

Novel tetrahydropyrimidinium / palladium system as a convenient catalyst: Suzuki coupling reactions of aryl chlorides

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Abstract

Four bis(3,4,5,6-tetrahydropyrimidinium) chlorides (**2a-d**) have been prepared and characterized by conventional spectroscopic methods and elemental analyses. A highly effective, easy to handle and environmentally benign process for palladium mediated Suzuki cross-coupling was developed. The *in situ* prepared three-component system Pd(OAc)₂ / bis(3,4,5,6-tetrahydropyrimidinium) chlorides (**2a-d**) and K₂CO₃ catalyses quantitatively the Suzuki cross-coupling of deactivated aryl chlorides.

Keywords : *N*-Heterocyclic carbene, tetrahydropyrimidinium, Suzuki, palladium, aryl chlorides, phenylboronic acid

Introduction

Reactions in which carbon-carbon bond formation took place are important in processes such as bioactive molecule synthesis, drugs and agrochemical synthesis. In particular, a metal catalyst offers a novel model for preparation of such molecules, quite large numbers of papers which predict spectroscopic and structural properties of transition metal complexes have appeared. In general, Suzuki cross-coupling reaction is interpreted as arising from the combination of organoboron compounds with electrophiles catalyzed by palladium complexes.^{1,2}

The C-Cl bond in chloroarenes is mainly used since chloroarenes are readily available inexpensive materials from an industrial point of view. Traditionally, however, the C-Cl bond in chloroarenes has been found to be comparatively inert.³ For a long time, the use of unactivated aryl chlorides as substrates in Suzuki-Miyaura cross-coupling was not feasible. Instead, more costly and less readily available aryl iodides and bromides were used. Buchwald⁴ and Fu⁵ were the first who independently developed catalyst systems based on electron-rich, sterically demanding phosphine ligands, which allow the Suzuki-Miyaura cross-coupling of many unactivated aryl chlorides. However, the major drawback of these is that the phosphine ligands

are comparatively difficult to prepare or rather expensive. Furthermore, tertiary phosphines require air-free handling to prevent their oxidation and are susceptible to P-C bond cleavage at elevated temperatures.⁶

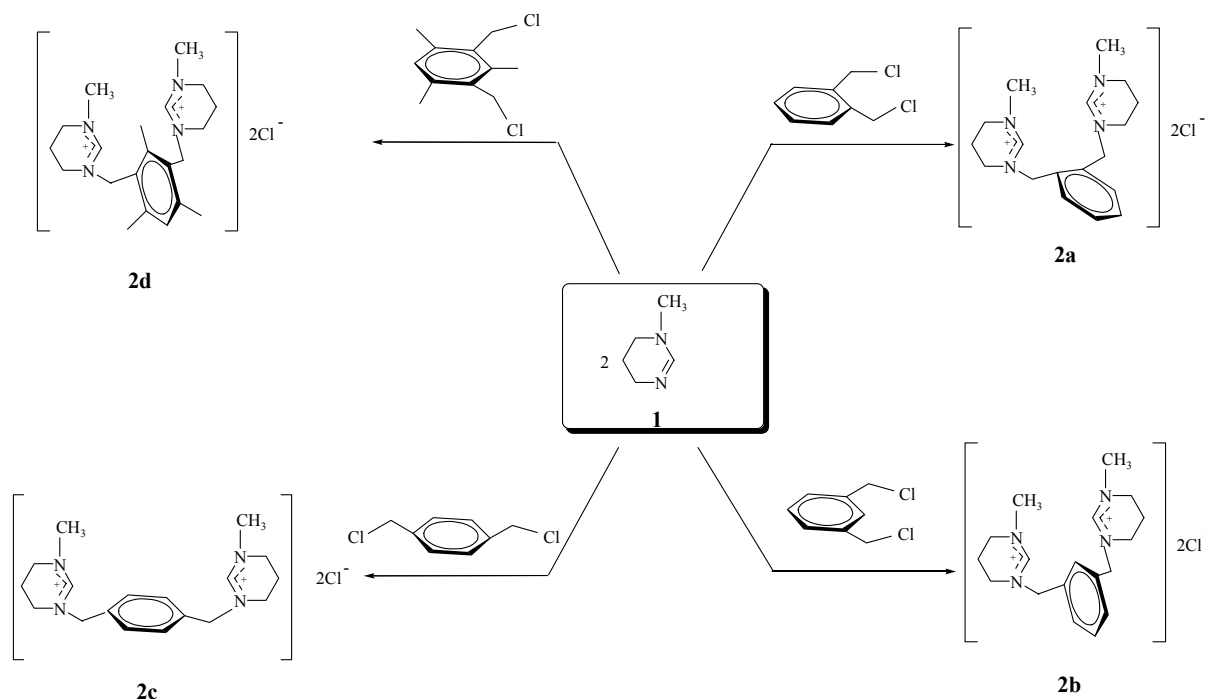
Transition metal complexes incorporating 1,3-diorganyl N-heterocyclic carbene (NHC) ligands, such as imidazol-2-ylidene, imidazolidin-2-ylidene, benzimidazol-2-ylidene and 3,4,5,6-tetrahydropyrimidin-2-ylidene have attracted a great deal of interest in recent years.⁷⁻¹⁴ They are often synthesised via reaction of an azol(in)ium salt (LHX) with a basic salt such as Pd(OAc)₂ to give M(NHC)L_m.

