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Methoxyaryl substituted palladium bis-NHC complexes – Synthesis and electronic effects

Dominik Munz [a], Christoph Allolio [a], Katrin Döring [b], Alexander Poethig [a,1], Thomas Doert [c,1], Heinrich Lang [b], Thomas Straßner [a,*]

[a] Physikalische Organische Chemie, Technische Universität Dresden, Bergstrasse 66, 01062 Dresden, Germany
[b] Institut für Chemie, Professur Anorganische Chemie, Technische Universität Chemnitz, Straße der Nationen 62, 09111 Chemnitz, Germany
[c] Anorganische Chemie, Technische Universität Dresden, Bergstrasse 66, 01062 Dresden, Germany

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ABSTRACT

A series of methoxyphenyl substituted chelated bis-*N*-heterocyclic carbene palladium(II) complexes has been synthesized and characterized by cyclovoltammetry, spectroscopy (NMR, IR), solid state structures and investigated by quantum chemical calculations. The results confirm that a methoxy functionality in *para* position at the aryl substituent enhances the donor properties of the ligand compared to a methoxy group in *ortho* or *meta* position.

1. Introduction

The discovery of a stable *N*-heterocyclic carbene (NHC) by Arduengo [1] in 1991 led to a new and rapidly advancing area of research. A large number of publications on NHC metal complexes has been published and reviewed in recent years [2–9]. Properties of NHC complexes include a high thermal stability as the ligands generally do not dissociate easily from the metal. There is also evidence indicating that carbene ligands are stronger π-donors than many phosphine based systems [10,11]. The catalytic activity of organometallic complexes is often linked to the donor properties of the ligands [12,13] and we therefore have been interested in finding ways to tune them. While in the past NHC ligands were assumed to be pure σ-donors, we believe that significant backbonding via the π-orbitals of the heterocycle has an effect on the donor properties [14,15].

Chelated palladium bis-NHC complexes have been shown to possess especially high stability against oxidizing and acidic conditions, making them suitable e.g. for the C–H activation of methane in trifluoroacetic acid [16,17]. They have also found wide application in *C,C* coupling reactions [18–24]. Recently, we were able to show that the catalytic activity of aryl substituted, chelated imidazoline-2-ylidene palladium and platinum complexes can be tuned by electron donating and withdrawing groups in *para* position on the aryl ring. Examples include the Heck reaction and the C–H activation of methane [25,26]. Scheme 1 shows the three different methoxyphenyl substituted bis-NHC palladium(II) complexes studied in this work.

The *para* methoxy substituted complex **3** was found to be a considerably more efficient catalyst than other *para* functionalized aryl substituted bis-NHC palladium complexes (*i.e.*, the analogous *para* bromophenyl or *para* nitrophenyl complexes) in the Heck reaction of aryl halogenides with styrene [25]. In the CH activation of methane we observed that electron donating substituted aryl bis-NHC complexes like for example **3** lead to lower turnover numbers than electron withdrawing substituted ones [27]. Therefore we decided to study the effect of the position of the activating methoxy groups in detail and synthesized new complexes where we varied their position on the aryl ring in order to further elucidate its effect on the electronic properties.

We expected differences for the resulting complexes based on resonance considerations as well as Hammett σ-constants: a methoxy group in *meta* position should not be able to act as a donor through its mesomeric effect and should instead become a net acceptor through the inductive effect of the electronegative oxygen. This is reflected by a change of sign in the corresponding

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[*] Corresponding author. Tel.: +4935146338571.
E-mail address: thomas.strassner@chemie.tu-dresden.de (T. Straßner).
[1] X-ray analysis.

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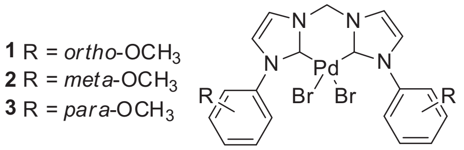


Scheme 1. Methoxyphenyl substituted chelated bis-NHC palladium(II) complexes.

Hammett parameter [28] and it should be possible to measure the effect, if π-donation from the aryl substituent has an influence on the metal.

In order to characterize the electronic effects of the ligands we employed different methods: cyclovoltammetry (CV), DFT calculations, NMR and IR spectroscopy. The direct experimental quantification of donor properties and other electronic effects by CV has already been proven to be a valuable tool for the characterization of NHC complexes [29–32] and it was employed in the determination of the Lever electronic parameter (LEP) [33] for a wide variety of common ligands. Also DFT calculations are widely applied for the estimation of donor effects [34,35]. Another way to determine the donor strength has been introduced by Tolman (TEP) [36]. In order to study the effect of the position of the methoxy group, we synthesized the new complexes **1** and **2**, which are isomers of the known complex **3** [25].

