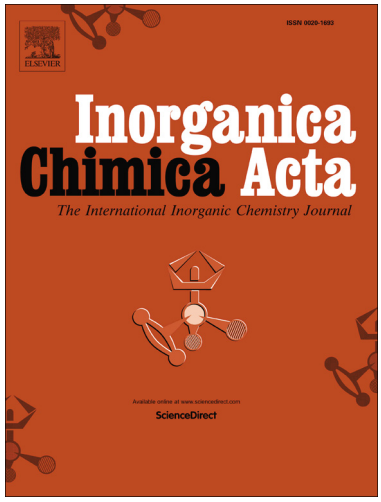


Research paper

Palladium(II) N-heterocyclic carbene complexes as catalysts for the direct arylation of pyrrole derivatives with aryl chlorides

Beyhan Yiğit, Nevin Gürbüz, Murat Yiğit, Zeynep Dağdeviren, İsmail Özdemir

PII: S0020-1693(16)31020-9
DOI: http://dx.doi.org/10.1016/j.ica.2017.05.047
Reference: ICA 17617

To appear in: *Inorganica Chimica Acta*

Received Date: 10 December 2016
Revised Date: 25 April 2017
Accepted Date: 22 May 2017

Please cite this article as: B. Yiğit, N. Gürbüz, M. Yiğit, Z. Dağdeviren, I. Özdemir, Palladium(II) N-heterocyclic carbene complexes as catalysts for the direct arylation of pyrrole derivatives with aryl chlorides, *Inorganica Chimica Acta* (2017), doi: http://dx.doi.org/10.1016/j.ica.2017.05.047

Palladium(II) N-heterocyclic carbene complexes as catalysts for the direct arylation of pyrrole derivatives with aryl chlorides

Beyhan Yiğit,[1] Nevin Gürbüz,[2,3] Murat Yiğit,[1*] Zeynep Dağdeviren,[1] İsmail Özdemir[2,3]

[1] *Department of Chemistry, Faculty of Science and Art, Adıyaman University, 02040 Adıyaman, Turkey*

[2] *Department of Chemistry, Faculty of Science and Art, Inönü University, 44280 Malatya, Turkey*

[3] *Catalysis Research and Application Center, Inönü University, 44280 Malatya, Turkey*

Abstract

Silver(I) N-heterocyclic carbene complexes were synthesized in good yields by the reactions of 1,3-dialkylperhydrobenzimidazolyum salts with silver(I) oxide and used as transmetallation reagents for the synthesis of palladium(II) N-heterocyclic carbene complexes. All of the complexes were characterized using elemental analysis, ^{1}H NMR and ^{13}C NMR spectroscopy. The catalytic activity of Pd(II)-NHC complexes in the direct arylation of pyrrole derivatives was investigated. These Pd(II)-NHC complexes showed the good catalytic performance for the direct arylation of pyrrole derivatives with readily available and inexpensive aryl chlorides. The arylation reactions regioselectively produced C2- or C5-arylation products in moderate to good yields by using 1 mol % of the palladium complex.

1. Introduction

N-Heterocyclic carbenes (NHC) have become one of the most widely used and investigated classes of ligands in organometallic chemistry, especially for the preparation of new metal-based catalysts since isolation of the first stable NHC species in 1991 by Arduengo [1, 2]. N-Heterocyclic carbenes are strong σ-donating and weak π-accepting ligands, and they form stable NHC complexes with transition metals [3-5]. A variety metal complexes of N-Heterocyclic carbenes have been synthesized and used as catalysts for many chemical transformations [6-15]. In particular, their palladium complexes have been successfully employed as highly active precatalysts for C-C and C-N coupling, and direct arylation reactions [16-21].

In recent years, the synthesis of arylated heterocycles have received considerable attention because of their biological and physical properties [22]. The arylation of heteroarenes with aryl

halides is one of the most valuable synthetic proceses for the preparation of arylated heteroarenes as it eliminates the preactivation of coupling components used in conventional methods such as Stille, Suzuki, Kumada or Negishi couplings [23-26]. In 1985, Ohta and co-workers reported that the arylation of heteroaromatics with aryl halides proceed in moderate to good yields using [$Pd(PPh_3)_4$] as the catalyst [27, 28]. Since then, the palladium-catalyzed direct arylation of heteroaryl derivatives via C-H bond activation using aryl halides has become a valuable method for the synthesis of arylated heterocycles [29-37].

Pyrroles are an important class of heterocyclic compounds because of their biological pharmacological activities [38, 39]. They have also been found in many drugs such as Atorvastatin, Fendosal and Tanaproget. Therefore, preparation of pyrrole derivatives has attracted increasing attention and several effective strategies have been developed for the synthesis of arylated pyrroles [40-50]. The direct arylation of pyrroles with aryl halides is one convenient methods for the introduction of aryl groups at C2 or C5 positions of pyrroles [51-60]. In most cases, palladium-catalyzed direct arylation of pyrroles were performed with aryl iodies and bromides [61-70]. Howewer, only a few examples on arylation of pyrroles using aryl chlorides have been reported, despite their lower cost and more easy availability [71-75]. For example, Daugulis and co-workers have reported the C2 or C5 arylation of pyrrole derivatives with various aryl chlorides using 5 mol % of $Pd(OAc)_2$ associated to 10 mol % of Cy_2P-*o*-biphenyl as the catalyst. The coupling products were obtained in 42-78% yields [71]. Despite the efficiency of palladium-N-Heterocyclic carbene systems in C-C and C-N coupling reactions, use of these complexes in direct arylation of heteroaromatics are relatively rare. So far, a few examples of (NHC)Pd-catalyzed direct arylation of nitrogen containing heterocycles have been reported. In 2006, Sames and co-workers have reported the direct arylation of pyrroles, indoles, imidazoles and imidazo[1,2-*a*]pyridines with bromobenzene and aryl iodides using palladium complexes with both phosphine and carbene ligands as catalyst [76]. Later, use of Pd-NHC complexes for the direct arylation of pyrroles, imidazoles and benzimidazoles with aryl halides was reported by the groups of Lee, Shao, Huynh and Liu [77-81]. To the best our knowledge, only one example of the direct arylation of pyrroles with aryl chlorides using N-heterocyclic carbene ligands has been reported by Doucet to date [75]. However, palladium complexses bearing a perhydrobenzimidazol-2-ylidene ligand have not yet been employed as catalyst for the direct arylation of pyrrole derivatives with aryl chlorides. Therefore, we now report the synthesis and characterization of new silver(I) and palladium(II) complexes with perhydrobenzimidazol-2-ylidene ligand and use of palladium complexes as catalysts for the direct C2- or C5-arylation of pyrrole derivatives with various aryl chlorides.

2. Experimental

2.1. Materials and methods

All reactions for the preparation of the silver(I) and palladium(II)-NHC complexes were carried out under argon in flame-dried glassware using standard Schlenk techniques. The solvents used were purified by distillation over the drying agents indicated and were transferred under Ar: THF, Et_2O (Na/K alloy), CH_2Cl_2 (P_4H_{10}), hexane, toluene (Na). All reagents were purchased from Sigma-Aldrich, Merck and Fluka. All ^{1}H- and ^{13}C-NMR were recorded in $CDCl_3$ using a Bruker AC300P FT spectrometer operating at 300.13 MHz (^{1}H) or 75.47 MHz (^{13}C). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in hertz. FT-IR spectra were recorded as KBr pellets in the range 400-4000 cm^{-1} on a Mattson 1000 spectrophotometer (wavenumbers, cm^{-1}). GC were measured by GC-FID on a Agilent 6890N gas chromatograph equipped with an HP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness. Melting points were measured in open capillary tubes with an Electrothermal-9200 melting point apparatus and uncorrected. Elemental analyses were performed at Inönü University research center.

