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Azetidines as ligands in the Pd(II) complexes series

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Abstract

The preparation of palladium (II) complexes having sterically congested azetidines as ligands is described. Diastereomerically pure α-alkylamino and α-alkylimino azetidines react with Na_2PdCl_4 to afford the corresponding bidendate Pd(II) complexes, whereas 2-cyano azetidines can be used to access bidendate Pd(II) complexes containing an amino-imidate moiety. Preliminary study of the catalytic activity of these new complexes in the Suzuki cross-coupling reaction is presented.

Keywords: Azetidine; Diamine; Imine; Imidate; Palladium complex

1. Introduction

Saturated 4-membered ring aza-heterocycles, namely azetidines, represent an understudied class of heterocycles. Recent advances in the synthesis and reactivity of chiral non racemic azetidines [1–6] are driven by the fact that such strained heterocycles can be found in several natural products or synthetic drugs of biological relevance as well as in the field of enantioselective catalysis [7]. In the latter case, combination of azetidines used as ligands and transition metals such as Rh [3] or Zn [1–6,8–10] proved, respectively, efficient for enantioselective cyclopropanation and addition of diethylzinc to aldehydes or ketones. To the best of our knowledge, combination of azetidines with palladium was reported only twice. The first example describes the intervention of a palladium species in a ring opening process involving four subsequent steps on azetidine substrates [11]. The second example reports the use of *N*-benzylazetidines as substrates for the synthesis of a cyclopalladated dimeric complex [12].

In this paper, we report the selective preparation of new palladium (II) complexes having various azetidine ligands (Fig. 1). The design of these new bidendate strained ligands comprises two chelation sites, the first being the heterocyclic nitrogen atom, the second one being an additional alkylamine, alkylimine or alkylimidate moiety, located in the 2-position of the azetidine. In addition, preliminary results showing the catalytic activities of the complexes bearing a diamine, an amine–imine or an amine–imidate ligand are also reported.

In order to examine the possible use of azetidines as ligands in palladium-mediated catalysis, we focused on the synthesis and isolation of chiral, Pd(II)-diamino complexes.

2. Results and discussion

2.1. Diamine complexes

Diamines **1** and **2** were prepared in good yield according to our previously described methodology [13], and

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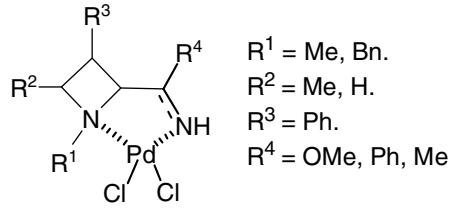
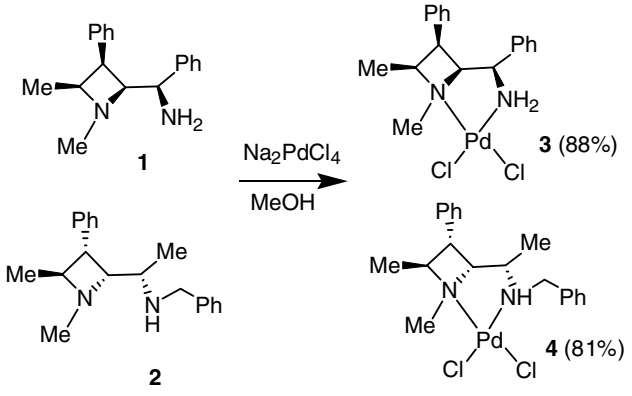


Fig. 1. General structure of the Pd(II) complexes with azetidine ligands.

were reacted with Na_2PdCl_4 under classical conditions [14] to give the expected Pd(II) complexes in high yields (Scheme 1). The reaction proceeds smoothly at room temperature in freshly distilled methanol. After a few hours, precipitation of the complexes is observable. After additional 24 h, the precipitated complexes are collected by filtration. These palladium complexes are stable on air and their purification by silica gel chromatography afforded **3** (88%) and **4** (81%) respectively as yellow and brownish crystalline solids.

