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An *N*-heterocyclic carbene-palladium-η³-allyl chloride complex for the Suzuki-Miyaura coupling of aryl halides

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ABSTRACT

An unsymmetrical, well-defined *N*-heterocyclic carbene-palladium-η³-allyl chloride complex has been synthesized and used as an efficient catalyst for the Suzuki-Miyaura cross-coupling of aryl bromides and activated aryl chlorides. The catalyst provides moderate to high yields of cross-coupling products at 50 °C in 2 hours, using 1 mol % of the catalyst and isopropyl alcohol as solvent.

1. Introduction

The Suzuki-Miyaura cross-coupling is one of the most useful methodologies for carbon-carbon bond formation and it is widely used for biaryl synthesis. Palladium catalysts with phosphines ligands were initially employed and are still extensively used to catalyze biaryl formation between aryl halides, triflates, and others, with boronic acids and esters [1-3]. However, upon the report of the first isolated *N*-heterocyclic carbene (NHC) [4], NHC's properties as ligands for metals were recognized and a new venue for their complexes in catalysis was opened [5]. NHCs became alternative ligands to phosphines for metal-catalyzed reactions because they have strong σ-donating properties and form stronger bonds with the metal [6,7]. During the last 20 years, NHC's are becoming complementary ligands to phosphines. Their catalytic activity is strongly related to the steric environment of palladium imposed by the *N*-substituents in the imidazolidene [8-10]. NHCs have been used intensively for carbon-carbon bond formation in cross-coupling reactions [7,11,12], even for alkyl electrophiles [13]. They have also been used as ligands for ruthenium complexes in ring closing metathesis [14-16]. While most of NHC's used in cross-coupling reactions are symmetrically substituted, unsymmetrical ligands allow diversification of steric bulkiness in the vicinity of a metal complex allowing fine tuning of reactivity [17-20]. The synthesis of nonsymmetrical carbenes precursors can be done by an imidazole alkylation, allowing the synthesis of several NHC precursors using different alkyl chains [18,21-23]. The use of well-defined NHC-Palladium complexes avoids the use of an excess of the ligand, they also have the advantage of their stability and easy handling [24]. We previously reported a highly active palladium-NHC-palladacycle complex for the Suzuki-Miyaura cross-coupling of aryl iodides reaction [18]. We report herein a new well-defined non-symmetrical [(NHC)-palladium-(allyl)Cl] catalyst for the Suzuki-Miyaura cross-coupling of aryl bromides and chlorides.

2. Experimental

2.1. Instrumentation

Melting points were recorded on a Fisher-Johns melting point apparatus and are uncorrected. ^{1}H NMR was recorded on a Bruker Ultra Shield-300 (300 MHz). Chemical shifts are reported in parts per million (ppm) down field from TMS, using

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residual $CDCl_3$ as an internal standard (7.24 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constant(s) and integration. ^{13}C NMR was recorded on a Bruker Ultra Shield (75 MHz). Chemical shifts are reported in parts per million (ppm) down field from TMS, using the middle resonance of $CDCl_3$ (77.23 ppm) as an internal standard. High-resolution mass spectra (HRMS) were obtained from Nebraska Center for Mass Spectrometry, University of Nebraska-Lincoln, Lincoln, NE.

2.2. Synthesis

All chemicals were purchased from Aldrich or Fisher and used as received at least otherwise is indicated. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Potassium *tert*-butoxide was purified by sublimation before used; 1-(2,6-diisopropylphenyl)-1*H*-imidazole was synthesized by a reported method [25]. Dichloromethane was distilled under nitrogen from calcium hydride prior to its use. All glassware was oven dried.