2.1. Synthesis of perhydrobenzimidazolium salts, 1

A mixture of *N,N'*-dialkyl-1,2-diaminocyclohexane (4.2 mmol), NH_4Cl (4.2 mmol) and triethyl orthoformate (10 mL) was heated for 12 h at 110 °C. Upon cooling to room temperature, colorless crystals were obtained. These were filtered off, washed with diethyl ether (3 × 15 mL) and dried under vacuum. The crude product was recrystallized from EtOH / Et_2O.

2.2. Synthesis of silver(I)-NHC complexes, 2

A solution of the appropriate perhydrobenzimidazolium chloride (1.08 mmol), Ag_2O (0.54 mmol) and activated molecular sieves 4Å in dichloromethane (25 mL) was stirred for 24 h at room temperature in the dark conditions, covered with aluminum foil under argon. The reaction mixture was filtered through celite, and the solvent was removed under reduced pressure. The crude product was recrystallized from dichloromethane:hexane (1:2) at room temperature. The resulting white solid was isolated by filtration and dried in vacuum.

2.2.1. Chloro-1,3-bis(4-ethylbenzyl)perhydrobenzimidazol-2-ylidenesilver(I), 2a

Yield: 0.47 g, 87%; en: 151-152 °C. ^{1}H NMR ($CDCl_3$) δ: 1.18-1.24 (m, 4H, NCHCH$_2$C*H*$_2$C*H*$_2$CH$_2$CHN), 1.73-1.80 and 2.01-2.05 (m, 4H, NCHC*H*$_2$CH$_2$CH$_2$C*H*$_2$CHN), 2.88-2.99 (m, 2H, NC*H*CH$_2$CH$_2$CH$_2$CH$_2$C*H*N), 1.25 (t, 6H, *J* = 7.56 Hz, CH$_2$C$_6$H$_4$CH$_2$C*H*$_3$-4), 2.65 (q, 4H, *J* = 7.42 Hz, CH$_2$C$_6$H$_4$C*H*$_2$CH$_3$-4), 4.41, 4.62, 4.90 and 5.08 (d, 4H, *J* = 15.0 Hz, C*H*$_2$C$_6$H$_4$CH$_2$CH$_3$-4), 7.19 and 7.25 (d, 8H, *J* = 7.4 Hz, CH$_2$C$_6$*H*$_4$CH$_2$CH$_3$-4). ^{13}C NMR ($CDCl_3$) δ: 23.8 (NCHCH$_2$*C*H$_2$*C*H$_2$CH$_2$CHN), 28.5 (NCH*C*H$_2$CH$_2$CH$_2$*C*H$_2$CHN), 53.3 (N*C*HCH$_2$CH$_2$CH$_2$CH$_2$*C*HN), 15.4 (CH$_2$C$_6$H$_4$CH$_2$*C*H$_3$-4), 16.6 (CH$_2$C$_6$H$_4$*C*H$_2$CH$_3$-4), 66.4 (*C*H$_2$C$_6$H$_4$CH$_2$CH$_3$-4), 127.4, 128.3, 132.2 and 144.3 (CH$_2$*C*$_6$H$_4$CH$_2$CH$_3$-4). Anal. Calc. for $C_{25}H_{33}AgClN_2$: C, 59.46; H, 6.54; N, 5.55. Found: C,59.55; H, 6.62; N, 5.48%.

2.2.2. Chloro-1,3-bis(2,4-dimethylbenzyl)perhydrobenzimidazol-2-ylidenesilver(I), 2b

Yield: 0.46 g, 85%; en: 184-185 °C. ^{1}H NMR ($CDCl_3$) δ: 1.11-1.38 (m, 4H, NCHCH$_2$C*H*$_2$C*H*$_2$CH$_2$CHN), 1.70-1.79 and 1.86-1.90 (m, 4H, NCHC*H*$_2$CH$_2$CH$_2$C*H*$_2$CHN), 3.04-3.16 (m, 2H, NC*H*CH$_2$CH$_2$CH$_2$CH$_2$C*H*N), 2.32 and 2.33 (s, 12H, CH$_2$C$_6$H$_3$(C*H*$_3$)$_2$-2,4), 4.50, 4.72, 4.90 and 5.02 (d, 4H, *J* = 15.1 Hz, C*H*$_2$C$_6$H$_3$(CH$_3$)$_2$-2,4), 6.87-7.28 (m, 6H, CH$_2$C$_6$*H*$_3$(CH$_3$)$_2$-2,4). ^{13}C NMR ($CDCl_3$) δ: 23.4 (NCHCH$_2$*C*H$_2$*C*H$_2$CH$_2$CHN), 28.4 (NCH*C*H$_2$CH$_2$CH$_2$*C*H$_2$CHN), 48.2 (N*C*HCH$_2$CH$_2$CH$_2$CH$_2$*C*HN), 20.9 and 21.0 (CH$_2$C$_6$H$_3$(*C*H$_3$)$_2$-2,4), 67.7 (*C*H$_2$C$_6$H$_3$(CH$_3$)$_2$-2,4), 126.9, 128.7, 130.2, 131.1, 135.6 and 137.7 (CH$_2$*C*$_6$H$_3$(CH$_3$)$_2$-2,4). Anal. Calc. for $C_{25}H_{33}AgClN_2$: C, 59.46; H, 6.54; N, 5.55. Found: C,59.54; H, 6.59; N, 5.51%.

2.2.3. Chloro-1,3-bis(3,4-dimethoxybenzyl)perhydrobenzimidazol-2-ylidenesilver(I), 2c

Yield: 0.46 g, 82%; en: 186-187 °C. ^{1}H NMR ($CDCl_3$) δ: 1.08-1.28 (m, 4H, NCHCH$_2$C*H*$_2$C*H*$_2$CH$_2$CHN), 1.72-1.78 and 2.04-2.08 (m, 4H, NCHC*H*$_2$CH$_2$CH$_2$C*H*$_2$CHN), 2.90-2.93 (m, 2H, NC*H*CH$_2$CH$_2$CH$_2$CH$_2$C*H*N), 3.88 and 3.89 (s, 12H, CH$_2$C$_6$H$_3$(OC*H*$_3$)$_2$-3,4), 4.57 and 4.85 (d, 4H, *J* = 15.0 Hz, C*H*$_2$C$_6$H$_3$(OCH$_3$)$_2$-3,4), 6.82-6.88 (m, 6H, CH$_2$C$_6$*H*$_3$(OCH$_3$)$_2$-3,4). ^{13}C NMR ($CDCl_3$) δ: 23.8 (NCHCH$_2$*C*H$_2$*C*H$_2$CH$_2$CHN), 28.1 (NCH*C*H$_2$CH$_2$CH$_2$*C*H$_2$CHN), 53.3 (N*C*HCH$_2$CH$_2$CH$_2$CH$_2$*C*HN), 55.9 and 56.1 (CH$_2$C$_6$H$_3$(O*C*H$_3$)$_2$-3,4), 66.4 (*C*H$_2$C$_6$H$_3$(OCH$_3$)$_2$-3,4), 110.9, 111.2, 120.2, 127.5, 148.9 and 149.3 (CH$_2$*C*$_6$H$_3$(OCH$_3$)$_2$-3,4). Anal. Calc. for $C_{25}H_{33}AgClN_2O_4$: C, 52.77; H, 5.80; N,4.92. Found: C,52.82; H, 5.74; N, 4.96%.