Complexes **3** and **4** were fully characterized. Single crystals suitable for X-ray analysis could be obtained by slow evaporation of an ethyl acetate solution. Both ORTEP drawings are depicted in Fig. 2 [15].



Scheme 1. Synthesis of diamino complexes **3** and **4**.

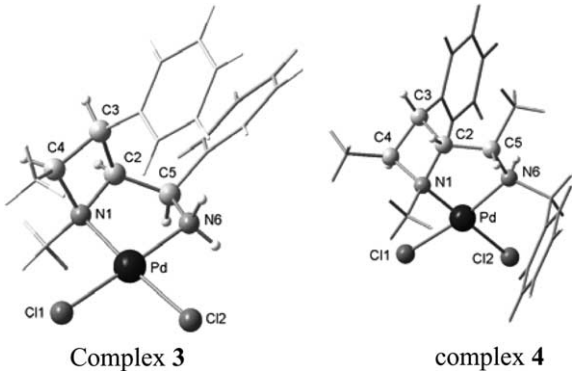


Fig. 2. ORTEP drawings of complexes **3** and **4**.

Selected bond lengths and angles are presented in Table 1. For example, Pd–N(1), Pd–C(2) as well as N(1)–C(2) bond lengths in complexes **3** and **4** are very close but not identical. In addition, the asymmetric structures of both complexes result in significant variations in bond lengths between palladium and nitrogen atoms (Pd–N(1) = 2.075 Å compared to Pd–N(6) = 2.049 Å in complex **3** and Pd–N(1) = 2.074 Å compared to Pd–N(6) = 2.042 Å in complex **4**).

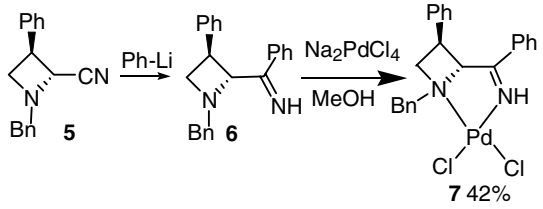
It is worth to note that only bidendate structures were obtained. No traces of bismonodendate type complexes were detected, even by using various ratios of substrate/palladium source.

2.2. Amino-imine complexes

We next envisioned the rigidification of the carbon-based link between the two chelating nitrogen atoms and turned our attention to the amino-imine combination. The preparation of complex **7** bearing an amino-imine type ligand is depicted in Scheme 2. 2-Cyanoazetidine **5** was reacted with PhLi in toluene at 5–10 °C to give the corresponding imine **6** [16]. Under classical conditions (Na_2PdCl_4, MeOH), complex **7** could be isolated in moderate yield (42%) from crude imine **6**, thus demonstrating that the flexibility of bidendate strained ligands in the azetidine series is modulable.

Table 1
Selected list of bond lengths (Å) and angles (°) for **3** and **4**

	3	**4**
Bonds		
Pd–Cl(2)	2.284	2.307
Pd–Cl(1)	2.300	2.318
Pd–N(1)	2.075	2.074
Pd–N(6)	2.049	2.042
N(1)–C(2)	1.518	1.507
Pd–C(2)	2.921	2.921
Angles		
N(1)–Pd–N(6)	85.0	84.9
Pd–N(1)–C(2)	107.8	109.8
C(5)–N(6)–Pd	110.0	111.2
N(1)–C(2)–C(5)	113.0	113.2
N(6)–C(5)–C(2)	108.5	111.0
N(1)–Pd–Cl(2)	93.2	89.9
N(6)–Pd–Cl(1)	89.6	93.9



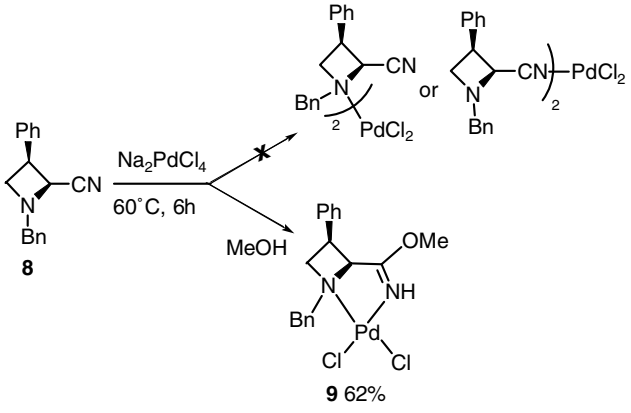
Scheme 2. Synthesis of amino-imine complex **7**.