2.2.1. Synthesis of 3-benzhydryl-1-(2,6-diisopropylphenyl)-1H-imidazol-3-ium chloride

A glass vial (10 mL) provided with a stirring bar was charged with 1-(2,6-diisopropylphenyl)-1*H*-imidazole (1 equivalent) and (chloromethylene)dibenzene (1 equivalent). The vial was capped and heated at 100-110 °C overnight. The imidazolium salt was obtained in quantitative yield and used without further purification. Color: White solid. M.p.: 225.1-225.9 °C. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 10.22 (s, 1H, NCH=N), 8.51 (s, 1H, C_4-H imidazol-3-ium), 7.58 (s, 1H, C_5-H imidazol-3-ium), 7.45 (t, 1H, *J* = 7.8 Hz, Ar-H), 7.29-7.37 (m, 10H, Ar-H), 7.18- 7.22 (m, 3H, Ar-H, Ar-C*H*-Ar), 2.22-2.35 (m, 2H, CH_3-C*H*-CH_3), 1.11 (t, 12 H, *J* = 6.6 Hz, 2x[CH_3-CH-CH_3]). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 145.2, 139.2, 136.9, 131.8, 130.2, 129.2, 129.1, 128.3, 124.6, 123.8, 122.3, 66.1, 22.7, 24.3, 24.0. HRMS (TOF MS EI+): calculated for $C_{28}H_{31}N_2$ $[M-2H]^+$ 393.2331, Found: 393.2330.

2.2.2. Synthesis of allyl(1-benzhydryl-3-(2,6-diisopropyl phenyl)-1,3-dihydro-2H-imidazol-2-ylidene)palladium(II) chloride

A flame dried 25 mL round-bottom flask provided with a stirring bar was charged with silver (I) oxide (0.368 g, 1.590 mmol) and 3-benzhydryl-1-(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium chloride (1.202 g, 2.79 mmol), capped with a rubber septum and reflushed with argon. Then, dichloro methane (15 mL) freshly distilled from CaH_2 under nitrogen was added and the mixture was stirred under argon for 12 h. Afterwards, the reaction mixture was filtered through a celite pad and the solution concentrated under vacuum. The crude was mixed with pentane and the solid crushed, decanting the pentane solution, repeating this procedure 3 times. The solid was dried under high vacuum and used for the next reaction without isolation.

In a glove box, a flame dried 25 mL round bottom flask was charged with mono((3-benzhydryl-1-(2,6-diisopropylphenyl)-1*H*-imidazol-3-ium-2-yl)silver(I)) chloride (1.300 g, 2.417 mmol) and allylpalladium chloride dimer (0.442 g, 1.208 mmol), and then dichloromethane (16 mL) was added. The reaction mixture was allowed to react for 2 h at rt. Afterwards, the reaction was filtered off through a pad of celite, the filtrate concentrated under vacuum. The crude was mixed with pentane and the solid crushed, decanting the pentane solution, repeating this procedure 3 times and purified by column chromatography using a mixture dichloromethane: acetone (99:1). Yield: 1.367 g, 83% overall yield from the two steps. Color: Pale yellow solid. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.93 (s, 1H, Ar-CH-Ar), 7.17-7.41 (m, 13H, Ar-H), 6.92 (d, 1H, *J* = 1.8 Hz, C_4-H imidazol-3-ium), 6.82 (d, 1H, *J* = 1.8 Hz, C_5-H imidazol-3-ium), 4.6 (dddd, 1H, J_1=13.6 Hz, J_2 = 12.3 Hz, J_3 = 7.5 Hz, J_4 = 6.9 Hz, CH_2-C*H*-CH_2), 3.98 (dd, 1H, *J* = 7.5, 7.2 Hz, CH_2-CH-CH_2), 2.95- 3.04 (m, 1H, CH_3-C*H*-CH_3), 2.79 (d, 1H, *J* = 13.6 Hz, CH_2-CH-CH_2), 2.61 (m, 1H, CH_3-C*H*-CH_3), 2.54 (d, 1H, *J* = 15.6 Hz, CH_2-CH-CH_2), 1.33 (d, 3H, *J* = 6.7 Hz, CH_3-CH-CH_3), 1.29 (d, 1H, *J* = 12.4 Hz, CH_2-CH-CH_2), 1.22 (d, 3H, *J* = 6.7 Hz, CH_3-CH-CH_3), 1.08 (dd, 6H, *J* = 7.7, 7.3 Hz, CH_3-CH-CH_3). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 185.5, 146.6, 145.8, 140.3, 139.3, 135.9, 136.0, 129.8, 129.4, 128.7, 128.5, 128.2, 127.8, 124.0, 123.5, 123.1, 120.4, 114.6, 72.4, 67.1, 48.7, 28.3, 26.2, 26.0, 23.4, 22.9. HRMS (TOF MS EI+): Calculated for $C_{31}H_{35}N_2Pd^{104}$ 539.1841, found 539.1888.