2.2.4. Chloro-1,3-bis(2,4,5-trimethoxybenzyl)perhydrobenzimidazol-2-ylidenesilver(I), 2d

Yield: 0.71 g, 81%; en: 173-175 °C. ^{1}H NMR ($CDCl_3$) δ: 1.33-1.48 (m, 4H, NCHCH$_2$C*H*$_2$C*H*$_2$CH$_2$CHN), 1.68-1.72 and 1.76-1.81 (m, 4H, NCHC*H*$_2$CH$_2$CH$_2$C*H*$_2$CHN), 3.57-3.62 (m, 2H, NC*H*CH$_2$CH$_2$CH$_2$CH$_2$C*H*N), 3.81, 3.88 and 3.90 (s, 18H, CH$_2$C$_6$H$_2$(OC*H*$_3$)$_3$-2,4,5), 4.50 ve 4.82 (d, 4H, *J* = 14.7 Hz, C*H*$_2$C$_6$H$_2$(OCH$_3$)$_3$-2,4,5), 6.49 and 6.84 (s, 4H, CH$_2$C$_6$*H*$_2$(OCH$_3$)$_3$-2,4,5). ^{13}C NMR ($CDCl_3$) δ: 23.2 (NCHCH$_2$*C*H$_2$*C*H$_2$CH$_2$CHN), 28.5 (NCH*C*H$_2$CH$_2$CH$_2$*C*H$_2$CHN), 44.3 (N*C*HCH$_2$CH$_2$CH$_2$CH$_2$*C*HN), 56.2, 56.6 and 56.9 (CH$_2$C$_6$H$_2$(O*C*H$_3$)$_3$-2,4,5), 58.8 (*C*H$_2$C$_6$H$_2$(OCH$_3$)$_3$-2,4,5), 97.4, 113.7, 115.1, 143.0, 149.7 and 151.9 (CH$_2$*C*$_6$H$_2$(OCH$_3$)$_3$-2,4,5). Anal. Calc. for $C_{27}H_{37}AgClN_2O_6$: C, 51.55; H, 5.88; N,4.45. Found: C, 51.59; H, 5.84; N, 4.48%.

2.2.5. Chloro-1,3-bis(2,3,4-trimethoxybenzyl)perhydrobenzimidazol-2-ylidenesilver(I), 2e

Yield: 0.61 g, 79%; en: 160-162 °C. ^{1}H NMR ($CDCl_3$) δ: 1.15-1.36 (m, 4H, NCHCH$_2$C*H*$_2$C*H*$_2$CH$_2$CHN), 1.67-1.71 and 1.74-1.78 (m, 4H, NCHC*H*$_2$CH$_2$CH$_2$C*H*$_2$CHN), 3.80-3.84 (m, 2H, NC*H*CH$_2$CH$_2$CH$_2$CH$_2$C*H*N), 3.86, 3.87 and 3.90 (s, 18H, CH$_2$C$_6$H$_2$(OC*H*$_3$)$_3$-2,3,4), 4.42 and 4.93 (d, 4H, *J* = 15.0 Hz, C*H*$_2$C$_6$H$_2$(OCH$_3$)$_3$-2,3,4), 6.62-6.67 and 6.96-7.02 (m, 4H, CH$_2$C$_6$*H*$_2$(OCH$_3$)$_3$-2,3,4). ^{13}C NMR ($CDCl_3$) δ: 24.0 (NCHCH$_2$*C*H$_2$*C*H$_2$CH$_2$CHN), 28.3 (NCH*C*H$_2$CH$_2$CH$_2$*C*H$_2$CHN), 45.6 (N*C*HCH$_2$CH$_2$CH$_2$CH$_2$*C*HN), 56.0, 58.7 and 60.8 (CH$_2$C$_6$H$_2$(O*C*H$_3$)$_3$-2,3,4), 67.0 (*C*H$_2$C$_6$H$_2$(OCH$_3$)$_3$-2,3,4), 107.2, 121.2, 123.8, 142.1, 151.9 and 153.8 (CH$_2$*C*$_6$H$_2$(OCH$_3$)$_3$-2,3,4). Anal. Calc. for $C_{27}H_{37}AgClN_2O_6$: C, 51.55; H, 5.88; N,4.45. Found: C, 51.61; H, 5.82; N, 4.50%.

2.3. Synthesis of palladium(II)-NHC complexes, 3

A solution of required silver(I)-NHC complex (0.82 mmol) and $PdCl_2(PhCN)_2$ (0.41 mmol) in dichloromethane (20 mL) was stirred for 24 h at room temperature in the dark. Then, the resulting mixture was filtered through celite, and the solvent was removed under reduced pressure. The crude product was recrystallized from dichloromethane:diethyl ether (1:2) at room temperature. The white crystals were filtered off, washed with diethyl ether (3 x 10 mL) and dried under vacuum.

2.3.1. Bis[1,3-bis(4-ethylbenzyl)perhydrobenzimidazol-2-ylidene]dichloropalladium(II), 3a

Yield: 0.31 g, 85%, mp 255 °C. IR, υ: 1514 cm^{-1} (NCN). ^{1}H NMR ($CDCl_3$) δ: 0.98-1.16 (m, 8H, NCHCH$_2$C*H*$_2$C*H*$_2$CH$_2$CHN), 1.58-1.60 and 1.84-1.86 (m, 8H, NCHC*H*$_2$CH$_2$CH$_2$C*H*$_2$CHN), 2.88-2.90 (m, 4H, NC*H*CH$_2$CH$_2$CH$_2$CH$_2$C*H*N), 1.21 (t, 12H, *J* = 7.8 Hz, CH$_2$C$_6$H$_4$CH$_2$C*H*$_3$-4), 2.61 (q, 8H, *J* = 7.5 Hz, CH$_2$C$_6$H$_4$C*H*$_2$CH$_3$-4), 4.96, 5.08, 5.41 and 5.54 (d, 8H, *J* = 15.3 Hz, C*H*$_2$C$_6$H$_4$CH$_2$CH$_3$-4), 7.07 and 7.48 (d,

16H, *J* = 7.8 Hz, $CH_2C_6H_4CH_2CH_3$-4). ^{13}C NMR ($CDCl_3$) δ: 23.9 ($NCHCH_2CH_2CH_2CH_2CHN$), 28.5 ($NCHCH_2CH_2CH_2CH_2CHN$), 51.9 ($NCHCH_2CH_2CH_2CH_2CHN$), 15.4 ($CH_2C_6H_4CH_2CH_3$-4), 18.9 ($CH_2C_6H_4CH_2CH_3$-4), 66.3 ($CH_2C_6H_4CH_2CH_3$-4), 127.7, 128.4, 133.6 and 143.1 ($CH_2C_6H_4CH_2CH_3$-4), 203.8 (Pd-*C*). Anal. Calc. for $C_{50}H_{64}N_4PdCl_2$: C, 66.85; H, 7.13; N, 6.23. Found: C, 66.89; H, 7.17; N, 6.21%.