Although substrate **5** is substituted by a benzyl group, it is worth noting that no traces of cyclopalladated complex was formed. Thus, complex **7** was selectively prepared through a coordination mode involving both nitrogen atoms in an 1,2-amino-imine combination.

2.3. Amino-imidate complexes

We next tried to prepare new Pd(II) complexes by using 2-cyano azetidines. In this case both the intracyclic nitrogen atom and the cyano group located in the 2-position of the azetidine ring may individually serve as ligand. It was then debatable whether the nitrile group would participate in the complexation process and act as a ligand. In fact, 2-cyanoazetidine **8** when treated with Na_2PdCl_4 in THF at 60 °C for 24 h, did not afford bismonodendate complexes even by modifying the substrate–palladium precursor ratio (Scheme 3).

In contrast, we discovered that using methanol as the solvent lead to the selective formation of amino-imidate based complex **9** (62%) [17]. Spectroscopic data of complex **9** are in good agreement with its structure. The ^{13}C NMR spectrum displays a set of six aromatic CH (δ = 128.7, 129.0, 129.1, 131.8, 132.3 and 133.6 ppm) and two quaternary carbons (δ = 128.4 and 129.7 ppm) which accounts for two residual mono-substituted phenyl groups. Signal indicating the presence of a nitrile group could not be detected. In contrast, signals at 176.1 ppm in ^{13}C NMR and 3.19 ppm in ^{1}H NMR spectra confirmed the formation of the imidate moiety. As depicted in Fig. 3, amino-imidate complexes **10** and **11** with different substitution pattern have been similarly prepared from the parent 2-cyanoazetidines, respectively, in 72% and 58% yields.



Scheme 3. Synthesis of amino-imidate complex **9**.

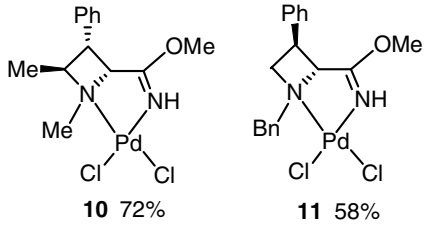


Fig. 3. Structure of complexes **10** and **11** with bidentate amino-imidate ligands.

2.4. Suzuki cross-coupling reactions

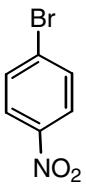
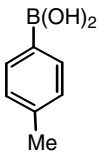
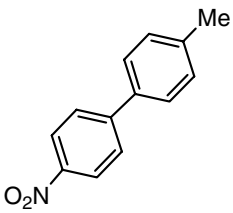
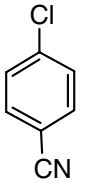
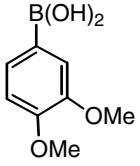
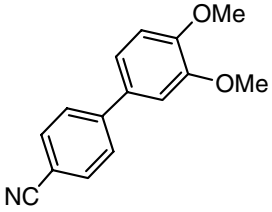
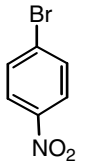
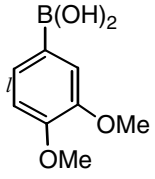
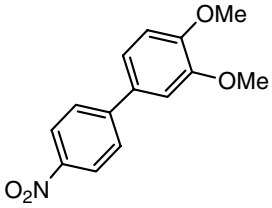
At this stage, it was debatable whether these new Pd (II) complexes bearing azetidinic diamino, amino-imine or amino-imidate ligands could be involved in a catalytic process. With this aim, complexes **4**, **7** and **11** were tested in the Suzuki coupling reaction and preliminary results are shown in Table 2. For example, 4-Nitrobromobenzene was reacted with 4-tolylboronic acid under classical conditions (solvent: DMF–water and base: 2.5 eq. K_2CO_3) with low catalyst loadings (1–2%). The expected biaryl product was obtained in good to high yields irrespective of the ligand structure (Table 2, entries 1–3) leading to the first examples of Suzuki reaction using azetidine ligands in the palladium catalytic species.

