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N4-Tetradentate Dicarboxyamidate/Dipyridyl Palladium Complexes as Robust Catalysts for the Heck Reaction of Deactivated Aryl Chlorides

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The palladium-catalyzed Heck reaction is one of the "power tools of contemporary organic synthesis".[1] It is used for the olefination of aryl halides, and has found application in natural products synthesis, materials science, and bioorganic chemistry.[2] The olefination of chloroarenes is of immense importance, since C–Cl bond activation contributes to the fundamental understanding of the reactivity of such very stable bonds and they are cheaper and more widely available than their bromide or iodide counterparts.[3] In particular, the activation of deactivated aryl chlorides has become a challenging task. In the past, phosphine complexes and P-donor palladacycles have been used for the activation of deactivated aryl chlorides.[4] However, phosphorus-containing ligands are expensive, toxic, and sensitive to air and temperature. Consequently phosphine-free Pd-catalyzed olefination of deactivated aryl chlorides has become highly desirable.

Among the phosphine-free catalysts, N-based palladacycles, N-heterocyclic carbenes (NHCs), and carbocyclic carbenes containing catalysts have performed well in the olefination of aryl chlorides.[5] The activity of catalysts is however essentially limited to activated and non-activated substrates. A key feature of several homogeneous catalytic systems is the stabilization of the active catalysts, which depends on the ligand stability, chelation or steric shielding of the metal center, and the strength of the metal–ligand bond. In recent years, transition-metal complexes containing N-donor ligands with amide functionality have received much attention and have shown that the anionic amide (deprotonated amide) ligands strongly donate electrons to the metal center thus stabilizing various oxidation states of metals.[6]

We believe that such ionic-type amidate bonding in palladium complexes could impart larger thermodynamic stabilization to active metal species thus rendering a metal electron-rich and therefore facilitate oxidative addition of aryl chlorides in the C–C cross coupling reactions.[7–14] In addition, the amide ligands have advantages over P-donor ligands due to their facile synthesis and their stability in air. Despite having these appealing characteristics, the amidate complexes are relatively unexplored in the field of catalysis. This is particularly the case for the Heck reaction. Herein, we present our studies on the utility of palladium(II) complexes of tetradentate dicarboxyamide/dipyridyl ligands as catalysts for the Heck reaction of deactivated aryl chlorides and olefins.

As depicted in Scheme 1, the new chelating tetradentate ligands **5a** and **5b** are readily accessible in four steps starting with the amino acid precursors L-phenyl alanine and L-valine, **1a** and **1b**, respectively. The square-planar palladium complexes **6a** and **6b** were readily prepared by treatment of the ligands with $Pd(OAc)_2$ in THF at room temperature. The bis(amide) ligand (**5a**) and its amidate palladium complex (**6a**) were structurally characterized by X-ray crystallography (see Figure 1 for complex **6a** and Supporting Information for the ligand **5a**). The ligand contains amide hydrogen atoms and in contrast, the amidate palladium complex displays tetradentate N4 coordination via N atoms of two different functions, namely amidate (deprotonated amide) (N1 and N2) and pyridine (N3 and N4). The coordination geometry around the palladium center is slightly distorted from ideal square-planar, as elucidated by bond angles and inter-planar angles around the metal atom (Figure 1). The solution structure of the palladium complexes was studied by ^{1}H NMR and ^{13}C NMR spectroscopy, and these studies

