b) K. W. Anderson, S. L. Buchwald, *Angew. Chem.* **2005**, *117*, 6329–6333; *Angew. Chem. Int. Ed.* **2005**, *44*, 6173–6177; c) B. Saito, G. C. Fu, *J. Am. Chem. Soc.* **2007**, *129*, 9602–9603; d) O. Diebolt, P. Braunstein, S. P. Nolan, C. S. J. Cazin, *Chem. Commun.* **2008**, 3190–3192; e) J. R. Naber, S. L. Buchwald, *Adv. Synth. Catal.* **2008**, *350*, 957–961; f) K. L. Billingsley, S. L. Buchwald, *Angew. Chem.* **2008**, *120*, 4773–4776; *Angew. Chem. Int. Ed.* **2008**, *47*, 4695–4698; g) D.-H. Lee, J.-Y. Jung, I. M. Lee, M.-J. Jin, *Eur. J. Org. Chem.* **2008**, 356–360; h) C. M. So, C. P. Lau, F. Y. Kwong, *Org. Lett.* **2007**, *9*, 2795–2798; i) C. M. So, C. P. Lau, A. S. C. Chan, F. Y. Kwong, *J. Org. Chem.* **2008**, *73*, 7731–7734; j) C. M. So, C. C. Yeung, C. P. Lau, F. Y. Kwong, *J. Org. Chem.* **2008**, *73*, 7803–7806; k) F. Yee Kwong, W. H. Lam, C. H. Yeung, K. S. Chan, A. S. C. Chan, *Chem. Commun.* **2004**, 1922–1923.

[5] a) N. Kataoka, Q. Shelby, J. P. Stambuli, J. F. Hartwig, *J. Org. Chem.* **2002**, *67*, 5553–5566; b) Q. Shelby, N. Kataoka, G. Mann, J. F. Hartwig, *J. Am. Chem. Soc.* **2000**, *122*, 10718–10719; c) G. Mann, C. Incarvito, A. L. Rheigold, J. F. Hartwig, *J. Am. Chem. Soc.* **1999**, *121*, 3224–3225; d) C. H. Burgos, T. E. Barder, X. Huang, S. L. Buchwald, *Angew. Chem.* **2006**, *118*, 4427–4432; *Angew. Chem. Int. Ed.* **2006**, *45*, 4321–4326; e) T. Schulz, C. Torborg, B. Schäffner, J. Huang, A. Zapf, R. Kadyrov, A. Boerner, M. Beller, *Angew. Chem.* **2009**, *121*, 936–939; *Angew. Chem. Int. Ed.* **2009**, *48*, 918–921.

[6] a) A. F. Littke, G. C. Fu, *Angew. Chem.* **2002**, *114*, 4350–4386; *Angew. Chem. Int. Ed.* **2002**, *41*, 4176–4211; b) see Ref. [5d]; c) see Ref. [5a]; d) S.-I. Kuwabe, K. E. Torraca, S. L. Buchwald, *J. Am. Chem. Soc.* **2001**, *123*, 12202–12206.

[7] a) Q. Shen, J. F. Hartwig, *J. Am. Chem. Soc.* **2006**, *128*, 10028–10029; b) M. C. Willis, *Angew. Chem.* **2007**, *119*, 3470–3472; c) D. S. Surry, S. L. Buchwald, *J. Am. Chem. Soc.* **2007**, *129*, 10354–10344; d) see Ref. [1g].

[8] a) V. V. Grushin, W. J. Marshall, *Organometallics* **2007**, *26*, 4997–5002; b) V. V. Grushin, *Chem. Eur. J.* **2002**, *8*, 1006–1014; c) D. A. Watson, M. Su, G. Teverovskiy, Y. Zhang, J. Garcia-Fortanet, T. Kinzel, S. L. Buchwald, *Science* **2009**, *325*, 1661–1664; d) D. V. Yandulov, N. T. Tran, *J. Am. Chem. Soc.* **2007**, *129*, 1342–1358.

[9] a) See Ref. [1f]; b) A. G. Sergeev, A. Spannenberg, M. Beller, *J. Am. Chem. Soc.* **2008**, *130*, 15549–15563; c) A. Brennführer, H. Neumann, S. Klaus, T. Riermeier, J. Almena, M. Beller, *Tetrahedron* **2007**, *63*, 6252–6258; d) R. Jennerjahn, I. Piras, R.

Jackstell, R. Franke, K.-D. Wiese, M. Beller, *Chem. Eur. J.* **2009**, *15*, 6383–6388.

[10] a) M. Guino, K. K. M. Hii, *Chem. Soc. Rev.* **2007**, *36*, 608–617; b) Y.-C. Yang, T.-Y. Luh, *J. Org. Chem.* **2003**, *68*, 9870–9873; c) see Ref. [3c]; d) C. A. Parrish, S. L. Buchwald, *J. Org. Chem.* **2001**, *66*, 3820–3827.