2.2.3. General procedure for the Suzuki-Miyaura cross-coupling of aryl halides

In a glove box a dry vial (10 mL) provided with a stirring bar was charged with KOtBu (1.1 mmol), K_3PO_4 (1.5 mmol), the aryl halide (1 mmol), 2.5 mL of dry isopropyl alcohol, and 0.5 mL of a stock solution of the catalyst in isopropanol (1 mol %). The mixture was capped and heated at 50 °C for 2 h. Afterwards, the reaction solution was cooled down to ambient temperature, 2 mL of water were added, the mixture was extracted with ethyl acetate, 3 times x 2 mL. The organic solution was dried with sodium sulfate, concentrated *in vacuo* and purified by column chromatography using a mixture of 0 to 20 % of ethyl acetate and hexane.

1-([1,1'-Biphenyl]-3-yl)ethan-1-one: Yield: 93.5 %. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.17 (dd, 1H, *J* = 1.6, 1.3 Hz, Ar-H), 7.90-7.94 (m, 1H, Ar-H), 7.76-7.79 (m, 1H, Ar-H), 7.59-7.62 (m, 2H, Ar-H), 7.50 (dd, 1H, *J* = 7.8, 7.7 Hz, Ar-H), 7.43-7.48 (m, 2H, Ar-H), 7.34-7.40 (m, 1H, Ar-H), 2.64 (s, 3H, ArCO-CH_3).

[1,1'-bBiphenyl]-4-yl(phenyl)methanone: Yield: 95.1 %. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.87 (dd, 2H, *J* = 9.6, 8.4 Hz, Ar-H), 7.81-7.84 (m, 2H, Ar-H), 7.55-7.61 (m, 5 H, Ar-H), 7.45-7.51 (m, 4H, Ar-H), 7.37-7.42 (m, 1H, Ar-H).

1-Phenylnaphthalene: Yield: 80.4 %. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.85-792 (m, 3H, Ar-H), 7.40-7.55 (m, 9H, Ar-H).

4-Methoxy-1,1'-biphenyl: Yield: 94.2 %. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.50-7.56 (m, 4H, Ar-H), 7.37-7.43 (m, 2H, Ar-H), 7.26-7.32 (m, 1H, Ar-H), 6.95-7.00 (m, 2H, Ar-H), 3.84 (s, 3H, Ar-OCH_3).

4-Methyl-1,1'-biphenyl: Yield: 90.3 % (4-bromotoluene), 48.5 % (4-chlorotoluene). ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.09-7.12 (m, 2H, Ar-H), 7.03-7.00 (m, 2H, Ar-H), 6.92-6.97 (m, 2H, Ar-H), 6.82-6.87 (m, 1H, Ar-H), 6.76-6.79 (m, 2H, Ar-H), 1.92 (s, 3H, Ar-CH_3).