Research in this area was principally motivated by the use of these complexes as catalyst precursors. Many different catalytic applications of NHC complexes have been described.¹⁵⁻¹⁷ Palladium-catalysed cross-coupling reactions are particularly attractive because of their versatility for formation of C-C bonds.¹⁸⁻²⁰ Sterically hindered, electron-rich alkyl phosphines²¹ and carbene²² ligands have received growing interest in recent years. Yet, the phosphine ligands and the phosphine-palladium complexes are labile to air and moisture at high temperatures, placing significant limits on their synthetic utility. Therefore, from a practical point of view, the development of more stable ligands leading to more reactive catalysts have gained importance for palladium-catalyzed Heck and Suzuki coupling reactions. Recently, nucleophilic N-heterocyclic carbenes (NHC's)²³ with stronger σ -donor properties than the bulky tertiary phosphines²⁴, have emerged as a new family of ligands. In contrast to metal phosphine complexes, the metal-NHC complexes appear to be extraordinarily stable towards heat, air and moisture due to the high dissociation energies of the metal-carbon bond.²⁵

The development of new ligands or the application of existing ligands in these reactions, particularly those involving aryl chlorides as substrates, is still of considerable importance. Recently, we have improved procedures Heck and Suzuki reactions of aryl chlorides making use of novel ligands 1,3-bis(dialkyl)imidazolium and benzimidazolinium salts.²⁶ Although the nature of the NHC ligand on complexes have tremendous influence on the rate of catalyzed reactions, the use of 3,4,5,6-tetrahydropyrimidinium ligands in coupling reactions is a neglected area. In order to find more efficient palladium catalysts we have prepared a series of new bis(3,4,5,6-tetrahydropyrimidinium) chlorides (**2**) (Scheme 1). We now report on the use of the *in situ* generated catalytic system composed of commercially available and stable reagents, Pd(OAc)₂ as palladium source, bis(3,4,5,6-tetrahydropyrimidinium) chlorides (**2a-d**) as a carbene precursor and K₂CO₃ as a base for cross coupling of aryl chlorides with phenylboronic acid.

Results and Discussion

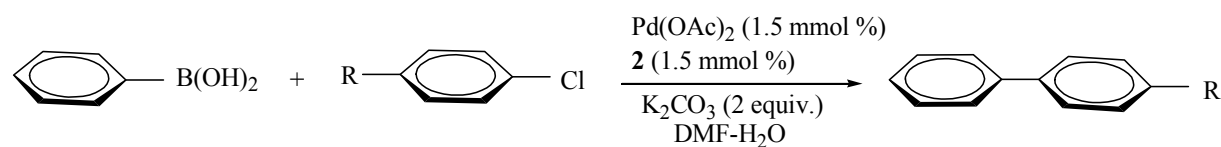
Bis(3,4,5,6-tetrahydropyrimidinium) chlorides (**2a-d**) are conventional NHC precursors. According to Scheme 1, the salts (**2a-d**) were obtained in almost quantitative yield by quarternization of 1-methyl(3,4,5,6-tetrahydropyrimidine)²⁷ in DMF with bis(chloromethyl) benzenes²⁶.