Although reaction conditions were not optimized, it should be noted that reactions involving aryl bromides as substrates proceed with high conversion within a few hours [18]. Combinations of electron rich boronic acids with either electron poor or electron rich aromatic halides have been successfully tested leading to variously substituted biphenyl derivatives. Moreover, catalytic systems based on palladium and congested azetidine ligands seem not only efficient in the aromatic bromide series but also in the more reluctant chloride series. Indeed, under the above mentioned catalytic conditions, chlorobenzene and 4-cyanochlorobenzene gave the corresponding biaryl coupling product in 51% yield (entry 4). It is also worthy to note that catalyst loadings could be lowered to 0.1% without decrease of yields and conversions (entry 5). These complexes proved to be particularly stable and could be stored on air several month without any appreciable depletion of their catalytic activities.

3. Conclusion

In summary, a modulable synthesis of new palladium (II) complexes bearing sterically congested azetidine ligands was developed. The use of diamine, amino-imine and amino-imidate ligands selectively led to bidendate palladium (II) complexes whose structures were confirmed by X-ray analysis. Preliminary results concerning the use of rigid *N*,*N*-bound palladium complexes as catalysts in the Suzuki cross-coupling reaction proved efficient for electron rich and electron poor aromatic bromides and chlorides. High yields and conversions were obtained using low (0.1%) catalyst loadings. The potential of these new complexes in asymmetric catalysis is under investigation.

Table 2
Suzuki coupling: aromatic substrates, Pd(II) catalysts and yields

Entry	Arylhalide	Boronic acid	Ligand type	Conditions	Biaryl	Yield (%)
1			Diamino **4**	Cat(1%), 100 °C, 6 h		77
2			Amino-imine **7**	Cat(1%), 100 °C, 5 h		85
3			Amino-imidate **11**	Cat(1%), rt, 18 h		61
4			Amino-imine **7**	Cat(2%), 100 °C, 6 h		51
5			Amino-imidate **11**	Cat(0.1%), 100 °C, 6 h		87

4. Experimental

4.1. General methods

NMR spectra were recorded on a Bruker AC spectrometer at 200 or 300 (^{1}H) and 75 (^{13}C) MHz. Low resolution mass spectra were recorded on a HP MS Eingin 5989B, in positive electrospray mode using a Branford Analytica source. Ranges of mass peaks reported here are characteristic of the isotopic dispersion in molecules containing Pd and Cl atoms. Solvents were freshly distilled prior to use. THF was distilled from sodium/benzophenone ketyl and MeOH was distilled from MgI_2. All other reagents were commercially available and were used as received. All reactions were carried under an inert atmosphere of argon unless otherwise stated. Biphenyl products listed in this paper are known in the chemical literature [19–21], except for 4-cyano-3′,4′-dimethoxy-2,2′-biphenyl (vide infra).

4.2. Synthesis of imine (*6*)

To a solution of 2-cyano azetidine **5** (1 mmol, 250 mg) in dry THF (10 mL) at 0 °C was added Phenyllithium (2 mmol) under argon. After stirring for 20 min, MeOH (10 mL) was added. After 1 h, the reaction was quenched with a saturated aqueous NH_4Cl solution (5 mL) and extracted with AcOEt (3 × 10 mL). The combined organic extracts were washed with brine, dried over magnesium sulfate, filtered and evaporated under reduced pressure. The resulting solid residue was triturated with petroleum ether, filtered and washed with small amounts of cold ether to obtain the crude imine which was used without further purification. ^{1}H NMR (200 MHz) δ: 7.6 (d, J = 7.5 Hz, 2H), 7.30 (m, 10H), 7.10 (m, 3H), 4.73 (d, J = 8.8 Hz, 1H), 3.90 (m, 2H), 3.55 (m, 3H).

