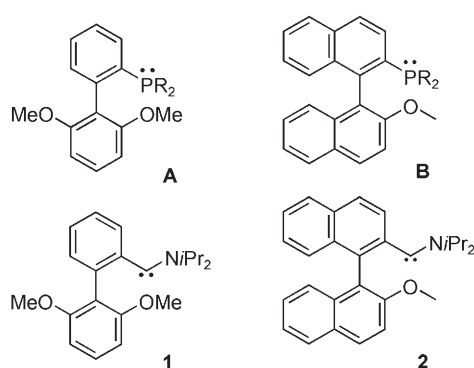


Palladium–Oxygen and Palladium–Arene Interactions in Complexes Derived from Biaryl Aminocarbenes: Comparison with Biaryl Phosphanes**

Joan Vignolle, Heinz Gornitzka, Bruno Donnadieu, Didier Bourissou,* and Guy Bertrand*

The spectacular progress in homogeneous catalysis can be attributed largely to the development of a diverse range of ligand frameworks. The fine-tuning of steric and electronic factors has led to extremely active and selective catalysts. A good example is the recent advances that have been made in Pd-catalyzed cross-coupling reactions with biaryl phosphanes (Scheme 1).^[1] Efforts to rationalize the unique behavior of



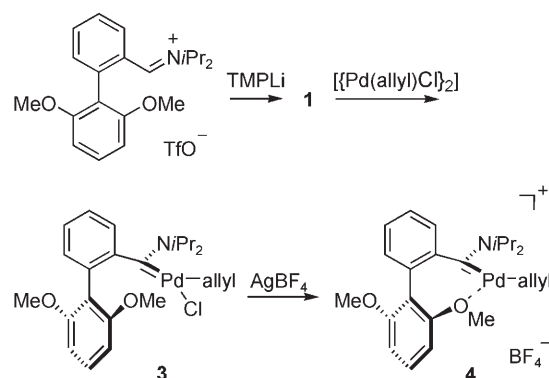
Scheme 1. Structures of the biaryl phosphanes **A** and **B**, and of the related biaryl aminocarbenes **1** and **2**.

these ligands have led to the substantiation both experimentally and computationally of the critical role of weak Pd–arene and Pd–X (X = O or N) interactions.^[2–6]

The development of N-heterocyclic carbenes as ligands also represents a major breakthrough in homogeneous catalysis.^[7] Our interest in increasing further the structural variety of available stable carbenes^[8] prompted us to inves-

tigate the possibility of preparing monoaminocarbenes (MACs)^[9] that feature the same topology as that of biaryl phosphanes.^[10–12] Herein we report the synthesis and characterization of the MACs **1** and **2**, which are related to **A** (SPhos: R = cyclohexyl) and MeO-MOP (**B**),^[13] respectively. We show that the coordination of these carbenes to the $\text{Pd}(\text{allyl})^+$ fragment is accompanied by secondary interactions, albeit of a markedly different nature to those encountered with the corresponding biaryl phosphanes. A rare Pd–oxygen contact was authenticated structurally by using the stable biphenylcarbene **1**, and spectroscopic evidence for an unprecedented, reversible Pd–arene interaction was obtained when the persistent binaphthylcarbene **2** was used as a ligand.

The carbene **1** was obtained readily by treatment of the corresponding iminium triflate^[14] with 2,2,6,6-tetramethylpiperidinolithium (TMPLi) in THF at -80°C (Scheme 2). The MAC **1** is stable indefinitely in solution at room temperature and was characterized unambiguously on the basis of a



Scheme 2. Neutral and cationic allyl palladium(II) complexes derived from the biphenyl MAC **1**. Tf = trifluoromethanesulfonyl.

^{13}C NMR signal at $\delta = 305$ ppm.^[11a,b] The in situ coordination of **1** upon treatment with $[\{\text{Pd}(\text{allyl})(\mu\text{-Cl})\}_2]$ afforded the corresponding air-stable complex **3** in 63% yield.^[14] In the solid state,^[15] the MAC complex **3** exhibits typical Pd–C (2.03 Å) and C–N (1.31 Å) bond distances,^[12,16] but no secondary interaction. To favor the participation of the biphenyl skeleton in the coordination, complex **3** was treated with AgBF_4 in CH_2Cl_2 . The pronounced desymmetrization of the two methoxy groups ($\delta_{\text{H}} = 4.12/3.68$ ppm, $\delta_{\text{C}} = 71.6/56.1$ ppm) upon cationization strongly supports the formation of a Pd–O contact. This hypothesis was confirmed by an X-ray diffraction study (Figure 1). The short Pd–O distance