Scheme 1. Synthesis of carbene precursors.

The structures of **2** were determined by their characteristic spectroscopic data and elemental analyses. ^{13}C NMR chemical shifts were consistent with the proposed structure; the imino carbon appeared as a typical singlet in the ^1H -decoupled mode at 154.1, 162.5, 153.9 and 162.4 ppm respectively for pyrimidinium salts **2a-d**. The ^1H NMR spectra of the pyrimidinium salts further supported the assigned structures; the resonances for C(2)-H were observed as sharp singlets at 8.54, 9.79, 9.13 and 9.70 ppm respectively for **2a-d**.

The palladium-catalyzed cross-coupling of arylboronic acids with aryl halides has been shown to proceed under a variety of conditions. A wide range of bases and solvents, as well as catalysts, have been employed with varying degrees of success according to the substrates²⁸. Here, various bis(3,4,5,6-tetrahydropyrimidinium) salts (**2a-d**) were compared as ligand precursors under the same reaction conditions. To survey the reaction parameters for the catalytic Suzuki reaction, Cs_2CO_3 , K_2CO_3 , and K_3PO_4 as base and DMF/ H_2O (1:1) and dioxane as solvent were used. We found that the reactions performed in DMF/ H_2O (1:1) with Cs_2CO_3 or K_2CO_3 as the base at 80 °C appeared to be best. We started our investigation with the coupling of *p*-chloroacetophenone and phenylboronic acid, in the presence of $\text{Pd}(\text{OAc})_2$ / carbene precursors (**2a-d**). The results obtained in the presence of **2a-d** are summarized (Table 1, entries 1-4). It is evident that the NHC precursors that contain pyrimidinium (**2a-d**) are the most effective of the examined salts.

Table 1. The Suzuki coupling reaction of aryl chlorides with phenylboronic acid

Entry	Ligand	R	Yield ^{a, b, c, d} (%)
1	2a	COCH ₃	90
2	2b	COCH ₃	85
3	2c	COCH ₃	82
4	2d	COCH ₃	92
5	2a	CH ₃	79
6	2b	CH ₃	74
7	2c	CH ₃	71
8	2d	CH ₃	83
9	2a	OCH ₃	83
10	2b	OCH ₃	82
11	2c	OCH ₃	71
12	2d	OCH ₃	87
13	2a	CHO	82
14	2b	CHO	80
15	2c	CHO	73
16	2d	CHO	85

^a Reaction conditions : 1.0 mmol of R-C₆H₄Cl-*p*, 1.5 mmol of phenylboronic acid, 2 mmol K₂CO₃, 1.50 mmol % Pd(OAc)₂, 1.50 mmol % **2**, DMF-H₂O (3 / 3 mL), ^b purity of compounds is checked by NMR and yields are based on aryl chloride. ^c All reactions were monitored by TLC, ^d temperature 80 °C, 5h.

Under those conditions, *p*-chloroacetophenone, *p*-chlorotoluene, *p*-chloroanisole and *p*-chlorobenzaldehyde, react very cleanly with phenylboronic acid in goods yields (Table 1, Entries 4, 8, 12 and 16). Our results from the screening of four pyrimidinium salts, for Suzuki cross-coupling reaction are summarized in Table 1.