4.3. General procedure for preparation of Pd(II) complexes

To a mixture of sodium tetrachloropalladate (II) (0.45 mmol, 145 mg) in freshly distilled and thoroughly degassed appropriate solvent (5 mL) was added the ligand (0.46 mmol). The red solution was allowed to stand for 4 h at room temperature. After removal of the solvent under reduced pressure or filtration of the precipitate, the solid was purified by flash chromatography on silica gel (AcOEt) to afford the expected palladium (II) complexes.

*4.3.1. Complex **3** (88%)*

IR (KBr): 3310, 3253, 3055, 3030 cm^{-1}. ^1H NMR (DMSO-d_6) δ: 8.49 (d, J = 6.5 Hz, 2H), 7.40 (m, 3H), 7.15 (m, 3H), 6.69 (d, J = 7 Hz, 2H), 5.21 (br s, 2H), 4.10 (d, J = 6.5 Hz, 1H), 3.84 (m, 1H), 3.48 (m, 2H), 2.05 (d, J = 6.2 Hz, 3H), 1.42 (s, 3H). ^{13}C NMR δ: 133.9, 133.3, 132.1, 128.9, 128.4, 128.2, 128.0, 126.3, 79.9, 71.9, 62.4, 52.0, 44.8, 17.6. Anal. Calc. for $C_{18}H_{22}Cl_2N_2Pd$: C, 48.72; H, 5.00; N, 6.31. Found: C, 48.59; H, 4.92; N, 6.21%. MS (*m*/*z*): 446–454 $[LPdClMeCN]^+$.

*4.3.2. Complex **4** (81%)*

IR (KBr): 3204, 3029 cm^{-1}: ^1H NMR (DMSO-d_6) δ: 8.73 (d, J = 7.2 Hz, 2H), 8.01 (dd, J = 2 and 6.6 Hz, 2H), 7.61 (m, 2H), 7.40 (m, 4H), 5.20 (brs, 1H), 4.55 (d, J = 13 Hz, 1H), 3.70 (m, 12H), 3.25 (d, J = 13 Hz, 1H), 3.05 (m, 2H), 2.52 (s, 3H), 1.47 (d, J = 6.8 Hz, 3H). ^{13}C NMR δ: 135.4, 133.5, 130.5(2CH), 129.5, 129.0, 128.9, 128.8, 77.5, 68.2, 59.1, 51.2, 47.0, 41.8, 16.2, 11.5. Anal. Calc. for $C_{20}H_{26}Cl_2N_2Pd$: C, 50.92; H, 5.56; N, 5.94. Found: C, 51.03; H, 5.35; N, 5.95%. MS (*m*/*z*): 472–482 $[LPdClMeCN]^+$.

*4.3.3. Complex **7** (42%)*

IR (KBr): 3416, 3030, 1637 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.30 (m, 15H), 4.40 (d, J = 8.3 Hz, 1H), 3.89 (d, J = 12.9 Hz, 2H), 3.78 (m, 1H), 3.70 (d, J = 12.7 Hz, 1H), 3.33 (m, 2H). ^{13}C NMR δ: 185.0, 135.6, 134.1, 131.8, 131.7, 129.8(2CH), 129.5, 129.3, 129.0, 128.4, 127.5, 126.5, 83.6, 66.6, 64.6, 44.1. Anal. Calc. for $C_{23}H_{22}Cl_2N_2Pd$: C, 54.84; H, 4.40; N, 5.56. Found: C, 54.61; H, 4.30; N, 5.29%. MS (*m*/*z*): 446–454 $[LPdClMeCN]^+$.