2.3.2. Bis[1,3-bis(2,4-dimethylbenzyl)perhydrobenzimidazol-2-ylidene]dichloropalladium(II), 3b

Yield: 0.32 g, 84%, mp 290-292 °C. IR, υ: 1497 cm^{-1} (NCN). ^1H NMR ($CDCl_3$) δ: 0.97-1.28 (m, 8H, $NCHCH_2CH_2CH_2CH_2CHN$), 1.55-1.64 (m, 8H, $NCHCH_2CH_2CH_2CH_2CHN$), 2.96-2.99 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$), 2.08 and 2.27 (s, 24H, $CH_2C_6H_3(CH_3)_2$-2,4), 4.83, 4.95, 5.13 and 5.21 (d, 8H, *J* = 16.2 Hz, $CH_2C_6H_3(CH_3)_2$-2,4), 6.8 (s, 4H, $CH_2C_6H_3(CH_3)_2$-2,4), 6.97 and 7.45 (d, 8H, *J* = 7.5 Hz and, *J* = 7.8 Hz, $CH_2C_6H_3(CH_3)_2$-2,4). ^{13}C NMR ($CDCl_3$) δ: 23.9 ($NCHCH_2CH_2CH_2CH_2CHN$), 28.2 ($NCHCH_2CH_2CH_2CH_2CHN$), 48.7 ($NCHCH_2CH_2CH_2CH_2CHN$), 19.3 and 20.9 ($CH_2C_6H_3(CH_3)_2$-2,4), 67.4 ($CH_2C_6H_3(CH_3)_2$-2,4), 126.6, 128.3, 130.5, 131.6, 135.0 and 136.1 ($CH_2C_6H_3(CH_3)_2$-2,4), 205.2 (Pd-*C*). Anal. Calc. for $C_{50}H_{64}N_4PdCl_2$: C, 66.85; H, 7.13; N, 6.23. Found: C, 66.87; H, 7.18; N, 6.25%.

2.3.3. Bis[1,3-bis(3,4-dimethoxybenzyl)perhydrobenzimidazol-2-ylidene]dichloropalladium(II), 3c

Yield: 0.53 g, 79%, mp 249-250 °C. IR, υ: 1513 cm^{-1} (NCN). ^1H NMR ($CDCl_3$) δ: 0.98-1.26 (m, 8H, $NCHCH_2CH_2CH_2CH_2CHN$), 1.59-1.62 and 1.86-1.90 (m, 8H, $NCHCH_2CH_2CH_2CH_2CHN$), 2.82-2.88 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$), 3.84 and 3.87 (s, 24H, $CH_2C_6H_3(OCH_3)_2$-3,4), 4.87, 5.02, 5.44 and 5.65 (d, 8H, *J* = 15.0 Hz, $CH_2C_6H_3(OCH_3)_2$-3,4), 6.65-6.92 and 7.28-7.43 (m, 12H, $CH_2C_6H_3(OCH_3)_2$-3,4). ^{13}C NMR ($CDCl_3$) δ: 23.9 ($NCHCH_2CH_2CH_2CH_2CHN$), 28.1 ($NCHCH_2CH_2CH_2CH_2CHN$), 51.9 ($NCHCH_2CH_2CH_2CH_2CHN$), 55.7 and 56.5 ($CH_2C_6H_3(OCH_3)_2$-3,4), 66.1 ($CH_2C_6H_3(OCH_3)_2$-3,4), 110.4, 111.4, 120.2, 128.9, 148.3 and 149.2 ($CH_2C_6H_3(OCH_3)_2$-3,4), 203.3 (Pd-*C*). Anal. Calc. for $C_{50}H_{64}N_4O_8PdCl_2$: C, 58.50; H, 6.24; N, 5.46. Found: C, 58.55; H, 6.27; N, 5.49%.

2.3.4. Bis[1,3-bis(2,4,5-trimethoxybenzyl)perhydrobenzimidazol-2-ylidene]dichloropalladium(II), 3d

Yield: 0.35 g, 75%, mp 258-260 °C. IR, υ: 1511 cm^{-1} (NCN). ^1H NMR ($CDCl_3$) δ: 0.98-1.16 (m, 8H, $NCHCH_2CH_2CH_2CH_2CHN$), 1.47-1.58 and 1.81-1.85 (m, 8H, $NCHCH_2CH_2CH_2CH_2CHN$), 3.45-3.46 (m, 4H, $NCHCH_2CH_2CH_2CH_2CHN$), 3.72, 3.84 and 3.85 (s, 36H, $CH_2C_6H_2(OCH_3)_3$-2,4,5), 5.03 and 5.53 (d, 8H, *J* = 15.3 Hz, $CH_2C_6H_2(OCH_3)_3$-2,4,5), 6.39 and 7.55 (s, 8H, $CH_2C_6H_2(OCH_3)_3$-2,4,5). ^{13}C NMR ($CDCl_3$) δ:

23.6 (NCHCH$_2$*C*H$_2$*C*H$_2$CH$_2$CHN), 28.0 (NCH*C*H$_2$CH$_2$CH$_2$*C*H$_2$CHN), 43.9 (N*C*HCH$_2$CH$_2$CH$_2$CH$_2$*C*HN), 56.0, 56.6 and 56.8 (CH$_2$C$_6$H$_2$(O*C*H$_3$)$_3$-2,4,5), 58.6 (*C*H$_2$C$_6$H$_2$(OCH$_3$)$_3$-2,4,5), 97.1, 113.8, 117.0, 143.5, 148.5 and 150.6 (CH$_2$*C*$_6$H$_2$(OCH$_3$)$_3$-2,4,5), 204.1 (Pd-C). Anal. Calc. for $C_{54}H_{72}N_4O_{12}PdCl_2$: C, 56.56; H, 6.28; N, 4.88. Found: C, 56.59; H, 6.31; N, 4.92%.