[*] Dr. J. Vignolle, Dr. H. Gornitzka, Dr. D. Bourissou
Université Paul Sabatier
Laboratoire Hétérochimie Fondamentale et Appliquée
UMR-CNRS 5069
118, route de Narbonne, 31062 Toulouse cedex 09 (France)
Fax: (+33) 5-6155-8204
E-mail: dbouriss@chimie.ups-tlse.fr
Dr. J. Vignolle, B. Donnadieu, Prof. G. Bertrand
UCR-CNRS Joint Research Chemistry Laboratory (UMI 2957)
Department of Chemistry, University of California
Riverside, CA 92521-0403 (USA)
Fax: (+1) 951-827-2725
E-mail: gbertran@mail.ucr.edu

[**] We thank the NIH (grant R01 GM 68825), CNRS, UPS, and RHODIA for financial support of this research.

Supporting information for this article is available on the WWW under <http://www.angewandte.org> or from the author.

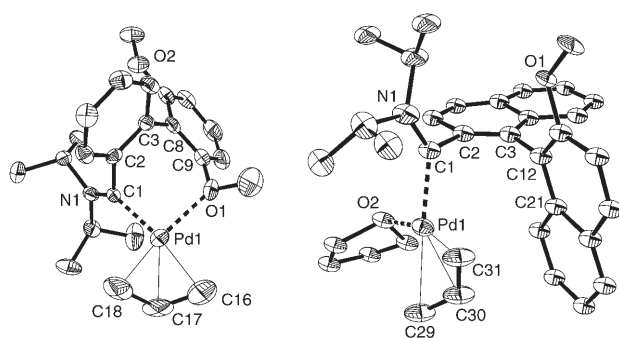


Figure 1. Molecular views (thermal ellipsoids at 50% probability) of complexes **4** (left) and **7** (right) in the solid state. Hydrogen atoms are omitted for clarity.

(2.21 Å)^[17] indicated unambiguously the presence of a bonding interaction. This Pd–O contact contrasts markedly with the Pd–arene interactions commonly encountered in the related SPhos and MeO-MOP complexes,^[3c,4a,d,f] a difference that may be attributed to the different orientations of the C_{carbene}–Pd and P–Pd bonds with respect to the biphenyl skeleton (Pd–C_{carbene}–C_{ipso}–C_{ortho}: 78° in **3**, 86° in **4** versus Pd–P–C_{ipso}–C_{ortho}: 0–10°). Surprisingly, evidence for such Pd–O contacts has been observed only once for biaryl phosphanes, by NMR spectroscopy.^[4c]

We then turned our attention to the binaphthylaminocarbenes **2**, which is related to MeO-MOP (**B**). The corresponding iminium salt was deprotonated with KHMDS at –80 °C in THF (Scheme 3).^[14] Carbene **2** is only moderately stable at room temperature (*t*_{1/2} ≈ 30 min) and was therefore characterized at –78 °C. Its structure was confirmed unambiguously on the basis of the diagnostic ¹³C NMR signal observed at δ = 307 ppm. In situ coordination of **2** to {Pd(allyl)Cl} occurred at

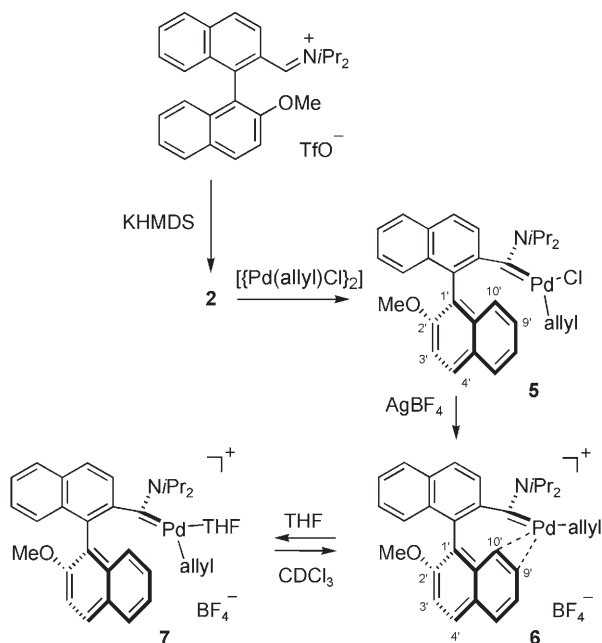
low temperature to give the air-stable complex **5** in 47% yield.^[14] X-ray diffraction analysis indicated the absence of a secondary interaction.