[11] a) S. S. Pröckl, W. Kleist, K. Köhler, *Tetrahedron* **2005**, *61*, 9855–9859; b) K. Köhler, R. G. Heidenreich, S. S. Soomro, S. Pröckl, *Adv. Synth. Catal.* **2008**, *350*, 2930–2936; c) W. Kleist, J.-K. Lee, K. Köhler, *Eur. J. Inorg. Chem.* **2009**, 261–266; d) M. Lamblin, L. Nassar-Hardy, J.-C. Hierso, E. Fouquet, F.-X. Felpin, *Adv. Synth. Catal.* **2010**, *352*, 33–79; e) Y. Monguchi, Y. Fujita, K. Endo, S. Takao, M. Yoshimura, Y. Takagi, T. Maegawa, H. Sajiki, *Chem. Eur. J.* **2009**, *15*, 834–837; f) M.-J. Jin, D.-H. Lee, *Angew. Chem.* **2010**, *122*, 1137–1140; *Angew. Chem. Int. Ed.* **2010**, *49*, 1119–1122; g) S. Wittmann, A. Schätz, R. N. Grass, W. J. Stark, O. Reiser, *Angew. Chem.* **2010**, *122*, 1911–1914; *Angew. Chem. Int. Ed.* **2010**, *49*, 1867–1870.

[12] a) N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.* **2006**, *348*, 609–679; b) L. Yin, J. Liebscher, *Chem. Rev.* **2007**, *107*, 133–173; c) M. T. Reetz, E. Westermann, *Angew. Chem.* **2000**, *112*, 170–173; *Angew. Chem. Int. Ed.* **2000**, *39*, 165–168; d) M. T. Reetz, J. G. de Vries, *Chem. Commun.* **2004**, *14*, 1559–1563; e) M. Beller, H. Fischer, K. Kühlein, C.-P. Reisinger, W. A. Herrmann, *J. Organomet. Chem.* **1996**, *520*, 257–259.

[13] M.-J. Jin, D.-H. Lee, *Angew. Chem.* **2010**, *122*, 1137–1140; *Angew. Chem. Int. Ed.* **2010**, *49*, 1119–1122.

[14] W. A. Herrmann, B. Cornils, *Angew. Chem.* **1997**, *109*, 1074–1095; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 1048–1067.

[15] a) T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2083; b) P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926–3945; *Angew. Chem. Int. Ed.* **2000**, *39*, 3773–3789; c) R. Sheldon, *Chem. Commun.* **2001**, 2399–2407.

[16] For a review, see a) B. C. Gates, *Chem. Rev.* **1995**, *95*, 511–522; for selected examples, see b) P. Wasserscheid, W. Keim, *Angew. Chem.* **2000**, *112*, 3926–3945; *Angew. Chem. Int. Ed.* **2000**, *39*, 3772–3789; c) H. Olivier-Bourbigou, L. Magna, *J. Mol. Catal. A* **2002**, *182–183*, 419–437; d) *Ionic Liquids in Synthesis* (Eds.: P. Wasserscheid, T. Welton), Wiley-VCH, Weinheim, **2002**.

[17] P. Wasserscheid, *Chem. Unserer Zeit* **2003**, *37*, 52–63.

[18] a) B. E. Ketz, A. P. Cole, R. M. Waymouth, *Organometallics* **2004**, *23*, 2835–2837; b) M. G. Gardiner, W. A. Herrmann, C.-P. Reisinger, J. Schwarz, M. Spiegler, *J. Organomet. Chem.* **1999**, *572*, 239–247.

[19] For recent examples on copper-catalyzed hydroxylations, see a) A. Tlili, N. Xia, F. Monnier, M. Taillefer, *Angew. Chem.* **2009**, *121*, 8881–8884; *Angew. Chem. Int. Ed.* **2009**, *48*, 8725–8728; b) D. Zhao, N. Wu, S. Zhang, P. Xi, X. Su, J. Lan, J. You, *Angew. Chem.* **2009**, *121*, 8885–8888; *Angew. Chem. Int. Ed.* **2009**, *48*, 8729–8732.

[20] For related recycling of ligands in hydroformylation reactions, see a) J. N. H. Reek, A. J. van der Linden, A. Marson, P. W. N. M. van Leuween, *Adv. Synth. Catal.* **2002**, *344*, 293–298; b) A. E. Sollewijn Gelpke, J. J. N. Veerman, M. Schreuder Goedheijt, P. C. J. Kramer, P. W. N. M. van Leeuwen, H. Hiemstra, *Tetrahedron* **1999**, *55*, 6657–6670.