2.3.5. Bis[1,3-bis(2,3,4-trimethoxybenzyl)perhydrobenzimidazol-2-ylidene]dichloropalladium(II), 3e

Yield: 0.48 g, 73%, mp 224-225 °C. IR, υ: 1495 cm^{-1} (NCN). ^{1}H NMR ($CDCl_3$) δ: 0.89-1.13 (m, 8H, NCHCH$_2$C*H*$_2$C*H*$_2$CH$_2$CHN), 1.57-1.66 and 1.87-1.89 (m, 8H, NCHC*H*$_2$CH$_2$CH$_2$C*H*$_2$CHN), 3.50-3.55 (m, 4H, NC*H*CH$_2$CH$_2$CH$_2$CH$_2$C*H*N), 3.79, 3.81 and 3.82 (s, 36H, CH$_2$C$_6$H$_2$(OC*H*$_3$)$_3$-2,3,4), 4.87 and 5.65 (d, 8H, *J* = 15.3 Hz, C*H*$_2$C$_6$H$_2$(OCH$_3$)$_3$-2,3,4), 6.59-6.66 and 7.65-7.70 (m, 8H, CH$_2$C$_6$*H*$_2$(OCH$_3$)$_3$-2,3,4). ^{13}C NMR ($CDCl_3$) δ: 24.0 (NCHCH$_2$*C*H$_2$*C*H$_2$CH$_2$CHN), 27.9 (NCH*C*H$_2$CH$_2$CH$_2$*C*H$_2$CHN), 44.6 (N*C*HCH$_2$CH$_2$CH$_2$CH$_2$*C*HN), 55.8, 58.7 and 60.7 (CH$_2$C$_6$H$_2$(O*C*H$_3$)$_3$-2,3,4), 66.8 (*C*H$_2$C$_6$H$_2$(OCH$_3$)$_3$-2,3,4), 107.6, 122.7, 125.0, 141.5, 151.3 and 152.7 (CH$_2$*C*$_6$H$_2$(OCH$_3$)$_3$-2,3,4), 204.8 (Pd-*C*). Anal. Calc. for $C_{54}H_{72}N_4O_{12}PdCl_2$: C, 56.56; H, 6.28; N, 4.88. Found: C, 56.60; H, 6.33; N, 4.91%.

2. 4. General procedure for the direct arylations

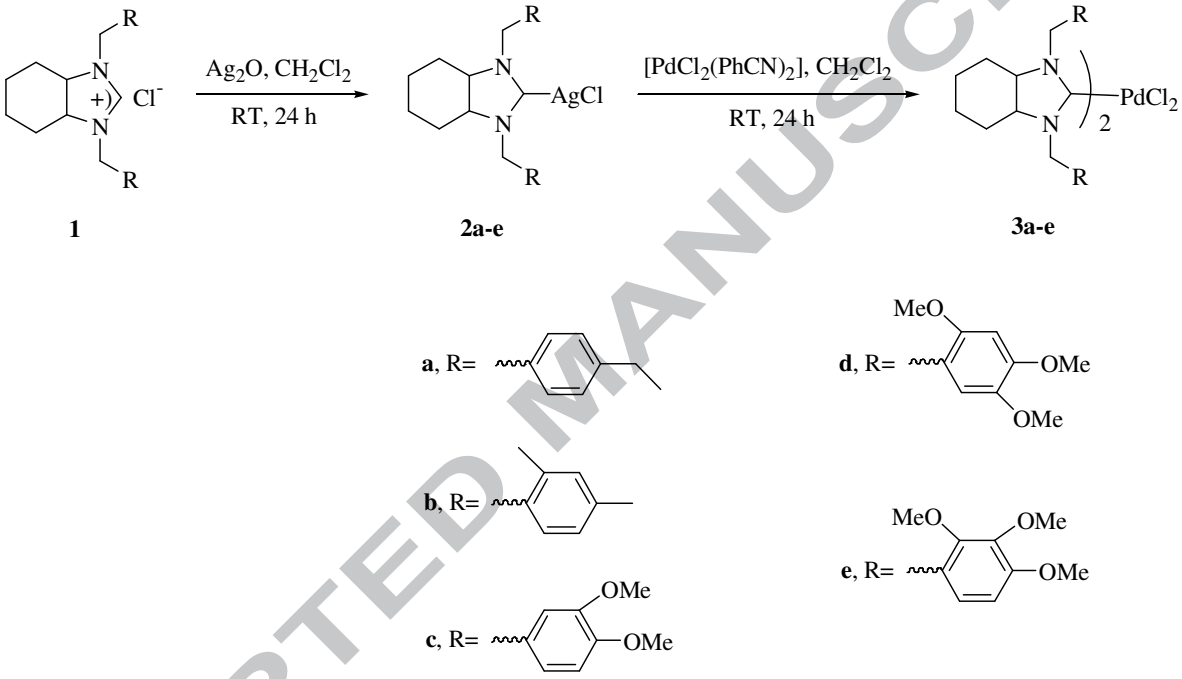
The heteroaryl derivative (2 mmol), aryl chloride (1 mmol) and KOAc (2 mmol) were introduced in a Schlenk tube equipped with a magnetic stirring bar. Pd complex (0.01 mmol) and DMAc (2 mL) were added and the Schlenk tube was purged several times with argon. The Schlenk tube was placed in a preheated oil bath at 150 °C, the reaction mixture was stirred for 20 h. Then, the reaction mixture was analysed by gas chromatography to determine the conversion of the aryl chloride. The solvent was removed by heating the reaction vessel under vacuum and the residue was charged directly onto a silica-gel column. The products were eluted by using an appropriate ratio of diethyl ether and pentane.

3. Results and discussion

3.1. Synthesis of Ag(I) and Pd(II)-NHC complexes

The symmetrical 1,3-dialkylperhydrobenzimidazolium salts as NHC precursors were obtained in high yields from the cyclization of the *N,N'*-dialkylcyclohexan-1,2-diamines with triethyl orthoformate and ammonium chloride [82, 83]. Treatment of the perhydrobenzimidazolium salts

with Ag_2O in dichloromethane at room temperature in the dark afforded the expected silver complexes Ag(I)-NHC **2a-e** (Scheme 1). The silver-NHC complexes **2a-e** were obtained in high yields as white solids, soluble in halogenated solvents. The formation of Ag(I)-NHC complexes **2a-e** were confirmed by the disappearance of the resonance signals of perhydrobenzimidazolium C2 proton in the ^{1}H NMR spectra and C2 carbon in ^{13}C NMR spectra. In the **2a-e** complexes, the resonances for carbene carbon were not detected, which has also been mentioned in the literature and given as a reason for the fluxional behavior of the NHC complexes [84, 85].



Scheme 1. The synthesis of palladium(II)-NHC complexes.

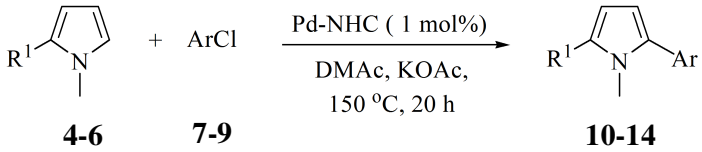
Several methods are available for the synthesis of Pd(II)-NHC complexes, which have been described in the literature. Among them, a facile and more general method is the generation of a silver(I)-NHC complex, followed by transfer of the carbene unit to palladium metal. This reaction has successfully been applied to a variety of metals, including ruthenium, rhodium, iridium, gold and nickel [86]. The palladium(II)-NHC complexes **3a-e** were prepared by treating $PdCl_2(PhCN)_2$ with silver(I)-NHC complexes as a carbene transfer reagent in dichloromethane at room temperature (Scheme 1). An instant precipitation of AgCl indicated successfully the carbene transfer onto

palladium to form palladium(II)-NHC complexes **3a-e.** These complexes were obtained in high yields and appeared to be stable both in solution and in solid states against air, light and moisture. The new complexes were characterized by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis techniques, which support the proposed structures. They show a characteristic $\upsilon_{(NCN)}$ band at 1514, 1497, 1513, 1511 and 1495 cm^{-1} for **3a**, **3b, 3c, 3d** and **3e** respectively. NMR analyses of the complexes showed that the N-heterocyclic carbene ligands transferred from silver complexes to palladium center. The ^{13}C NMR spectra of the Pd-NHC complexes exhibited a singlet resonance of the C2 carbon at 203.8, 205.2, 203.3, 204.1 and 204.8 ppm respectively for **3a-e**. This is consistent with reported values for $[PdCl_2(NHC)_2]$ complexes. The results obtained from the elemental analysis of the complexes **2a-e** and **3a-e** are in agreement with the theoretical requirements of their structures. The geometry of these complexes was not defined, as suitable single crystals of these complexes for X-ray diffraction studies could not be obtained.