Conclusions

In conclusion, we have developed a new type of easily prepared bis(3,4,5,6-tetrahydropyrimidinium) salts (**2a-d**) useful as ligands for the Suzuki-Miyaura coupling reaction. Through the use of **2** and Pd(OAc)₂ as a pre-catalyst mixture, aryl halides undergo efficient coupling reactions with C₆H₅B(OH)₂ in the presence of K₂CO₃. Several trends are readily apparent. First, the procedure is simple and does not require induction periods. Second, the scope

of this reaction is broad and includes aryl chlorides that are activated or deactivated. Third, all ligands led to good conversions at low catalyst concentration (1.5 mmol %). The procedure is simple and efficient towards various aryl halides and does not require induction periods.

Experimental Section

General Procedures. All reactions for the preparation of 1-methyl-3,4,5,6-tetrahydropyrimidine (**1**) and bis(1-methyl-3,4,5,6-tetrahydropyrimidine) chlorides²⁷ (**2a-d**) were carried out under argon using standard Schlenk-type flasks. Test reactions for the catalytic activity of catalysts in the Suzuki cross-coupling reactions were carried out in air. All reagents were purchased from the Aldrich Chemical Co. The solvents, were distilled prior to use: Et₂O over Na, DMF over BaO, EtOH over Mg.

All ¹H and ¹³C-NMR were registered in DMSO-d₆. ¹H NMR and ¹³C NMR spectra were recorded using a Bruker AC300P FT spectrometer operating at 300.13 MHz (¹H), 75.47 MHz (¹³C). Chemical shifts (δ) are given in ppm relative to TMS and coupling constants (*J*) in Hz. Infrared spectra were recorded as KBr pellets in the range 400-4000 cm⁻¹ on a ATI UNICAM 1000 spectrometer. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and are uncorrected. Elemental analyses were performed by TUBITAK (Ankara, Turkey) Microlab.

Preparation of 3,3'-dimethyl-1,1'-(1,2-bismethylenebenzene)(3,4,5,6-tetrahydropyrimidinium) chloride, (2a). To a solution of 1-methyl-3,4,5,6-tetrahydropyrimidine (0.98 g, 10 mmol) in DMF (10 mL) 1,2-bis(chloromethyl)benzene (0.87 g, 5 mmol) was added slowly and the resulting mixture was stirred at room temperature for 5h. Diethyl ether (10 mL) was added to obtain a white crystalline solid which was filtered off. The solid was washed with diethylether (3x 10 mL) dried under vacuum and the crude product was recrystallized from ethanol/diethylether. mp = 150-151 °C, and the yield was 1.65 g, 89 %, ν_(CN) = 1511 cm⁻¹. Anal. Cal. For C₁₈H₂₈N₄Cl₂; C: 58.22, H: 7.60, N: 15.09; found C: 58.25, H: 7.56, N: 15.10. ¹H NMR (δ, DMSO-d₆): 2.13 (q, *J* = 6,0 Hz, 4H, NCH₂CH₂CH₂N); 3.29 and 3.48 (t, *J* = 5,6 Hz, 8H, NCH₂CH₂CH₂N); 3.33 (s, 6H, NCH₃); 4.88 (s, 4H, CH₂C₆H₄CH₂); 7.46 (m, 4H, CH₂C₆H₄CH₂); 8.54 (s, 2H, NCHN); ¹³C{¹H}NMR (δ,DMSO-d₆): 41.5 (NCH₂CH₂CH₂N); 42.3 and 44.9 (NCH₂CH₂CH₂N); 18.7 (NCH₃); 54.9 (CH₂C₆H₄CH₂); 132.6, 129.4 and 129.3 (CH₂C₆H₄CH₂); 154.1 (NCHN).

Preparation of 3,3'-dimethyl-1,1'-(1,3-bismethylenebenzene)(3,4,5,6-tetrahydropyrimidinium) chloride, (2b). Compound **2b** was prepared in the same way as **2a** from 1-methyl-3,4,5,6-tetrahydropyrimidine (0.98 g, 10 mmol) in DMF (10 mL) 1,3-Bis(chloromethyl)benzene (0.87 g, 5 mmol) was added slowly to give white crystals of **2b**. mp = 117-118 °C, and the yield was 1.57 g, 85 %, ν_(CN) = 1509 cm⁻¹. Anal. Cal. For C₁₈H₂₈N₄Cl₂; C: 58.22, H: 7.60, N: 15.09; found C: 58.20, H: 7.63, N: 15.11. ¹H NMR