[1,1'-Biphenyl]-4-carbaldehyde: Yield: 60.8 %. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 10.04 (s, 1H, Ar-CO-H), 7.93-7.95 (d, 2H, *J* = 8.1 Hz, Ar-H), 7.73-7.75 (d, 2H, *J* = 8.2 Hz, Ar-H), 7.61-7.64 (m, 2H, Ar-H), 7.38-7.50 (m, 3H, Ar-H).

2-Chloro-1,1'-biphenyl: Yield: 50.1 %. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.57-7.61 (m, 2H, Ar-H), 7.29-7.46 (m, 7H, Ar-H).

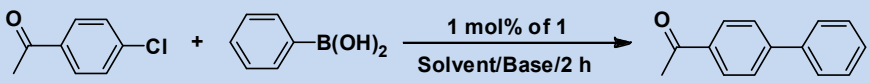
1-([1,1'-Biphenyl]-4-yl)ethan-1-one: Yield: 95.0 %. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.01 (d, 2H, *J* = 8.4 Hz, Ar-H ($COCH_3$), ortho), 7.67 (d, 2H, *J* = 8.4 Hz, Ar-H($COCH_3$), meta), 7.60-7.63 (m, 2H, ArH), 7.36-7.48 (m, 3H, Ar-H), 2.63 (s, 3H, Ar-$COCH_3$).

1-(4'-Methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one: Yield: 93.0. ^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 8.01 (d, 2H, *J* = 8.4 Hz, Ar-H($COCH_3$), ortho), 7.63 (d, 2H, *J* = 8.4 Hz, Ar-H($COCH_3$), meta), 7.56 (d, 2H, *J* = 8.8 Hz, Ar-H(OCH_3), meta), 6.98 (d, 2H, *J* = 8.8 Hz, Ar-H(OCH_3), ortho), 3.85 (s, 3H, Ar-OCH_3), 2.61 (s, 3H, Ar-$COCH_3$).

3. Results and discussion

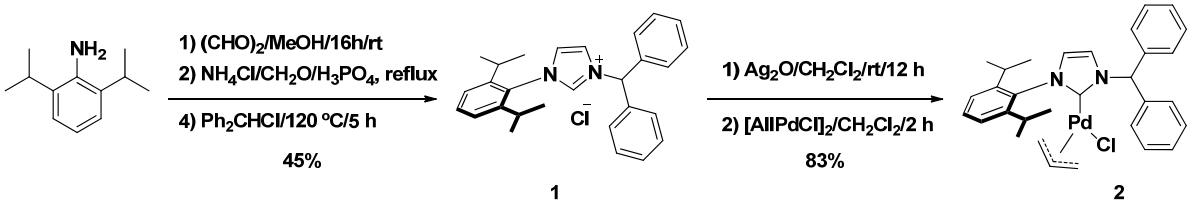
Because the bulkiness around the metal is critical for the catalytic activity of palladium-NHC complexes, we sought to determine whether a combination of a rigid *N*-2,6-diisopropyl

Table 1. Screening of reaction conditions.



Entry [a]	Base	Solvent	Yield (%) [b]
1 [c]	K_3PO_4	THF	15.5
2 [c]	K_3PO_4	THF/Water	18.3
3 [c,d]	K_3PO_4	Dioxane	21.4
4 [e]	NaOH	*i*PrOH	86.4
5	KO*t*-Bu	THF	0.80
6	KO*t*-Bu	Toluene	0.80
7 [d,f]	KO*t*-Bu/Cs_2CO_3	Dioxane	64.4
8	KO*t*-Bu	*i*PrOH	88.3
9	KO*t*-Bu	EtOH	66.4
10	KO*t*-Bu	MeOH	8.30
11 [g]	KO*t*-Bu/K_3PO_4	*i*PrOH	38.7
12 [h]	KO*t*-Bu/K_3PO_4	*i*PrOH	95.0

[a] Reaction conditions: 4'-chloroacetophenone (1 mmol), phenylboronic acid (1.3 mmol), base (1.1 mmol), 3 mL of solvent, 2 h, 50 °C.
[b] Average yield of two experiments, isolated yields.
[c] With 3 equiv of K_3PO_4.
[d] At 80 °C.
[e] With 1.5 equiv.
[f] With 10 mol% of KOtBu and 1.5 mol of Cs_2CO_3.
[g] With 10 mol% of KOtBu and 3 mol of K_3PO_4.
[h] With 1.1 mmol of KOtBu and 1.5 mol of K_3PO_4.