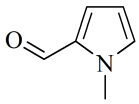
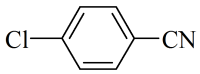
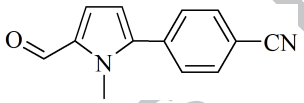
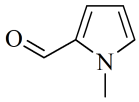
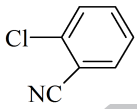
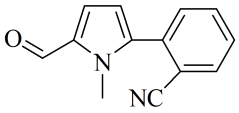
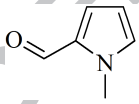
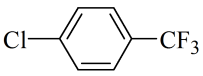
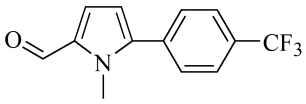
3.2. Catalytic studies: Direct arylation of pyrroles with ary chlorides using 3a-e as catalyst

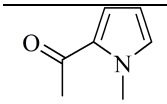
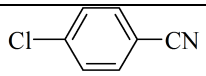
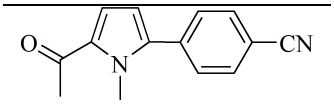
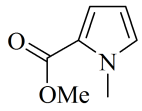
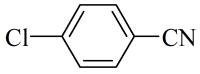
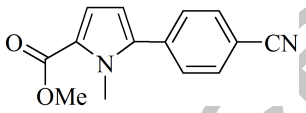
The arylation of pyrroles is an important field of research in organic synthesis due to their biological and physical properties, and it provides a cost-effective and environmentally attractive procedure for the preparation of arylpyrroles. The first examples of direct arylation of pyrroles by using aryl chlorides as the coupling partners and Pd-NHC complexes as the catalyst was reported by Doucet and co-workers [75]. They found that the treatment of electron-deficient aryl chlorides with pyrroles derivatives in the presence of 1mol% a Pd-NHC complex gave the corresponding arylation products in moderate to good yields. Based on previous results, in this study, N,N-dimethylacetamide (DMAc) and potassium acetate (KOAc) were selected as the solvent and base. The catalytic reactions were performed at 150 ^{o}C for 20 h under argon in the presence of complexes **3a-e**. Under these reaction conditions, pyrrole derivatives were reacted with aryl chlorides bearing electron-withdrawing groups at the *para* or *ortho* position to produce the arylated products in moderate to good yields (Tables 1, 2). A wide range of functional groups on both pyrroles and aryl chlorides such as aldehyde, acetyl, ester, cyano and trifluoromethyl were well tolerated during the course of this reaction.

Table 1. Direct arylation of pyrrole derivatives with aryl chlorides.[a]



4-6 **7-9** **10-14**

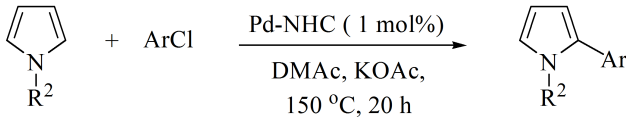
Entry	Pyrrole	ArCl	Pd-NHC	Product	Yield(%)[b]
1			**3a**		77
2			**3b**		50
3	**4**	**7**	**3c**	**10**	47
4			**3d**		60
5			**3e**		62
6			**3a**		74
7			**3b**		76
8	**4**	**8**	**3c**	**11**	80
9			**3d**		68
10			**3e**		75
11			**3a**		81
12			**3b**		65
13	**4**	**9**	**3c**	**12**	68
14			**3d**		51
15			**3e**		46
16			**3a**		96
17			**3b**		93
18			**3c**		93

19	 **5**	 **7**	**3d**	 **13**	93
20			**3e**		92
21	 **6**	 **7**	**3a**	 **14**	94
22			**3b**		91
23			**3c**		90
24			**3d**		89
25			**3e**		72

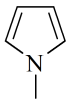
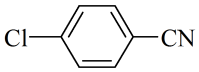
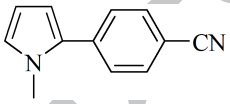
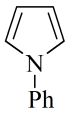
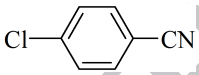
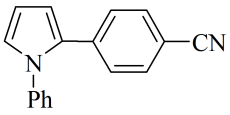
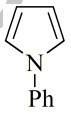
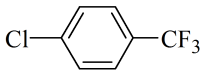
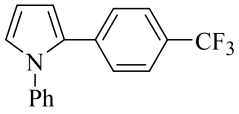
[a]Reaction conditions: Pd-NHC (0.01 mmol), aryl chloride (1 mmol), pyrroles (2 mmol), KOAc (2 mmol), DMAc (3 mL), 20 h, 150 ^{o}C. [b]GC yields using dodecane as internal standard in an average of two runs and stucture of compound was checked by NMR.

Initially, the reaction of 1-methylpyrrole-2-carboxaldehyde (**4**) with 4-chlorobenzonitrile (**7**) was examined in the presence of complexes **3a-e** as catalysts and KOAc as base in N,N-dimethylacetamide at 150 ^{o}C. Regioselective arylation on only the C5 position of 1-methylpyrrole-2-carboxaldehyde (**4**) was observed, because the hydrogen at the 2- and 5-position of pyrrole is more reactive than that of 3- and 4-position [69], and good yields of the coupling product (**10**) were obtained with complexes **3a** and **3e** (Table 1, entries 1 and 5). Then, 2-chlorobenzonitrile (**8**) and 4-(trifluoromethyl)chlorobenzene (**9**) were reacted with 1-methylpyrrole-2-carboxaldehyde (**4**) in the presence of complexes **3a-e** (Table 1, entries 6-15). When the 2-chlorobenzonitrile (**8**) was used as the coupling partners, the best yields (76% and 80%) were achieved with catalysts **3b** and **3c** to give **11**. 4-(Trifluoromethyl)chlorobenzene (**9**) also gave the product **12** in good yields (Table 1, entries 11-15). Next, we examined the reactions of 4-chlorobenzonitrile (**7**) with 2-acetyl-1-methylpyrrole (**5**) and methyl 1-methylpyrrole-2-carboxylate (**6**) under the same reaction conditions (Table **1**). The reaction of 2-acetyl-1-methylpyrrole (**5**) with 4-chlorobenzonitrile (**7**) gave the expected product **13** in 92-96% yields (Table 1, entries 16-20). Methyl 1-methylpyrrole-2-carboxylate (**6**) also reacts with 4-chlorobenzonitrile (**7**) to give **14** in 72-94% yields with complexes **3a-e** (Table 1, entries 21-25).