We anticipated that the *anti* orientation of the methoxy substituent with respect to the palladium center would preclude a Pd–O interaction in the corresponding cationic complex. To determine whether the binaphthyl skeleton may engage in Pd–arene interactions, the cationic complex **6** was prepared by chloride abstraction with AgBF₄ in CH₂Cl₂. The signals for the methoxy groups remained virtually unchanged in the NMR spectra (Δδ_H = 0.16 ppm, Δδ_C = 1.9 ppm), in agreement with the absence of a Pd–O contact in **6**. Careful inspection of the ¹³C NMR spectrum revealed that two of the signals for the carbon atoms of the binaphthyl skeleton are shifted upfield to a significant extent in this cationic complex (δ = 99.3 and 112.0 ppm in **6** versus δ > 122 ppm in **5**). This situation is reminiscent of that observed for some binaphthylphosphane complexes^[4d–f] and strongly suggests weak η² coordination of the naphthyl backbone to the Pd center. The two diagnostic high-field signals observed for **6** were assigned unambiguously to C9' and C10' on the basis of 2D NMR experiments (see Scheme 3 for atom numbering). This interaction contrasts with the η² bonding through C1'/C2' encountered in the related MeO-MOP complexes. In fact, Pd–arene interactions involving the remote ring of the binaphthyl skeleton, as observed in **6**, are unknown in biaryl phosphanes. In the case of **6**, the interaction most likely results from the configuration of the binaphthyl axis.

Crystals of **6** suitable for X-ray diffraction analysis could only be obtained upon cooling a solution of **6** in THF to –30 °C. The modest quality of the crystallographic data precludes discussion of the geometric parameters, but the connectivity of the complex was established unambiguously (Figure 1). Thus, a 1:1 adduct **7** was formed by the coordination of one THF molecule to the Pd center and removal of the Pd–arene interaction. The dissolution of **7** in CDCl₃ returned **6** along with free THF in a further illustration of the hemilabile character of the aminobinaphthylcarbene **2**.

Thus, as observed for the related biaryl phosphanes SPhos and MeO-MOP, the coordination of the biaryl aminocarbenes **1** and **2** to the {Pd(allyl)}⁺ fragment is accompanied by secondary interactions. The formal replacement of the phosphane group with an aminocarbene moiety influences markedly the relative positions of the metal fragment and the biaryl skeleton, so that unusual Pd–O and Pd–arene interactions are found with the hybrid ligands **1** and **2**. Biaryl aminocarbenes further expand the structural diversity of bidentate ligands based on aminocarbenes.^[18] Their hemilabile character,^[19] which has been substantiated spectroscopically by reversible competition between η² naphthyl coordination and coordination by THF, may offer interesting perspectives in catalysis.

Complex **3** derived from the biphenylaminocarbene **1** was evaluated as a catalyst for the α arylation of propiophenone.^[20,21] With a precatalyst loading of 2 mol %, bromobenzene underwent quantitative coupling with propiophenone at room temperature within 15 h. Although the reaction proceeded more slowly, chlorobenzene also acted as an effective arylating agent under the same conditions.^[14] According to



Scheme 3. Neutral and cationic allyl palladium(II) complexes derived from the binaphthyl MAC **2**. HMDS = hexamethyldisilazane.

these preliminary results, the MAC complex **3** competes with the most active phosphane-based catalysts reported to date for the coupling of aryl bromides. Indeed, binap (2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl) ligands,^[20] bis(diarylphosphanyl)ferrocene derivatives,^[21] and biphenylphosphanes^[22a,b] are typically used at temperatures higher than 50 °C, and only PtBu_3 ,^[21b] DtBPF (1,1'-bis(di-*tert*-butylphosphanyl)ferrocene),^[21b] and binaphthyl(dialkyl)phosphanes^[22c] were found to be suitable for the coupling of aryl bromides at room temperature. The reaction of chlorobenzene at room temperature is also encouraging, as, until now, aryl chlorides have only been coupled at high temperatures,^[20,21b,22a,b,23] except with cyclic alkyl aminocarbenes.^[24] Given the superiority of cyclic carbenes over their acyclic counterparts as robust ligands for transition metals,^[25] better catalytic results can be expected with cyclic biaryl aminocarbenes, the preparation of which is under active investigation.