(δ , DMSO- d_6): 1.94 (q, $J = 6.0$ Hz, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$); 3.29 and 3.48 (t, $J = 5.6$ Hz, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$); 3.26 (s, 6H, NCH_3); 4.66 (s, 4H, $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$); 7.73 (s, 1H, $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$); 7.14 (m, 3H, $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$); 9.79 (s, 2H, NCHN); $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , DMSO- d_6): 42.2 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$); 42.3 and 44.9 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$); 18.9 (NCH_3); 57.8 ($\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$); 154.6, 134.8, 129.4, 129.1 and 128.5 ($\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$); 162.5 (NCHN).

Preparation of 3,3'-dimethyl-1,1'-(1,4-bismethylenebenzene)(3,4,5,6-tetrahydropyrimidinium) chloride, (2c). Compound **2c** was prepared in the same way as **2a** from 1-methyl-3,4,5,6-tetrahydropyrimidine (0.98 g, 10 mmol) in DMF (10 mL) 1,4-bis(chloromethyl)benzene (0.87 g, 5 mmol) was added slowly to give white crystals of **2c**.

mp = 282-283 °C, and the yield was 1.72 g, 93 %, $\nu_{\text{CN}} = 1512 \text{ cm}^{-1}$. Anal. Cal. For $\text{C}_{18}\text{H}_{28}\text{N}_4\text{Cl}_2$: C: 58.22, H: 7.60, N: 15.09; found C: 58.19, H: 7.61, N: 15.08. ^1H NMR (δ , DMSO- d_6): 1.92 (q, $J = 5.1$ Hz, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$); 3.33 and 3.16 (t, $J = 5.1$ Hz, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$); 3.21 (s, 6H, NCH_3); 4.71 (s, 4H, $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$); 7.45 (s, 4H, $\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$); 9.13 (s, 2H, NCHN); $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , DMSO- d_6): 41.8 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$); 41.9 and 44.5 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$); 18.7 (NCH_3); 56.9 ($\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$); 135.2, 129.7, 129.2 and 129.0 ($\text{CH}_2\text{C}_6\text{H}_4\text{CH}_2$); 153.9 (NCHN).

Preparation of 3,3'-dimethyl-1,1'-(2,4-bismethylenemesitylene)(3,4,5,6-tetrahydropyrimidinium) chloride, (2d). Compound **2d** was prepared in the same way as **2a** from 1-methyl-3,4,5,6-tetrahydropyrimidine (0.98 g, 10 mmol) in DMF (10 mL) 2,4-Bis(chloromethyl)mesitylene (1.08 g, 5 mmol) was added slowly to give white crystals of **2d**.

mp = 264-265 °C, and the yield was 1.86 g, 90 %, $\nu_{\text{CN}} = 1508 \text{ cm}^{-1}$. Anal. Cal. For $\text{C}_{21}\text{H}_{34}\text{N}_4\text{Cl}_2$: C: 61.01, H: 8.29, N: 13.55; found C: 61.04, H: 8.27, N: 13.54. ^1H NMR (δ , DMSO- d_6): 2.04 (q, $J = 4.8$ Hz, 4H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$); 3.13 and 3.46 (t, $J = 5.1$ Hz, 8H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$); 3.37 (s, 6H, NCH_3); 4.94 (s, 4H, $\text{CH}_2\text{C}_6\text{H}(\text{CH}_3)_3\text{-1,3,5)}\text{CH}_2$); 6.88 (s, 1H, $\text{CH}_2\text{C}_6\text{H}(\text{CH}_3)_3\text{-1,3,5)}\text{CH}_2$); 2.28 and 2.39 (s, 9H, $\text{CH}_2\text{C}_6\text{H}(\text{CH}_3)_3\text{-1,3,5)}\text{CH}_2$); 9.70 (s, 2H, NCHN); $^{13}\text{C}\{^1\text{H}\}$ NMR (δ , DMSO- d_6): 41.0 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$); 42.2 and 45.1 ($\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$); 18.4 (NCH_3); 52.3 ($\text{CH}_2\text{C}_6\text{H}(\text{CH}_3)_3\text{-1,3,5)}\text{CH}_2$); 153.8, 139.9, 139.0, 131.6 and 127.7 ($\text{CH}_2\text{C}_6\text{H}(\text{CH}_3)_3\text{-1,3,5)}\text{CH}_2$); 20.6 and 16.5 ($\text{CH}_2\text{C}_6\text{H}(\text{CH}_3)_3\text{-1,3,5)}\text{CH}_2$); 162.4 (NCHN).