Table 2. Direct arylation of 1-methylpyrrole and 1-phenylpyrrole with aryl chlorides.[a]



15, 16 **7, 9** **17-19**

Entry	Pyrrole	ArCl	Pd-NHC	Product	Yield(%)[b]
1			**3a**		91
2			**3b**		94
3	**15**	**7**	**3c**	**17**	92
4			**3d**		94
5			**3e**		97
6			**3a**		83
7			**3b**		76
8	**16**	**7**	**3c**	**18**	79
9			**3d**		80
10			**3e**		94
11			**3a**		18
12			**3b**		52
13	**16**	**9**	**3c**	**19**	44
14			**3d**		35
15			**3e**		28

[a]Reaction conditions: Pd-NHC (0.01 mmol), aryl chloride (1 mmol), pyrroles (2 mmol), KOAc (2 mmol), DMAc (3 mL), 20 h, 150 °C. [b]GC yields using dodecane as internal standard in an average of two runs and stucture of compound was checked by NMR.

Finally, we also investigated the arylation of the 1-methylpyrrole (**15**) and 1-phenylpyrrole (**16**) with aryl chlorides. Under the same reaction conditions, only C2-arylated products were obtained in good yields (Table 2, entries 1-15), bisarylated products were not isolated. 1-Methylpyrrole was efficiently arylated with 4-chlorobenzonitrile in 91-97% yields, but slightly lower yields (76-94%) were observed for 1-phenylpyrrole (Table 2, entries 6-10). Among the tested complexes, palladium complexes (**3c-e**) with methoxy substituents on benzyl group exhibited high catalytic activities compared to that bearing methyl or ethyl substituents (**3a, b**) for the arylation of pyrrole derivatives and high yields were obtained with complexs **3c**.

4. Conclusion

In summary, silver(I) and palladium(II) NHC complexes were successfully synthesized and characterized by elemental analysis and spectroscopic methods. The catalytic activities of the palladium complexes were investigated in direct C2 or C5 arylation of pyrrole derivatives in the presence of potassium acetate. Although aryl chlorides possesed poor reactivity, arylation of pyrrole derivatives proceeded efficiently with Pd(II)-NHC complexes, and all complexes exhibited high catalytic activities in these reactions. Furthermore, the catalyst loading was lower, compared to previous reports. This method is cost-effective and environmentally attractive for the preparation of arylpyrroles because it is use inexpensive aryl chlorides and KOAc as the coupling partners and the base, reduces the number of reaction steps and produces less waste. It should be noted that these arylation reactions are very selective, such that in all cases, only the C2 or C5-arylated products were formed; the 3- or 4-arylated products were not detected by GC analysis of the reaction mixtures.

Acknowledgements

We thank the Adıyaman University Research Fund (FEFMAP/2015-0004) and İnönü University Research Fund (İÜBAP: 2015/41-Güdümlü) for financial support of this work

References

[1] A. J. Arduengo III, R. L. Harlow, M. Kline, J. Am. Chem. Soc. 113 (1991) 361.

[2] W. A. Herrmann, Angew. Chem. 114 (2002) 1342.

[3] L. Jafarpour, S. P. Nolan, Adv. Organomet. Chem. 46 (2000) 181.

[4] E. Peris, R. H. Crabtree, Coord. Chem. Rev. 248 (2004) 2239.

[5] P. De Fremont, N. Marion, S. P. Nolan, Coord. Chem. Rev. 253 (2009) 862.

[6] J. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaughnessy, L. M. Alcazar-Roman, J. Org. Chem. 64 (1999) 5575.

[7] A. C. Hillier, G. A. Grasa, M. S. Viciu, H. M. Lee, C. Yang, S. P. Nolan, J. Organomet. Chem. 653 (2002) 69.

[8] M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, Tetrahedron Lett. 40 (1999) 2247.

[9] G. Occhipinti, H. R. Bjorsvik, V. R. Jensen, J. Am. Chem. Soc. 128 (2006) 6952.

[10] A. Zaph, M. Beller, Chem. Eur. J. 7 (2001) 2908.

[11] S. K. Yen, L. L. Koh, F. H. Hahn, H. V. Huynh, T. S. A. Hor, Organometallics 35 (2006) 5105.

[12] M. Yiğit, B. Yiğit, İ. Özdemir, E. Çetinkaya, B. Çetinkaya, Appl. Organometal. Chem. 20 (2006) 322.

[13] M. C. Jahnke, M. Hussain, F. Hupka, T. Pape, S. Ali, F. E. Hahn, K. J. Cavell, Tetrahedron 65 (2009) 909.

[14] M. G. Gardiner, W. A. Herrmann, C. P. Reisinger, J. Schwarz, M. Spiegler, J. Organomet. Chem. 572 (1999) 239.

[15] J. C. C. Chen, I. J. B. Lin, Organometallics 19 (2000) 5113.

[16] A. C. Hillier, G. A. Grasa, M. S. Viciu, H. M. Lee, C. Yang, S. P. Nolan, J. Organomet. Chem. 653 (2002) 69.

[17] F. Li, J. J. Hu, L. L. Koh, T. S. A. Hor, Dalton. Trans. 39 (2010) 5231.

[18] F. E. Hahn, M. C. Jahnke, V. Gomez-Benitez, D. Morales-Morales, T. Pape, Organometallics 24 (2005) 6458.

[19] J. F. Hartwig, M. Kawatsura, S. I. Hauck, K. H. Shaughnessy, L. M. Alcazar-Roman, J. Org. Chem. 64 (1999) 5575.

[20] İ. Özdemir, Y. Gök, Ö. Özeroğlu, M. Kaloğlu, H. Doucet, C. Bruneau, Eur. J. Inorg.

Chem. 12 (2010) 1798.

[21] E.Ö. Karaca, N. Gürbüz, İ. Özdemir, H. Doucet, O. Şahin, O. Büyükgüngör, B. Çetinkaya, Organometallics 34 (2015) 2487.

[22] J.J. Li, G.W. Gribble, Palladium in Heterocyclic Chemistry, Pergamon, Amsterdam, The Netherlands, 2000.

[23] C. Wolf, R. Lerebours, J. Org. Chem. 68 (2003) 7077.

[24] M. Allegretti, A. Arcadi, F. Marinelli, L. Nicolini, Synlett (2001) 609.

[25] M.G. Organ, M. Abdel-Hadi, S. Avola, N. Hadei, J. Nasielski, C.J. O'Brien, C. Valente, Chem. Eur. J. 13 (2006) 150.

[26] J.-M. L'Helgoual'ch, A. Seggio, F. Chevallier, M. Yonehara, E. Jeanneau, M. Uchiyama, F. Mongin, J. Org. Chem. 73 (2008) 177.

[27] Y. Akita, A. Inoue, K. Yamamoto, A. Ohta, Heterocycles 23 (1985) 2327.

[28] A. Ohta, Y. Akita, T. Ohkuwa, M. Chiba, R. Fukunaga, A. Miyafuji, T. Nakata, N. Tani, Y. Aoyagi, Heterocycles 31 (1990) 1951.

[29] I.V. Seregin, V. Gevoryan, Chem. Soc. Rev. 36 (2007) 1173.

[30] M. Parisien, D. Valette, K. Fagnou, J. Org. Chem. 70 (2005) 7578.

[31] M. Yiğit, B. Yiğit, Y. Gök, Inorg. Chim. Acta. 453 (2016) 23.