Experimental Section

All reactions and manipulations were carried out under an atmosphere of dry argon by using standard Schlenk techniques. All NMR spectra were recorded at 293 K unless otherwise stated.

Carbenes 1 and 2: A 1:1 mixture of the iminium precursor and TMPLi or KHMDS was cooled to -78°C , and $[\text{D}_8]\text{THF}$ was added. The suspension was warmed to room temperature and stirred for 30 min. ^{13}C NMR ($[\text{D}_8]\text{THF}$): $\delta_{\text{C}}(\text{carbene}) = 304.6$ (for **1**) and 307.1 ppm (for **2**).

Neutral complexes 3 and 5: $[\{\text{Pd}(\text{allyl})\text{Cl}\}_2]$ (0.45 equiv with respect to the iminium precursor) was added at -78°C to a freshly prepared solution of carbene **1** or **2** in THF (10 mL). The resulting solution was warmed to room temperature and stirred for 2 h. Workup and recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ afforded **3** or **5** as yellow crystals. ^{13}C NMR (CDCl_3): $\delta_{\text{C}}(\text{carbene}) = 253.9$ (for **3**) and 252.6 ppm (for **5**).

Cationic complexes 4 and 6: A 1:1 mixture of **3** or **5** and AgBF_4 (0.24 mmol) was cooled to -30°C , and CH_2Cl_2 (5 mL) was added. The resulting solution was warmed to room temperature and stirred for 30 min. Workup and recrystallization from $\text{CH}_2\text{Cl}_2/\text{Et}_2\text{O}$ at 5°C afforded **4** (0.114 g, 85%) as yellow crystals: ^{13}C NMR (CDCl_3 , -20°C): $\delta = 56.1$ (OCH_3), 71.6 (br, OCH_3), 245.7 ppm (br, $\text{C}_{\text{carbene}}$). Attempts to crystallize complex **6** (^{13}C NMR (CDCl_3 , 25°C): $\delta = 55.9$ (OCH_3), 99.3 ($\text{C}10'$), 112.0 ($\text{C}9'$), 246.7 ppm ($\text{C}_{\text{carbene}}$)) from THF at -30°C afforded the adduct **7** (260 mg, 69%) as brown crystals.

Received: October 24, 2007

Published online: February 13, 2008

Keywords: aminocarbenes · biaryls · coordination modes · metal–ligand interactions · palladium

- [1] For selected examples of Pd-catalyzed C–C, C–N, C–O, and C–B cross-coupling reactions with biaryl phosphanes, see: a) E. R. Strieter, D. G. Blackmond, S. L. Buchwald, *J. Am. Chem. Soc.* **2003**, *125*, 13978–13980; b) J. E. Milne, S. L. Buchwald, *J. Am. Chem. Soc.* **2004**, *126*, 13028–13032; c) T. E. Barder, S. D. Walker, J. R. Martinelli, S. L. Buchwald, *J. Am. Chem. Soc.* **2005**, *127*, 4685–4696; 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) K. L. Billingsley, T. E. Barder, S. L. Buchwald, *Angew. Chem.* **2007**, *119*, 5455–5459; *Angew. Chem. Int. Ed.* **2007**, *46*, 5359–5363.