Scheme 1

phenyl substituent and a flexible *N*-diphenylmethyl substituent could give an active catalysts for the Suzuki-Miyaura cross-coupling of aryl halides. The [(NHC)-palladium-(allyl)Cl] complex was synthesized by the silver transfer method [26], starting from the commercially available 2,6-diisopropylaniline [25], to provide the corresponding imidazole, which under treatment with net chlorodiphenylmethane provides the imidazolium salt **1**. The silver complex was treated with palladium allyl chloride producing catalyst **2** in good yield, Scheme 1.

The choice of solvent/base is crucial for the yield. Using as a model the reaction between 4'-chloroacetophenone and phenylboronic acid, different protic and non protic solvents were screened together with distinct bases, Table 1. The combination of non-protic solvents with different bases provided low yields (Entries 1, 3, 5, 6), except for the combination of dioxane with KO*t*-Bu/Cs_2CO_3 (Entry 7). Isopropanol with NaOH or KO*t*-Bu provided the highest yield, (Entries 4 and 8). The addition of 1.5 equivalent of K_3PO_4 improved the yield to 95%, (Entry 12). A catalytic amount of KO*t*-Bu (10 mol%) in combination with K_3PO_4 gave a lower yield than the one molar amount (Entry 11 *vs.* 12). The high activity for the Suzuki-Miyaura cross coupling of some catalysts in isopropanol with a base, it has been attributed to the reduction of the palladium complex by the isopropoxide formed from the reaction between the alcohol and a base [27]. Interestingly, ethanol and methanol gave lower yields, which may indicate that ethoxide and methoxide ions, formed from the reaction between the solvent and the base, are less efficient in reducing the palladium complex than KO*t*-Bu (Entries 9 and 10 *vs.* 12).

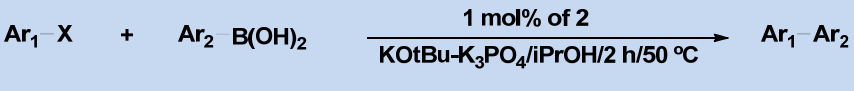
The substrate scope was explored, finding out that catalyst **2** shows a good catalytic activity for activated aryl chlorides, Table 2 (Entries 9 and 10). However, under these conditions, complex **2** provides moderate yields for non-activated aryl chlorides, (Entries 8 and 11). Nevertheless, the catalyst shows a good substrate scope for aryl bromides with excellent yields, even for deactivated substrates (Entries 3 to 5). Compared with other symmetric [28,29] and non-symmetric catalysts [30,31], complex **2** performs better, working under milder conditions and wider substrate scope.

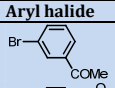
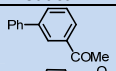
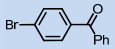
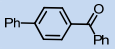
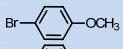
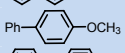
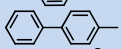
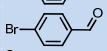
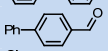
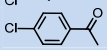
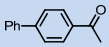
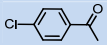
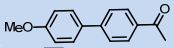
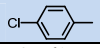
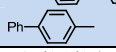
The bulkiness of the substituents distort their position in the complex, making the isopropyl and phenyl groups magnetically non-equivalent, as it is shown by the ^1H and ^{13}C NMR spectra of complex **2**. Intrigued for the NMR results, we wanted to observe the spatial distributions of the groups around the palladium center in the solid state. Crystals suitable for single-crystal X-ray diffraction were obtained from acetone, Figure 1. In this structure, the isopropyl and phenyl groups are above and below the plane, fitting around the metal center. However, they do not surround tightly the metal center as in other cases [8,10]. This fact could explain why the catalyst is active for aryl bromides and activated aryl chlorides, but moderately active for non-activated aryl chlorides, under the conditions employed. In fact, catalysts with more sterically demanding ligands are more active even for sterically demanding aryl chlorides [32,33]. The bulkiness around the metal could be responsible for the catalytic activity of the complex. Currently, we are synthesizing other complexes with different groups around the carbene.