[32] B. Yiğit, M. Yiğit, Z. Dağdeviren, İ. Özdemir, Transition Met. Chem. 41 (2016) 751.

[33] S. Akkoç, Y. Gök, İ. Ö. İlhan, V. Kayser, Beilstein J. Org. Chem. 12 (2016) 81.

[34] S. Akkoç, Y. Gök, Inorg. Chim. Acta. 429 (2015) 34.

[35] A. R. Martin, A. Chartoire, A.M.Z. Slavin, S.P. Nolan, Beilstein J. Org. Chem. 8 (2012) 1637.

[36] M. Brahim, H. B. Ammar, J. –F. Soule, H. Doucet, Beilstein J. Org. Chem. 12 (2016)

2197.

[37] S. Yanagisava, T. Sudo, R. Noyori, K. Itami, J. Am. Chem. Soc. 128 (2006) 11748.

[38] E. C. Taylor, R. A. Jones, Pyrroles, Wiley: New York, 1990.

[39] F. Bellina, R. Rossi, Tetrahedron 62 (2006) 7213.

[40] A. R. Katritzky, J. Li, M. F. Gordeev, Synthesis (1994) 93.

[41] Z. Xu, X. Lu, Tetrahedron Lett. 38 (1997) 3461.

[42] T. J. Donohoe, N. J. Race, J. F. Bower, C. K. A. Callens, Org. Lett. 12 (2010) 4094.

[43] D. J. Gorin, N. R. Davis, F. D. Toste, J. Am. Chem. Soc. 127 (2005) 11260.

[44] Q. Zheng, R. Hua, J. Jiang, L. Zhang, Tetrahedron 70 (2014) 8252.

[45] S. V. Kumar, B. Saraiah, G. Parameshwarappa, H. Ila, G. K. Verma, J. Org. Chem. 79 (2014) 7961.

[46] R. Zhu, L. Xing, Y. Liu, F. Deng, X. Wang, Y. Hu, J. Organomet. Chem. 693 (2008) 3897.

[47] J. Oyamada, T. Kitamura, Tetrahedron 65 (2009) 3842.

[48] C. A. Figueria, P. S. Lopes, P. T. Gomes, Tetrahedron 71 (2015) 4362.

[49] M. Krzeszewski, D. T. Gryko, J. Org. Chem. 80 (2015) 2893.

[50] G. Sun, S. Ren, X. Zhu, M. Huang, Y. Wan, Org. Lett. 18 (2016) 544.

[51] F. Bellina, R. Rossi, Tetrahedron 65 (2009) 10269.

[52] C. B. Bheeter, L. Chen, J. –F. Soule, H. Doucet, Catal, Sci. Technol. 6 (2016) 2005.

[53] H. –C. Ma, X. –Z. Jiang, J. Org. Chem. 72 (2007) 8943.

[54] J. A. Smith, S. Ng, J. White, Org. Biomol. Chem. 4 (2006) 2477.

[55] J. C. Antilla, J. M. Baskin, T. E. Barder, S. L. Buchwald, J. Org. Chem. 69 (2004) 5578.

[56] J. Nemeth, N. Debreczeni, M. Balint, Catal. Lett. 145 (2015) 1113.

[57] H. Bekolo, Can. J. Chem. 85 (2007) 42.

[58] T. Satoh, M. Miura, Chem. Lett. 36 (2007) 200.

[59] L. Wang, Z. Li, X. Qu, W. Peng, Chin. J. Chem. 33 (2015) 1015.

[60] P. Bizouard, C. Testa, V. A. Zinovyeva, J. Roger, J. –C. Hierso, Synlett 27 (2016) 1227.

[61] D. T. Gryko, O. Vakuliuk, D. Gryko, B. Koszarna, J. Org. Chem. 74 (2009) 9517.

[62] O. Vakuliuk, D. T. Gryko, Eur. J. Org. Chem. (2011) 2854.

[63] O. Vakuliuk, B. Koszarna, D. T. Gryko, Synthesis 17 (2011) 2833.

[64] K. Ueda, K. Amaike, R. M. Maceiczyk, K. Itami, J. Yamaguchi, J. Am. Chem. Soc. 136 (2014) 13226.

[65]. B. S. Cho, H. J. Bae, Y. K. Chung, J. Org. Chem. 80 (2015) 5302.

[66] R. Hosseinzadeh, M. Tajbakhsh, M. Alikarami, M. Mohadjerani, J. Heterocyclic Chem. 45 (2008) 1815.

[67] C. B. Bheeter, J. K. Bera, H. Doucet, Tetrahedron Letters 53 (2012) 509.

[68] Y. Xu, L. Zhao, Y. Li, H. Doucet, Adv. Synth. Catal. 355 (2013) 1423.

[69] L. Zhao, C. Bruneau, H. Doucet, ChemCatChem. 5 (2013) 255.

[70] Y. Fall, H. Doucet, M. Santelli, ChemSusChem. 2 (2009) 153.

[71] E. T. Nadres, A. Lazareva, O. Daugulis, J. Org. Chem. 76 (2011) 471.

[72] D. Roy, S. Mom, S. Royer, D. Lucas, J. -C. Hierso, H. Doucet, ACS Catal. 2 (2012) 1033.

[73] D. Roy, S. Mom, M. Beauperin, H. Doucet, J. -C. Hierso, Angew. Chem. Int. Ed. 40 (2010) 6650.

[74] L. -C. Campeau, P. Thansandote, Keith Fagnou, Org. Lett. 7 (2005) 1857.

[75] İ. Özdemir, N. Gürbüz, N. Kaloğlu, Ö. Doğan, M. Kaloğlu, C. Bruneau, H. Doucet,

Beilstein J. Org. Chem. 9 (2013) 303.

[76] B. B. Toure, B. S. Lane, D. Sames, Org. Lett. 8 (2006) 1979.

[77] P. V. Kumar, W. -S. Lin, J. -S. Shen, D. Nandi, H. M. Lee, Organometallics 30 (2011) 5160.

[78] D. Ghosh, H. M. Lee, Org. Lett. 14 (2012) 5534.

[79] Z. -S. Gu, W. -X. Chen, L. -X. Shao, J. Org. Chem. 79 (2014) 5806.

[80] S. Guo, H. V. Huynh, Organometallics 33 (2014) 2004.

[81] X. -X. He, Y. Li, B. -B. Ma, Z. Ke, F. -S. Liu, Organometallics 35 (2016) 2655.

[82] M. Yigit, Molecules 14 (2009) 2032.

[83] M. Murat, G. Bayam, B. Yiğit, İ. Özdemir, Heterocycles 87 (2013) 897.

[84] D. J. Nielsen, K. J. Cavell, B. M. Skelton, A. H. White, Inorg. Chim. Acta. 352 (2003) 143.

[85] B. Yiğit, Y. Gök, İ. Özdemir, S. Günal, J. Coord. Chem. 65(2012) 371.

[86] I. J. B. Lin, C. S. Vasam, Coord. Chem. Rev. 251 (2007) 642.

- The new Ag(I) and Pd(II)-NHC complexes were prepared.
- These complexes were characterized by elemental analysis, IR, ^{1}H, ^{13}C NMR pectroscopy.
- The new Pd^{II} complexes were tested as catalysts in direct arylation of pyrrole derivatives.