*4.3.4. Complex **9** (62%)*

IR (KBr): 3482, 3168, 3057, 1639 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 8.15 (m, 4H), 7.42 (m, 6H), 5.12 (d, J = 10 Hz, 1H), 5.03 (dd, J = 4 and 12 Hz, 1H), 4.83 (d, J = 11 Hz, 1H), 4.40 (m, 1H), 4.16 (m, 1H), 3.75 (d, J = 11 Hz, 1H), 3.20 (s, 3H). ^{13}C NMR δ: 176.1, 133.6, 132.3, 131.8, 129.6, 129.1, 129.0, 128.9, 128.7, 75.2, 65.8, 62.3, 55.1, 37.6. Anal. Calc. for $C_{18}H_{20}Cl_2N_2Pd$: C, 47.24; H, 4.40; N, 6.12. Found: C, 47.12; H, 4.46; N, 6.06%. MS (*m*/*z*): 460–468 $[LPdClMeCN]^+$.

*4.3.5. Complex **10** (72%)*

IR (KBr): 3483, 3199, 3029, 1636 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.90 (d, J = 10 Hz, 2H), 7.42 (m, 3H), 5.44 (m 1H), 4.85 (brs, 1H), 4.03 (brs, 1H), 3.48 (s, 3H), 3.12 (s, 3H), 1.57 (d, J = 6.8 Hz, 3H). ^{13}C NMR δ: 178.3, 133.6, 129.0, 128.7, 128.5, 76.1, 71.0, 56.1, 46.9, 40.6, 16.5. Anal. Calc. for $C_{13}H_{18}Cl_2N_2Pd$: C, 39.47; H, 4.59; N, 7.08. Found: C, 39.11; H, 4.46; N, 6.92%. MS (*m*/*z*): 398–405 $[LPdClMeCN]^+$.

*4.3.6. Complex **11** (58%)*

IR (KBr): 3492, 3169, 3058, 1639 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.95 (m, 2H), 7.50 (m, 3H), 7.35 (m, 3H), 7.10 (d, J = 7.7 Hz, 2H), 4.82 (m, 3H), 4.45 (d, J = 7.7 Hz, 1H), 3.72 (s, 3H), 3.55 (m 2H), 1.90 (brs, 1H). ^{13}C NMR δ: 176.4, 136.6, 131.8, 131.4, 129.8, 129.2, 129.1, 128.2, 126.7, 77.5, 65.8, 64.2, 56.8, 41.2. Anal. Calc. for $C_{18}H_{20}Cl_2N_2Pd$: C, 47.24; H, 4.40; N, 6.12. Found: C, 47.35; H, 4.62; N, 5.89%. MS (*m*/*z*): 460–468 $[LPdClMeCN]^+$.

4.4. Typical procedure for Suzuki reaction

Boronic acid (1.1 mmol), aryl halide (1 mmol) and K_2CO_3 (2.5 mmol) were successively added to the appropriate palladium (II) complex (0.01 mmol, Table 2) and the mixture was dried under vacuum for 1 h. Freshly distilled and degassed DMF (2 mL) followed by degassed water (0.2 mL) were next added. The reaction mixture was then allowed to stir at room temperature for 1 h and was heated at reflux. After completion of the reaction, water (10 mL) followed by AcOEt (5 mL) were added. The aqueous layer was separated and extracted with AcOEt (3 × 5 mL). The combined organic extracts were dried over magnesium sulfate, filtered and the solvent was removed under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the expected biaryl compounds.

4-cyano-3′,4′-dimethoxy-2,2′-biphenyl (51%). IR (KBr): 3075, 2222, 1247, 1220 cm^{-1}. ^1H NMR ($CDCl_3$) δ: 7.63 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 8.1 Hz, 2H), 7.09 (dd, J = 9.3 and 2.1 Hz, 1H), 7.01 (d, J = 2.1 Hz, 1H), 6.90 (d, J = 9.3 Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H). ^{13}C NMR δ: 149.5, 145.5, 134.2, 132.6, 131.9, 127.3, 119.8, 119.0, 111.6, 110.3, 56.0, 55.9.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2005.02.041.

References

[1] C. Agami, F. Couty, G. Evano, Tetrahedron: Asymmetry 13 (2002) 297.