4. Conclusion

We have synthesized a unsymmetrical, well-defined *N*-heterocyclic carbene-palladium-η3-allyl chloride complex, The catalysts at a concentration of 1 mol % promotes the cross-coupling of aryl bromides and activated aryl chlorides with boronic acids, under moderate conditions, with high yields.

Table 2. Suzuki-Miyaura cross-coupling of aryl halides with boronic acids, catalyzed by complex**2**.



Entry [a]	Aryl halide	Product	Yield (%) [b]
1			93.5
2			95.1
3			80.4
4			94.2
5			90.3
6			60.8 (93.0) [c]
7			50.1
8			95.0
9			93.0
10			48.5

[a] Reaction conditions: ArX (1 mmol), $ArB(OH)_2$ (1.3 mmol), $KOtBu/K_3PO_4$ (1.1/1.5 equiv), 3 mL of *i*PrOH, 2 h, 50 °C.
[b] Average yield of two experiments, isolated yields.
[c] Determined by NMR.

The straight forward synthesis makes it attractive to prepare families of *N*-heterocyclic carbene (NHC) precursors to moderate the steric characteristics and electronic properties around a metal center-NHC complex.

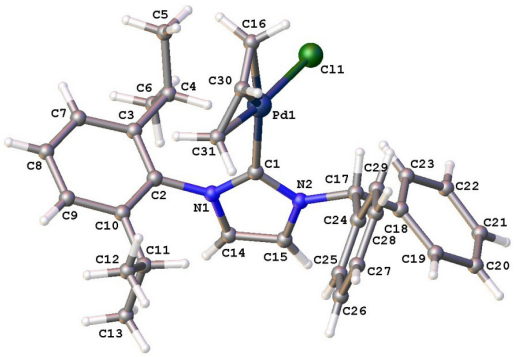


Figure 1. ORTEP of the complex **2**.