- [2] For an *o*-phenanthrylphosphane, see: J. Yin, M. P. Rainka, X.-X. Zhang, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 1162–1163.
- [3] For biphenylphosphanes, see: a) S. M. Reid, R. C. Boyle, J. T. Mague, M. J. Fink, *J. Am. Chem. Soc.* **2003**, *125*, 7816–7817; b) J. W. Faller, N. Sarantopoulos, *Organometallics* **2004**, *23*, 2008–2014; c) S. D. Walker, T. E. Barder, J. R. Martinelli, S. L. Buchwald, *Angew. Chem.* **2004**, *116*, 1907–1912; *Angew. Chem. Int. Ed.* **2004**, *43*, 1871–1876; d) T. E. Barder, M. R. Biscoe, S. L. Buchwald, *Organometallics* **2007**, *26*, 2183–2192.
- [4] For binaphthylphosphanes, see: a) P. Kočovský, S. Vyskočil, I. Císařová, J. Sejbál, I. Tišlerová, M. Smrčina, G. C. Lloyd-Jones, S. C. Stephen, C. P. Butts, M. Murray, V. Langer, *J. Am. Chem. Soc.* **1999**, *121*, 7714–7715; b) Y. Wang, X. Li, J. Sun, K. Ding, *Organometallics* **2003**, *22*, 1856–1862; c) W. J. Marshall, V. V. Grushin, *Organometallics* **2003**, *22*, 555–562; d) P. Dotta, P. G. A. Kumar, P. S. Pregosin, A. Albinati, S. Rizzato, *Organometallics* **2003**, *22*, 5345–5349; e) P. Dotta, P. G. A. Kumar, P. S. Pregosin, A. Albinati, S. Rizzato, *Organometallics* **2004**, *23*, 4247–4254; f) P. G. A. Kumar, P. Dotta, R. Hermatschweiler, P. S. Pregosin, A. Albinati, S. Rizzato, *Organometallics* **2005**, *24*, 1306–1314.
- [5] For Pd–arene interactions in biaryl phosphane palladium(I) dimers, see: a) U. Christmann, D. A. Pantazis, J. Benet-Buchholz, J. E. McGrady, F. Maseras, R. Vilar, *J. Am. Chem. Soc.* **2006**, *128*, 6376–6390; b) T. E. Barder, *J. Am. Chem. Soc.* **2006**, *128*, 898–904.
- [6] Pd–arene interactions have also been evidenced in arylated-alkyl palladium(II) complexes; see, for example: a) J. Cámpora, J. A. López, P. Palma, P. Valerga, E. Spillner, E. Carmona, *Angew. Chem.* **1999**, *111*, 199–203; *Angew. Chem. Int. Ed.* **1999**, *38*, 147–151; b) M. Catellani, C. Mealli, E. Motti, P. Paoli, E. Perez-Carreño, P. S. Pregosin, *J. Am. Chem. Soc.* **2002**, *124*, 4336–4346.
- [7] a) W. A. Herrmann, *Angew. Chem.* **2002**, *114*, 1342–1363; *Angew. Chem. Int. Ed.* **2002**, *41*, 1290–1309; b) C. M. Crudden, D. P. Allen, *Coord. Chem. Rev.* **2004**, *248*, 2247–2273; c) 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.
- [8] a) A. J. Arduengo III, *Acc. Chem. Res.* **1999**, *32*, 913–921; b) D. Bourissou, O. Guerret, F. P. Gabbaï, G. Bertrand, *Chem. Rev.* **2000**, *100*, 39–92; c) Y. Canac, M. Soleilhavoup, S. Conejero, G. Bertrand, *J. Organomet. Chem.* **2004**, *698*, 3857–3865.
- [9] a) S. Solé, H. Gornitzka, W. W. Schoeller, D. Bourissou, G. Bertrand, *Science* **2001**, *292*, 1901–1903; b) X. Cattoën, H. Gornitzka, D. Bourissou, G. Bertrand, *J. Am. Chem. Soc.* **2004**, *126*, 1342–1343.
- [10] For biphenyl NHCs, see: a) L. Delaude, M. Szyba, A. Demonceau, A. F. Noels, *Adv. Synth. Catal.* **2002**, *344*, 749–756; b) C. Flidél, A. Maisse-François, S. Bellemin-Laponnaz, *Inorg. Chim. Acta* **2007**, *360*, 143–148.
- [11] For binaphthyl NHCs, see: a) D. S. Clyne, J. Jin, E. Genest, J. C. Gallucci, T. V. Rajan Babu, *Org. Lett.* **2000**, *2*, 1125–1128; b) W.-L. Duan, M. Shi, G.-B. Rong, *Chem. Commun.* **2003**, 2916–2917; c) J. J. Van Veldhuizen, D. G. Gillingham, S. B. Garber, O. Kataoka, A. H. Hoveyda, *J. Am. Chem. Soc.* **2003**, *125*, 12502–12508; d) A. R. Chianese, R. H. Crabtree, *Organometallics* **2005**, *24*, 4432–4436.
- [12] Transition-metal complexes of heteroditopic (phosphane/amino-carbene) ligands that feature a biphenyl spacer were obtained from the corresponding cyclic C-amino phosphorus ylides: J. Vignolle, B. Donnadieu, D. Bourissou, M. Soleilhavoup, G. Bertrand, *J. Am. Chem. Soc.* **2006**, *128*, 14810–14811.
- [13] MOP is a generic term for 2-phosphanyl-2'-substituted 1,1'-binaphthyl and MeO-MOP stands for 2-phosphanyl-2'-methoxy-1,1'-binaphthyl; for applications of binaphthylphosphanes in asymmetric catalysis, see: a) T. Hayashi, *Acc. Chem. Res.* **2000**, *33*, 354–362; b) G. C. Lloyd-Jones, S. C. Stephen, M. Murray,