[2] F. Couty, D. Prim, Tetrahedron: Asymmetry 13 (2002) 2619.
[3] C. Agami, F. Couty, N. Rabasso, Tetrahedron Lett. 43 (2002) 4633.
[4] F. Couty, F. Durrat, D. Prim, Tetrahedron Lett. 44 (2003) 5209.
[5] F. Couty, G. Evano, N. Rabasso, Tetrahedron: Asymmetry 14 (2003) 2407.
[6] A. Carlin-Sinclair, F. Couty, N. Rabasso, Synlett (2003) 726.
[7] F. Couty, G. Evano, D. Prim, Mini-Rev. Org. Chem. 1 (2004) 133.
[8] P.J. Hermsen, J.G.O Cremers, L. Thijs, B. Zwanenburg, Tetrahedron Lett. 42 (2001) 4243.
[9] M. Shi, J.K. Jiang, Tetrahedron: Asymmetry 10 (1999) 1673.
[10] J. Wilken, S. Erny, S. Wassmann, J. Martens, Tetrahedron: Asymmetry 11 (2000) 2143.
[11] S.-I. Murahashi, N. Yoshimura, T. Tsumiyama, T. Kojima, J. Am. Chem. Soc. 105 (1983) 5002.
[12] A. Marinetti, P. Hubert, J.-P. Genêt, Eur. J. Org. Chem. (2000) 1815.
[13] F. Couty, G. Evano, D. Prim, J. Marrot, Eur. J. Org. Chem. (2004) 3893.
[14] V.V. Dunina, L.G. Kuz'mina, M.Y. Kazakova, O.N. Gorunova, Y.K. Grishin, E.I. Kazakova, Eur. J. Inorg. Chem. (1999) 1029.
[15] Crystal data and structure refinements for **3** and **4**: A colorless crystal ($0.70 \times 0.45 \times 0.06$ mm for **3** and $0.46 \times 0.14 \times 0.10$ mm for **4**) was analyzed with a Siemens SMART three-circle diffractometer equipped with a CCD bidimensional detector using Mo Kα monochromatized radiation ($\lambda = 0.71073$ Å). **3** – $C_{18}H_{22}Cl_2N_2Pd$, Monoclinic, space group $P2(1)$, $a = 6.8611(1)$ Å, $b = 13.3799(3)$ Å, $c = 10.4445(2)$ Å, $\beta = 106.871(1)°$. $V = 917.55(3)$ Å^3, $Z = 2$, $\rho_{calc} = 1.606$ g cm^{-3}, μ(Mo kα) = 1.303 mm^{-1}, $F(0\,0\,0) = 448$, 6437 reflections measured of which 3894 were independent, 211 refined parameters, $R_1 = 0.0345$, $wR_2 = 0.0870$. **4** – $C_{20}H_{26}Cl_2N_2Pd$, Orthorhombic, space group $P2(1)2(1)2(1)$, $a = 10.1524(1)$ Å, $b = 14.0255(1)$ Å, $c = 14.6409(2)$ Å, $V = 2084.75(4)$ Å^3, $Z = 4$, $\rho_{calc} = 1.503$ g cm^{-3}, μ(Mo Kα) = 1.151 mm^{-1}, $F(0\,0\,0) = 960$, 14,653 reflections measured of which 5452 were independent, 230 refined parameters, $R_1 = 0.0325$, $wR_2 = 0.0674$. Data reduction were performed with the SAINT software. The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using the SADABS program based on the method of Blessing. The structures were solved by direct methods and refined by full-matrix least-squares using the SHELX-TL package. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 253195 & 253196. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk].
[16] Imines derived from nucleophilic addition on 2-cyanoazetidines cannot be purified since they are hydrolyzed to 2-acylazetidines on silica gel. See Ref. [2].
[17] R.A. Michelin, M. Mozzon, R. Bertani, Coord. Chem. Rev. 147 (1996) 299.
[18] Various amounts of homocoupling products were obtained in addition to the expected biaryl product.
[19] H. Musso, H. Pietsch, Chem. Ber. 100 (1967) 2854.
[20] C.-H. Cho, H.-S. Yun, K. Park, J. Org. Chem. 68 (2003) 3017.
[21] K. Shudo, T. Ohta, T. Okamoto, J. Am. Chem. Soc. 103 (1981) 645.