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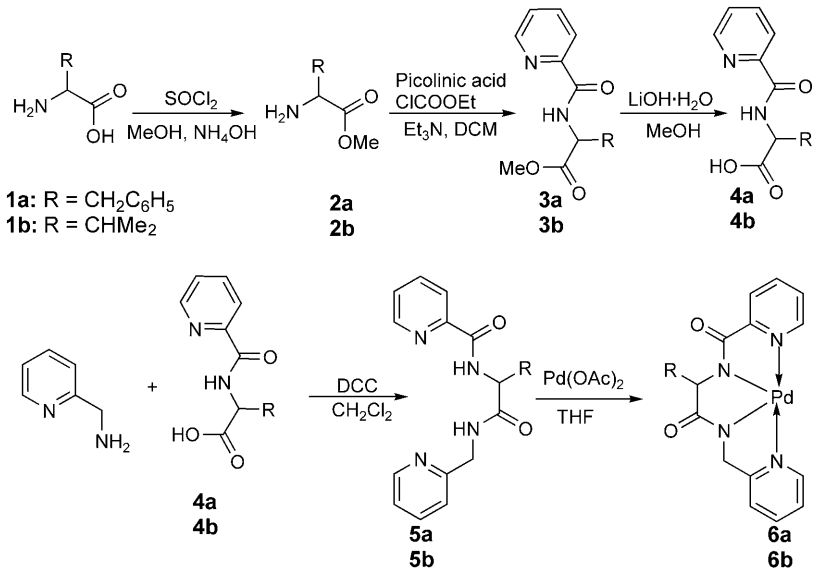


Scheme 1. Synthesis of dicarboxyamide/dipyridyl ligands **5a** and **5b** and their respective palladium complexes **6a** and **6b**.

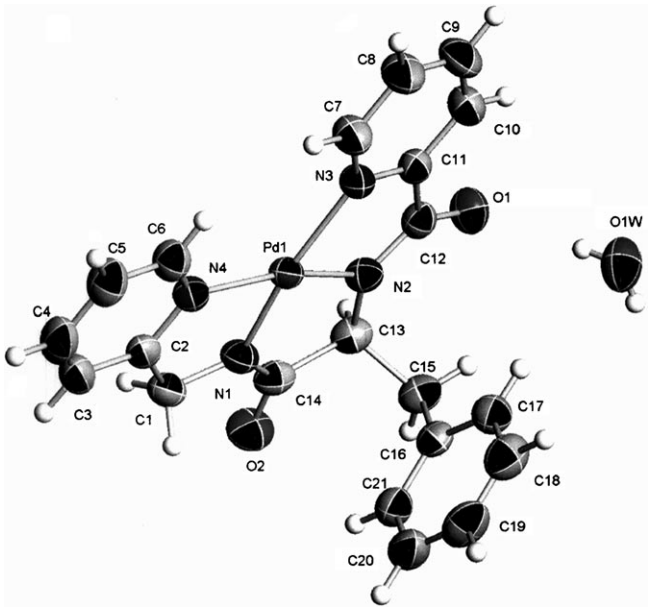


Figure 1. X-ray structure of the Pd^{II} complex **6a** with one molecule of water in the crystal (hydrogen atoms are included to highlight amidate anion bonding to palladium atom; ORTEP plot created at 50% probability). Selected bond lengths [Å] and bond angles [°]: Pd–N1 1.9276(17), Pd–N2 1.9426(16), Pd–N3 2.0744(16), Pd–N4 2.0650(16), C12–O1 1.244(2), C14–O2 1.240(3); N1-Pd-N2 83.12(6), N3-Pd-N4 114.08(6), N1-Pd-N3 163.90(6), N2-Pd-N4 165.02(6), N1-Pd-N4 81.90(6), N2-Pd-N3 80.90(6); dihedral angle [°] between the least-square planes (N1-Pd-N2) and (N3-Pd-N4) is 2.090(1)°, which is a measure of the deviation from square-planarity.

show presence of amidate bonding to palladium similar to that observed in the solid state (see the Supporting Information). Remarkably, both the palladium complexes **6a** and **6b** show high thermal stability up to 350 °C, as analyzed by thermogravimetric analysis (see the Supporting Information). The thermal robustness of the amidate palladium complexes is further confirmed by the absence of inactive palladium black in solution on heating in *N*,*N*-dimethylacetamide (DMA) at 160 °C for several days.