- C. P. Butts, S. Vyskočil, P. Kočovský, *Chem. Eur. J.* **2000**, *6*, 4348–4357; c) I. J. S. Fairlamb, G. C. Lloyd-Jones, S. Vyskočil, P. Kočovský, *Chem. Eur. J.* **2002**, *8*, 4443–4453; d) P. Kočovský, S. Vyskočil, M. Smrčina, *Chem. Rev.* **2003**, *103*, 3213–3245.
- [14] See the Supporting Information for details.
- [15] CCDC 664945 (3), CCDC 664946 (4), CCDC 664947 (5), and CCDC 664948 (7) 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] D. Kremzow, G. Seidel, C. W. Lehmann, A. Fürstner, *Chem. Eur. J.* **2005**, *11*, 1833–1853.
- [17] Similar Pd–O distances (2.20–2.22 Å) were observed in palladium(II) complexes of (2,6-dimethoxyphenyl)diphenylphosphane: J.-F. Ma, Y. Kojima, Y. Yamamoto, *J. Organomet. Chem.* **2000**, *616*, 149–156.
- [18] a) S. J. Roseblade, A. Ros, D. Monge, M. Alcarazo, E. Álvarez, J. M. Lassaletta, R. Fernandez, *Organometallics* **2007**, *26*, 2570–2578; b) Y. Canac, C. Duhayon, R. Chauvin, *Angew. Chem.* **2007**, *119*, 6429–6431; *Angew. Chem. Int. Ed.* **2007**, *46*, 6313–6315; c) O. Köhl, *Chem. Soc. Rev.* **2007**, *36*, 592–607; d) S. T. Liddle, I. S. Edworth, P. L. Arnold, *Chem. Soc. Rev.* **2007**, *36*, 1732–1744, and references therein.
- [19] IMes (1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) was recently found to behave as a bidentate hemilabile ligand towards tungsten fragments. Weak interactions were evidenced between the metal and a C=C bond of one mesityl ring: F. Wu, V. K. Dioumaev, D. J. Szalda, J. Hanson, J. A. Franz, R. M. Bullock, *Organometallics* **2007**, *26*, 5079–5090.
- [20] M. Palucki, S. L. Buchwald, *J. Am. Chem. Soc.* **1997**, *119*, 11108–11109.
- [21] a) B. C. Hamann, J. F. Hartwig, *J. Am. Chem. Soc.* **1997**, *119*, 12382–12383; b) M. Kawatsura, J. F. Hartwig, *J. Am. Chem. Soc.* **1999**, *121*, 1473–1478.
- [22] a) D. W. Old, J. P. Wolfe, S. L. Buchwald, *J. Am. Chem. Soc.* **1998**, *120*, 9722–9723; b) J. M. Fox, X. Huang, A. Chieffi, S. L. Buchwald, *J. Am. Chem. Soc.* **2000**, *122*, 1360–1370; c) T. Hamada, A. Chieffi, J. Ahman, S. L. Buchwald, *J. Am. Chem. Soc.* **2002**, *124*, 1261–1268.
- [23] a) A. Ehrentraut, A. Zapf, M. Beller, *Adv. Synth. Catal.* **2002**, *344*, 209–217; b) M. S. Viciu, R. F. Germaneau, S. P. Nolan, *Org. Lett.* **2002**, *4*, 4053–4056.
- [24] V. Lavallo, Y. Canac, C. Präsang, B. Donnadiou, G. Bertrand, *Angew. Chem.* **2005**, *117*, 5851–5855; *Angew. Chem. Int. Ed.* **2005**, *44*, 5705–5709.
- [25] Cyclic diaminocarbenes and alkyl aminocarbenes proved to be much more efficient ligands than their acyclic counterparts; see: a) W. A. Herrmann, K. Öfele, D. v. Preysing, E. Herdtweck, *J. Organomet. Chem.* **2003**, *684*, 235–248, and Ref. [24].