General procedure for the Suzuki coupling reaction

$\text{Pd}(\text{OAc})_2$ (1.5 mmol %), bis(*tetrahydropyrimidinium*) chloride, **2** (1.5 mmol %), aryl chloride (1.0 mmol), phenyl boronic acid (1.5 mmol), K_2CO_3 (2 mmol), water (3 mL)-DMF (3 mL) were added to a small Schlenk tube and the mixture was heated at 80 °C for 5 h. At the conclusion of the reaction, the mixture was cooled, extracted with Et_2O , filtered through a pad of silica gel with copious washing with Et_2O , concentrated and purified by flash chromatography on silica gel. The purity of the compounds was checked by GC and yields are based on aryl chloride, (see Table 1).

Acknowledgements

This work was financially supported by the Technological and Scientific Research Council of Turkey TÜBİTAK-CNRS (France) [TBAG-U/181 (106T716)] and İnönü University Research Fund (BAP:2004/Güz8).

References

1. (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *576*, 147. (c) Stanforth, S. P. *Tetrahedron* **1998**, *54*, 263. (d) Mingji, D.; Liang, B.; Wang, C.; You, Z.; Xiang, J.; Dong, G.; Chen, J.; Yang, Z. *Adv. Synth. Catal.* **2004**, *346*, 1669.
2. Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.
3. Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047.
4. (a) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 9722. (b) Wolfe, J. P.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **1999**, *38*, 2413. (c) Wolfe, J. P.; Singer, R. A.; Yang, B. H.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 9550.
5. (a) Littke, A. F.; Fu, G. C. *Angew. Chem. Int. Ed.* **1998**, *37*, 3387. (b) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020. (c) Liu, S.-Y.; Choi, M. J.; Fu, G. C. *Chem. Commun.* **2001**, 2408.
6. Herrmann, W. A. *Applied Homogeneous Catalysis with Organometallic Compounds*, Cornils, B.; Herrmann, W. A., Eds. VCH: Weinheim, 1996; p 712.
7. Arduengo III, A. J.; Krafczyk, R. *Chem. Unserer Zeit.* **1998**, *32*, 6.
8. Weskamp, T.; Böhm, V. P. W.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, *600*, 12.
9. Bourissou, D.; Guerret, O.; Gabbai, F. P.; Bertrand, G. *Chem. Rev.* **2000**, *100*, 39.
10. Magill, A. M.; McGuinness, D. S.; Cavell, K. J.; Britovsek, G. J. P.; Gibson, V. C.; White, J. P.; Williams, D. J.; White, A. H.; Skelton, B. W. *J. Organomet. Chem.* **2001**, *617-618*, 546.
11. Crudden, C. M.; Allen, D. P. *Coord. Chem. Rev.* **2004**, *248*, 2247.
12. Herrmann, W. A.; Schneider, S. K.; Öfele, K.; Sakamoto, M.; Herdtweck, E. *J. Organomet. Chem.* **2004**, *689*, 2441.
13. Mayr, M.; Wurst, K.; Ongania, K. H.; Buchmeiser, M. R. *Chem. Eur. J.* **2004**, *10*, 1256.
14. Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1290.
15. Perry, M. C.; Burgess, K. *Tetrahedron: Asymm.* **2003**, *14*, 951.
16. Peris, E.; Crabtree, R. H. *Coord. Chem. Rev.* **2004**, *248*, 2239.
17. Zapf, A.; Beller, M. *Chem. Commun.* **2005**, 431.
18. Bedford, R. B.; Cazin, C. S. J.; Holder, D. *Coord. Chem. Rev.* **2004**, *248*, 2283.
19. Wang, A. E.; Xie, J. H.; Wang, L. X.; Zhou, Q. L. *Tetrahedron* **2005**, *61*, 259.
20. Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020.