Owing to such high thermal stability of these complexes, we initially studied the Heck reaction of 4-chlorotoluene and 4-methylstyrene using 1 mol% of **6a** (relative to aryl chloride). To optimize the efficiency of our catalytic system, various reaction conditions were used, and the product mixture was analyzed by gas chromatography (Table 1). Among the different bases screened, $LiOH{\cdot}H_2O$ has a pronounced effect on the product yield and we obtained 74% yield using DMA as a solvent at 160 °C in 44 h (entry 7, Table 1).

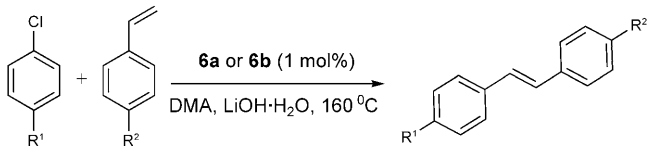
Table 1. Optimization of the Heck reaction of 4-chlorotoluene and 4-methylstyrene catalyzed by complex **6a**.[a]

Entry	Base (mmol)	Solvent	Conv. [%]	Yield [%][b]
1	K_2CO_3 (2)	DMA	22	15
2	K_3PO_4 (2)	DMA	12	5
3	NaOAc (2)	DMA	3	–
4	$NaHCO_3$ (2)	DMA	2	–
5	KOH (2)	DMA	5	–
6	$LiOH{\cdot}H_2O$ (2)	DMA	82	75
7	$LiOH{\cdot}H_2O$ (1.2)	DMA	80	74
8	$LiOH{\cdot}H_2O$ (1.2)	DMSO	3	–
9	$LiOH.H_2O$ (1.2)	DMF	8	–
10	$LiOH{\cdot}H_2O$ (1.2)	NMP	73	64

[a] Reaction conditions: 4-chlorotoluene (1 mmol), 4-methylstyrene (2 mmol), and **6a** (1 mol%) in solvent (3 mL) at 160 °C for 44 h. [b] Yield of isolated product.

Under our optimized reaction conditions, the maximum number of turnovers (TON ca. 620) was achieved with a catalyst loading of 0.1 mol% of **6a** (entry 2, Table 2). The activity of the catalyst **6b** was also tested for the Heck reaction, and the corresponding cross-coupled products were obtained in good yields (entries 3 and 4, Table 2). As can be seen, the reactions of less reactive aryl chlorides such as 4-chloroanisole, 4-chlorotoluene, and chlorobenzene with styrene and 4-methylstyrene, proceeded smoothly, and good yields were obtained under our experimental conditions (entries 5–8, Table 2). Unlike most previously reported systems for the Heck coupling of aryl chlorides, additional co-catalysts such as $[NBu_4]Br$[5a,b,11a,b] or $[PPh_4]Cl$[16] are not required in our catalytic system to achieve high catalytic activity. It is very clear from these results that both palladium complexes **6a**

Table 2. The Heck reaction of aryl chlorides catalyzed by Pd^{II} complexes **6a** and **6b**.[a]



Entry	R^1	R^2	Conv. [%]	Yield [%][b]	TON
1	CH_3	CH_3	80	74	74
2[c]	CH_3	CH_3	73	62	620
3[d]	CH_3	CH_3	81	73	73
4[d]	OCH_3	CH_3	69	62	62
5	OCH_3	CH_3	82	70	70
6	OCH_3	H	74	62	62
7	CH_3	H	72	60	60
8[e]	H	H	80	71	71
9[f]	CH_3	CH_3	89	80	80
10[f]	OCH_3	CH_3	85	75	75

[a] Unless otherwise noted, the reaction was carried out with aryl chloride (1 mmol), alkene (2 mmol), catalyst (1 mol%), $LiOH·H_2O$ (1.2 mmol) and DMA (3 mL) at 160°C for 44 h. [b] Yield of isolated product. [c] 0.1 mol% of the catalyst was used. [d] Catalyst **6b** was used. [e] Chlorobenzene (2 mmol) and styrene (1 mmol) under N_2 balloon pressure. [f] Reaction carried out using [nBu$_4$N]Br additive (20 mol% relative to aryl chlorides).

and **6b** are efficient and active for the Heck reaction of deactivated aryl chlorides and olefins.