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Supplementary material

CCDC 959838 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

References

[1]. Suzuki, A. *J. Organomet. Chem.* **1999**, *576(1-2)*, 147-168.
[2]. Miyaura, N.; Suzuki *Chem. Rev.* **1995**, *95*, 2457-2483.
[3]. Suzuki, A. Overview of the Suzuki Protocol with B, in Handbook of organopalladium chemistry for organic synthesis, E. -I. Negishi, Editor. John Wiley & Sons, 2002, p. 249-262.
[4]. Arduengo, A. J. III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*, 361-363.
[5]. Herrmann, W. A; Kocher, C. *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162-2187.
[6]. Diez-Gonzalez, S.; Marion, N.; Nolan, S. P. *Chem. Rev.* **2009**, *109*, 3612-3676.
[7]. Kantchev, E. A. B.; O'Brien, C. J.; Organ, M. G. *Angew. Chem. Int. Ed.* **2007**, *46*, 2768-2813.
[8]. Viciu, M. S.; Navarro, O.; Germaneau, R. F.; Kelly III, R. A.; Sommer, W.; Marion, N.; Stevens, E. D.; Cavallo, L.; Nolan, S. P. *Organometallics* **2004**, *23*, 1629-1635.
[9]. Nasielski, J.; Hadei, N.; Achonduh, G.; Kantchev, A. B.; O'Brien, C. J.; Lough, A.; Organ, M. G. *Chem. - Eur. J.* **2010**, *16*, 10844-10853.
[10]. Altenhoff, G.; Goddard, R.; Lehmann, C. W.; Glorius, F. *J. Am. Chem. Soc.* **2004**, *126*, 15195-15201.
[11]. Gstottmayr, C. W. K.; Bohm, V. P. W.; Herdtweck, E.; Grosche, M.; Herrmann, W. A. *Angew. Chem. Int. Ed.* **2002**, *41*, 1363-1365.
[12]. Grasa, G. A.; Viciu, M. S.; Huang, J.; Zhang, C.; Trudell, M. L.; Nolan, S. P. *Organometallics* **2002**, *21*, 2866-2873.
[13]. Eckhardt, M.; Fu, G. C. *J. Am. Chem. Soc.* **2003**, *125*, 13642-13643.
[14]. Fu, G. C.; Nguyen, S. T.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 9856-9857.
[15]. Huang, J.; Stevens, E. D.; Nolan, S. P.; Petersen, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 2674-2678.
[16]. Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem. Int. Ed.* **1998**, *37*, 2490-2493.
[17]. Ablialimov, O.; Kedziorek, M.; Torborg, C.; Malinska, M.; Wozniak, K.; Grela, K. *Organometallics* **2012**, *31*, 7316-7319.
[18]. Palencia, H.; Garcia-Jimenez, F.; Takacs, J. M. *Tetrahedron Lett.* **2004**, *45*, 3849-3853.
[19]. Faller, J. W.; Fontaine, P. P. *Organometallics* **2006**, *25*, 5887-5893.
[20]. Tornatzky, J.; Kannenberg, A.; Blechert, S. *Dalton Trans.* **2012**, *41*, 8215-8225.
[21]. Bouhrara, M.; Jeanneau, E.; Veyre, L.; Copereta, C.; Thieuleux, C. *Dalton Trans.* **2011**, *42*, 2995-2999.
[22]. Truscott, B. J.; Klein, R.; Kaye, P. T. *Tetrahedron Lett.* **2010**, *51*, 5041-5043.
[23]. Downing, S. P.; Danopoulos, A. A. *Organometallics* **2006**, *25*, 1337-1340.
[24]. Marion, N.; Nolan, S. P. *Acc. Chem. Res.* **2008**, *41*, 1440-1449.

[25]. Liu, J.; Chen, J.; Zhao, J.; Zhao, Y.; Li, L.; Zhang, H. *Synthesis* **2003**, *17,* 2661-2666.
[26]. Wang, H. M. J.; Lin, I. J. B. *Organometallics* **1998**, *17*, 972-975.
[27]. Fantasia, S.; Nolan, S. P. *Chem. Eur. J.* **2008**, *14*, 6987-6993.
[28]. Huynh, H. V.; Han, Y.; Ho, J. H. H.; Tan, G. K. *Organometallics* **2006**, *25*, 3267-3274.
[29]. Han, Y.; Hong, Y. T.; Huynh, H. V. *J. Organomet. Chem.* **2008**, *693 (19)*, 3159-3165.
[30]. Shi, M.; Qian, H. X. *Tetrahedron* **2005**, *61,* 4949-4955.
[31]. Paulose, T. A. P.; Olson, J. A.; Quail, J. W.; Foley, S. R. *J. Organomet. Chem.* **2008**, *693(21-22)*, 3405-3410.
[32]. Chartoire, A.; Lesieur, M.; Falivene, L.; Slawin, A. M. Z.; Cavallo, L.; Cazin, C. S. J.; Nolan, S. P. *Chem. - Eur. J.* **2012**, *18*, 4517-4521, S4517/1-S4517/25.
[33]. Organ, M. G.; Calimsiz, S.; Sayah, M.; Hoi, K. H.; Lough, A. J. *Angew. Chem. Int. Ed.* **2009**, *48*, 2383-2387.