21. Böhm, V. P. W.; Gstöttmayr, C. W. K.; Weskamp, T.; Herrmann, W. A. *J. Organomet. Chem.* **2000**, 595, 186.
22. Herrmann, W. A.; Weskamp, T.; Böhm, V. P. W. *Adv. Organomet. Chem.* **2001**, 48, 1.
23. Huang, J.; Schanz, H. J.; Stevens, E. D.; Nolan, S. P. *Organometallics* **1999**, 18, 2370.
24. Schwarz, J.; Böhm, V. P. W.; Gardiner, M. G.; Grosche, M.; Herrmann, W. A.; Hieringer, W.; Raudaschl-Sieber, G. *Chem. Eur. J.* **2000**, 6, 1773.
25. Herrmann, W. A.; Öfele, K.; Preysing, D.; Herdtweck, E. *J. Organomet. Chem.* **2003**, 684, 235.
26. (a) Gürbüz, N.; Özdemir, İ.; Demir, S.; Çetinkaya, B. *J. Mol. Catal. A:Chem.* **2004**, 209, 23. (b) Özdemir, İ.; Gök, Y.; Gürbüz, N.; Yaşar, S.; Çetinkaya, E.; Çetinkaya, B. *Polish J. Chem.* **2004**, 78, 2141. (c) Özdemir, İ.; Gök, Y.; Gürbüz, N.; Çetinkaya, E.; Çetinkaya, B. *Synt. Commun.* **2004**, 34, 4135. (d) Özdemir, İ.; Çetinkaya, B.; Demir, S.; Gürbüz, N. *Catal. Lett.* **2004**, 97, 37. (e) Özdemir, İ.; Gök, Y.; Gürbüz, N.; Çetinkaya, E.; Çetinkaya, B. *Heteroatom Chem.* **2004**, 15, 419. (f) Özdemir, İ.; Alıcı, B.; Gürbüz, N.; Çetinkaya, E.; Çetinkaya, B. *J. Mol. Catal. A:Chem.* **2004**, 217, 37. (g) Gürbüz, N.; Özdemir, İ.; Seçkin, T.; Çetinkaya, B. *J. Inorg. and Organomet. Polym.* **2004**, 14, 149. (h) Özdemir, İ.; Demir, S.; Yaşar, S.; Çetinkaya, B. *Appl. Organomet. Chem.* **2005**, 19, 55.
27. (a) Alıcı, B.; Çetinkaya, E.; Çetinkaya, B. *Heterocycles* **1997**, 45, 29. (b) Alıcı, B.; Özdemir, İ.; Gürbüz, N.; Çetinkaya, E.; Çetinkaya, B. *Heterocycles* **2005**, 65, 1439.
28. (a) Bedford, R. B.; Hazelwood, S. L.; Limmert, M.E. *Chem. Commun.* **2002**, 2610. (b) Walker, S. D.; Barder, T. E.; Martinelli, J. R.; Buchwald, S. L. *Angew. Chem. Int. Ed.* **2004**, 43, 1871. (c) Kabakla, G. W.; Wang, L.; Pagni R. M.; Hair, C. M.; Namboodiri, V. *Synthesis* **2003**, 2, 217. (d) Jiang, N.; Ragauskas, A. J. *Tetrahedron Lett.* **2006**, 47, 197. (e) Navarro, O.; Marion, N.; Oonishi, Y.; Kelly III, R. A.; Nolan, S. P. *J. Org. Chem.* **2006**, 71, 685. (f) Schneider, S. K.; Roembke, P.; Julius, G. R.; Loschen, C.; Raubenheimer, H. G.; Frenking, G.; Herrmann, W. A. *Eur. J. Inorg. Chem.* **2005**, 2973.