With regard to the stability and catalytic activity, the amidate palladium complexes are comparable to palladacycles. The unprecedented activity of **6a** and **6b** may be attributed to an amidate metal coordination achieved with high thermal stability such that the metal amidate unit is retained in the catalytic cycle. Above all it is expected that the strength of Pd–amidate bond and ligand chelation or steric shielding of the metal center have a far greater effect on the stabilization of the active catalysts. It is very likely that one of the main functions of the unsymmetrical dicarboxyamide/dipyridyl ligands during the reaction is to stabilize the palladium center and deliver an electron-rich and well-defined active lower valent palladium species at such a rate and in such manner that prevents decomposition to inactive bulk metal. To the best of our knowledge, this is the first report on the use of purely N-donor ligands that shows significant catalytic activity with deactivated aryl chlorides in the Heck reaction.

In conclusion, we have shown that highly active amidate/pyridyl palladium complexes for the Heck reaction of deactivated aryl chlorides can be constructed from readily available ligand precursors. The concept of using an anionic carboxyamide as an ancillary ligand for palladium demonstrated here provides a new opportunity for the development of phosphine-free transition metal catalysis. Kinetic and quantum-mechanical studies to determine the effect of the metal–amidate bond on the catalytic properties are in progress.

Experimental Section

Typical procedure for the synthesis of compounds (5a and 5b): *N*-(Pyridine-2-carbonyl)amino acid (20 mmol) and *N*,*N*′-dicyclohexylcarbodiimide (DCC) (20 mmol) were dissolved in dry dichloromethane (50 mL) and cooled down to 0°C. The solution was stirred for 30 min and then a solution of 2-(aminomethyl)pyridine (25 mmol) in dichloromethane (20 mL) was added dropwise over 15 min. After the addition, the mixture was warmed to room temperature and stirred for another 12 h. After filtration, the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate) to afford the compound as a white solid (83–84% yield).

Synthesis of dicarboxyamidate/dipyridyl palladium complexes (6a and 6b): The N4-donor ligand (**5a** or **5b**, 1 mmol) was added in one portion at room temperature to a stirred orange solution of palladium acetate (1 mmol) in THF (10 mL). Upon stirring the solution for 30 min, a pale yellow precipitate was obtained. This mixture was stirred for another 5 h at room temperature then filtered, and with washed THF (ca. 20 mL) to afford pure **6a** or **6b**. The complex (**6a**) was dissolved in methanol, and on slow evaporation of methanol at room temperature gave single crystals suitable for X-ray diffraction studies.

General procedure for the Heck reaction: The catalyst **6a** (4.6 mg, 1 mol%) was added to a solution of lithium hydroxide monohydrate (1.2 mmol), aryl chloride (1 mmol), and alkene (2 mmol) in *N*,*N*-dimethylacetamide (3 mL). The reaction mixture was heated to 160°C and the progress of reaction was monitored by GC. At the end of the reaction, the reaction solution was cooled to room temperature, treated with 1 N aq. HCl (1.5 mL), and extracted with ethyl acetate (3×10 mL). The combined organic phase was dried over Na_2SO_4. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate and hexane mixtures to afford the Heck product in high purity.

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Keywords: aryl chlorides · C–C coupling · Heck reaction · N ligands · oxidative addition · palladium

[1] a) K. C. Nicolaou, E. J. Sorensen, *Classics in Total Synthesis*, VCH, Weinheim, **1996**; b) R. F. Heck, *Comprehensive Organic Synthesis, Vol. 4* (Eds.: B. M. Trost, I. Flemming), Pergamon Press, Oxford, **1991**, ch. 3.4, p. 833; c) A. de Meijere, F. E. Meyer, *Angew. Chem.* **1994**, *106*, 2473–2506; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379–2411; d) W. Cabri, I. Caudiani, *Acc. Chem. Res.* **1995**, *28*, 2–7; e) T. Jeffery, *Adv. Met. Org. Chem.* **1996**, *5*, 153–260; f) S. Bräse, A. de Meijere in *Metal Catalyzed Cross-Coupling Reactions* (Eds.: P. J. Stang, F. Diederich), Wiley-VCH, New York, **1998**, ch. 3.

[2] a) J. T. Link, L. E. Overman in *Metal-Catalyzed Cross-Coupling Reactions* (Eds.: F. Diederich, P. J. Stang), Wiley-VCH, Weinheim, **1998**, ch. 6; b) *Step-Growth Polymers for High-Performance Materials* (Eds.: J. L. Hedrick, J. W. Labadie), *ACS Symposium Series*, *624*, American Chemical Society, Washington, DC, **1996**, ch. 1, 2, and 4; c) A. Häberli, C. J. Leumann, *Org. Lett.* **2001**, *3*, 489–492.

[3] a) V. V. Grushin, H. Alper, *Chem. Rev.* **1994**, *94*, 1047–1062; b) V. V. Grushin, H. Alper in *Activation of Unreactive Bonds and Organic Synthesis* (Ed.: S. Murai), Springer, Berlin, **1999**, p. 193.

[4] a) D. Morales-Morales, R. Redon, C. Yung, C. M. Jensen, *Chem. Commun.* **2000**, 1619–1620; b) Y. Ben-David, M. Portnoy, M. Gozin, D. Milstein, *Organometallics* **1992**, *11*, 1995–1996; c) M. Portnoy, Y. Ben-David, D. Milstein, *Organometallics* **1993**, *12*, 4734–4735; d) A. F. Littke, G. C. Fu, *J. Org. Chem.* **1999**, *64*, 10–11; e) A. F. Littke, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 6989–7000.

[5] a) R. B. Bedford, C. S. J. Cazin, D. Holder, *Coord. Chem. Rev.* **2004**, *248*, 2283–2321; b) W. A. Herrmann, K. Ofele, S. K. Schneider, E. Herdtweck, S. D. Hoffmann, *Angew. Chem.* **2006**, *118*, 3943–3947; *Angew. Chem. Int. Ed.* **2006**, *45*, 3859–3862; c) Q. Yao, M. Zabawa, J. Woo, C. Zheng, *J. Am. Chem. Soc.* **2007**, *129*, 3088–3089; d) D. F. Wass, M. F. Haddow, T. W. Hey, A. G. Orpen, C. A. Russell, R. L. Wingad, M. Green, *Chem. Commun.* **2007**, 2704–2706.

[6] a) A. K. Patra, M. Ray, R. Mukherjee, *Inorg. Chem.* **2000**, *39*, 652–657; b) M. Ray, D. Ghosh, Z. Shirin, R. Mukherjee, *Inorg. Chem.* **1997**, *36*, 3568–3572; c) M. Ray, R. Mukherjee, J. F. Richardson, R. M. Buchanan, *J. Chem. Soc. Dalton Trans.* **1993**, 2451–2457; d) A. K. Patra, R. Mukherjee, *Polyhedron* **1999**, *18*, 1317–1322; e) J. C. Noveron, M. M. Olmstead, P. K. Mascharak, *Inorg. Chem.* **1998**, *37*, 1138–1139; f) D. S. Marlin, M. M. Olmstead, P. K. Mascharak, *Inorg. Chem.* **1999**, *38*, 3258–3260; g) M. J. Bartos, C. Kidwell, K. E. Kauffmann, S. W. Gordon-Wylie, T. J. Collins, G. C. Clark, E. Münck, S. T. Weintraub, *Angew. Chem.* **1995**, *107*, 1345–1348; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1216–1219; h) K. Bowman-James, *Acc. Chem. Res.* **2005**, *38*, 671–678; i) S. O. Kang, R. A. Begum, K. Bowman-James, *Angew. Chem.* **2006**, *118*, 8048–8061; *Angew. Chem. Int. Ed.* **2006**, *45*,7882–7894; j) S. O. Kang, M. A. Hossain, K. Bowman-James, *Coord. Chem. Rev.* **2006**, *250*, 3038–3052.

[7] For recent reviews on the Heck reaction, see ref. [5a] and: a) N. J. Whitcombe, K. K. Mimi Hii, S. E. Gibson, *Tetrahedron* **2001**, *57*, 7449–7476; b) M. T. Reetz, J. G. de Vries, *Chem. Commun.* **2004**, 1559–1563; c) I. P. Beletskaya, A. V. Cheprakov, *Chem. Rev.* **2000**, *100*, 3009–3066; d) G. T. Crisp, *Chem. Soc. Rev.* **1998**, *27*, 427–436; e) V. Farina, *Adv. Synth. Catal.* **2004**, *346*, 1553–1582.

[8] For recent work on Heck–Mizoroki reactions: a) D. D. Pathak, H. Maheswaran, K. L. Prasanth, M. L. Kantam, *Synlett* **2007**, *5*, 757–760; b) B.-L. Lin, L. Liu, Y. Fu, S.-W. Luo, Q. Chen, Q.-X. Guo, *Organometallics* **2004**, *23*, 2114–2123; c) H. Hagiwara, Y. Sugawara, T. Hoshi, T. Suzuki, *Chem. Commun.* **2005**, 2942–2944; d) V. Calò, A. Nacci, A. Monopoli, E. Leva, N. Cioffi, *Org. lett.* **2005**, *7*, 617–620; e) S. Mukhopadhyay, G. Rothenberg, A. Joshi, M. Baidossi, Y. Sasson, *Adv. Synth. Catal.* **2002**, *344*, 348–354; f) S. S. Pröckl, W. Kleist, M. A. Gruber, K. Köhler, *Angew. Chem.* **2004**, *116*, 1917–1918; *Angew. Chem. Int. Ed.* **2004**, *43*, 1881–1882; g) R. K. Arvela, N. E. Leadbeater, *J. Org. Chem.* **2005**, *70*, 1786–1790; h) Q. Yao, E. P. Kinney, C. Zheng, *Org. Lett.* **2004**, *6*, 2997–2999.

[9] For ligand-free palladium, palladium colloids, and nanoparticulate palladium in Heck reactions, see: a) J. G. de Vries, *Dalton Trans.* **2006**, 421–429; b) I. P. Beletskaya, A. V. Cheprakov, *J. Organomet. Chem.* **2004**, *689*, 4055–4082; c) R. B. Bedford, M. E. Blake, C. P. Butts, D. Holder, *Chem. Commun.* **2003**, 466–467.

[10] For electron-rich sterically congested phosphine ligands in Heck reaction with aryl chloride substrates, see refs. [4b–e] and: a) M. Portnoy, Y. Ben-David, I. Rousso, D. Milstein, *Organometallics* **1994**, *13*, 3465–3479; b) M. R. Netherton, G. C. Fu, *Org. Lett.* **2001**, *3*, 4295–4298; c) K. H. Shaughnessy, P. Kim, J. F. Hartwig, *J. Am. Chem. Soc.* **1999**, *121*, 2123–2132; d) A. Ehrentraut, A. Zapf, M. Beller, *Synlett* **2000**, 1589–1592.

[11] For palladacycles in Heck reaction with aryl chloride substrates, see ref. [4a] and: a) W. A. Herrmann, C. Brossmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem.* **1995**, *17,* 1989; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*,1844–1848; b) W. A. Herrmann, C. Brossmer, C.-P. Reisinger, T. H. Riermeier, K. Öfele, M. Beller, *Chem. Eur. J.* **1997**, *3*, 1357–1364; c) R. B. Bedford, *Chem. Commun.* **2003**, 1787–1796; d) M. Albrecht, G. van Koten, *Angew. Chem.* **2001**, *113*, 3866–3898; *Angew. Chem. Int. Ed.* **2001**, *40*, 3750–3781; e) J. Dupont, M. Pfeffer, J. Spencer, *Eur. J. Inorg. Chem.* **2001**, 1917–1927; f) W. A. Herrmann, V. P. W. Böhm, C.-P. Reisinger, *J. Organomet. Chem.* **1999**, *576*, 23–41; g) D. A. Albisson, R. B. Bedford, P. N. Scully, *Tetrahedron Lett.* **1998**, *39*, 9793–9796; h) S. Iyer, C. Ramesh, *Tetrahedron Lett.* **2000**, *41*, 8981–8984; i) S. Iyer, A. Jayanthi, *Tetrahedron Lett.* **2001**, *42*, 7877–7878; j) Y. Wu, J. Hou, H. Yun, X. Cui, R. Yuan, *J. Organomet. Chem.* **2001**, *637–639*, 793–795; k) C. S. Consorti, M. L. Zanini, S. Leal, G. Ebeling, J. Dupont, *Org. Lett.* **2003**, *5*, 983–986.

[12] For N-heterocyclic carbenes (NHCs) in the Heck reaction with aryl chloride substrates, see: a) A. C. Hillier, G. A. Grasa, M. S. Viciu, H. M. Lee, C. Yang, S. P. Nolan, *J. Organomet. Chem.* **2002**, *653*, 69–82; b) W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Angew. Chem.* **1995**, *107*, 2602–2605; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371–2374; c) J. Schwarz, V. P. W. Böhm, M. G. Gardiner, M. Grosche, W. A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, *Chem. Eur. J.* **2000**, *6*, 1773–1780; d) W. A. Herrmann, C. P. Reisinger, M. Spiegler, *J. Organomet. Chem.* **1998**, *557*, 93–96; e) D. S. McGuiness, K. J. Cavell, *Organometallics* **2000**, *19*, 741–748; f) V. César, S. Bellemin-Laponnaz, L. H. Gade, *Organometallics* **2002**, *21*, 5204–5208; g) E. Peris, J. A. Loch, J. Mata, R. H. Crabtree, *Chem. Commun.* **2001**, 201–202; h) K. Selvakumar, A. Zapf, M. Beller, *Org. Lett.* **2002**, *4*, 3031–3033; i) S. Caddick, W. Kofie, *Tetrahedron Lett.* **2002**, *43*, 9347–9450; j) J. Liu, Y. Zhao, Y. Zhou, L. Li, T. Y. Zhang, H. Zhang, *Org. Biomol. Chem.* **2003**, *1*, 3227–3231.

[13] For carbocyclic carbenes in the Heck reaction with aryl chloride substrates, see refs. [5b–d] and: B. Dhudshia, A. N. Thadani, *Chem. Commun.* **2006**, 668–670.

[14] For the recent applications of N-donor ligands in palladium catalyzed cross-coupling reactions; see: a) S. Haneda, C. Ueba, K. Eda, M. Hayashi, *Adv. Synth. Catal.* **2007**, *349*, 833–835; b) C. Nájera, J. Gil-Moltó, S. Karlström, L. R. Falvello, *Org. Lett.* **2003**, *5*, 1451–1454; c) T. Schultz, N. Schmees, A. Pfaltz, *Appl. Organomet. Chem.* **2004**, *18*, 595–601; d) H. Weissman, D. Milstein, *Chem. Commun.* **1999**, 1901–1902; e) B. Tao, D. W. Boykin, *Tetrahedron Lett.* **2002**, *43*, 4955–4957; f) C. J. Mathews, P. J. Smith, T. Welton, *J. Mol. Catal. A: Chemical* **2003**, *206*, 77–82; g) V. Montoya, J. Pons, V. Branchadell, J. Garcia-Anton, X. Solans, M. Font-Bardia, J. Ros, *Organometallics* **2008**, *27*, 1084–1091.

[15] CCDC-689837 and CCDC-689838 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] M. T. Reetz, G. Lohmer, R. Schwickardi, *Angew. Chem.* **1998**, *110*, 492–495; *Angew. Chem. Int. Ed.* **1998**, *37*, 481–483.

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