2. Experimental

2.1. Material and methods

Solvents of at least 99.5% purity were used throughout this study. All other chemicals were obtained from common suppliers and used without further purification. THF and DMF were dried by standard procedures prior to use. 3,3′-Bis(4-methoxyphenyl)-[(1,1′-diimidazolin-2,2′-diylidene)methane] palladium(II) dibromide **3** was prepared according to published protocols [25]. Imidazoles **4** and **5** have been synthesized following a modified procedure which is described in detail in the Supplementary material.

^1H and ^{13}C NMR spectra were recorded with a Bruker AC 300 and Bruker DRX 500 P spectrometer. The spectra were referenced internally to the resonances of the solvent (^1H, ^{13}C). Elemental analyses were performed by the microanalytical laboratory of our institute using a EuroVektor Euro EA-3000 Elemental Analyzer. Melting and decomposition points were determined with a Wagner&Munz PolyTherm A melting point apparatus and are uncorrected. IR spectra were recorded with a Thermo Nicolet Avatar 360 E.S.P. (ATR) using a resolution of 1 cm^{-1}, 64 scans and an aperture of 100.0. The CV experiments were conducted in a custom made glass cell under an argon atmosphere using a Radiometer Analytical PGZ 100 VoltaLab potentiostat. The experiments were conducted at 25 °C using a platinum work and counter electrode. As reference electrode a non-aqueous calomel electrode was used. Acetonitrile with a concentration of 0.1 M TBA-PF_6 was employed as the solvent. The solvent and TBA-PF_6 were carefully dried prior to use. All organometallic compounds were added to achieve a concentration of $c = 0.1$ mmol. All cyclovoltammograms were measured at a scan rate of 100 mV s^{-1}. Positive mode ESI-MS spectra for the synthesized compounds were recorded on a Bruker Esquire MS with Ion Trap Detector on samples dissolved in NH_4OAc buffered methanol.

2.2. Synthesis of the complexes with bromide counterions

2.2.1. 3,3′-Bis(2-methoxyphenyl)-[(1,1′-diimidazolin-2,2′-diylidene) methane] palladium(II) dibromide (*1*)

200 mg (0.38 mmol) of 3,3′-Bis-(2-methoxyphenyl)-1,1′-methylene-diimidazolium-dibromide (**7**) and 80 mg (0.36 mmol) $[Pd(OAc)_2]$ were stirred in 5 mL DMSO at ambient temperature. After 2 h the formation of a white precipitate was observed. After 12 h the solution was heated at 60 °C for 4 h. At the end of the reaction the solvent was removed under reduced pressure and the resulting solid was washed twice with 3 mL of MeOH, MeCN and CH_2Cl_2. Volatiles were removed in vacuo to yield an off-white solid (0.17 g, 69% based on $[Pd(OAc)_2]$).

^1H NMR (500.13 MHz, DMSO-d_6, $T = 323$ K): δ 7.78 (s, 2H, NC*H*); 7.68–7.42 (m, 6H, Ar and NC*H*); 7.33–7.08 (m, 4H, Ar); 6.50 (s, 2H, NCH_2N); 3.83 (s, 6H, CH_3) ppm. ^{13}C NMR (125.77 MHz, DMSO-d_6, $T = 353$ K): δ 153.25 (i-*C* of Ar); 129.71 (*C*H); 128.06 (*C*H); 124.37 (*C*H); 120.70 (*C*H); 119.71 (*C*H); 112.68 (*C*H); 62.59 (CH_2); 54.83 (CH_3) ppm; carbene carbon atom signal not detected due to poor solubility. Mp. > 300 °C. MS (ESI): $m/z = 525.1$ $[PdL(OAc)]^+$, 547.0 $[PdLBr]^+$. *Anal.* Calc. for $C_{21}H_{20}N_4Br_2O_2Pd\cdot0.8\ C_2H_6SO$: C, 39.39; H, 3.63; N, 8.13; S, 3.72. Found: C, 39.51; H, 3.51; N, 8.31; S, 3.75%.

2.2.2. 3,3′-Bis(3-methoxyphenyl)-[(1,1′-diimidazolin-2,2′-diylidene) methane] palladium(II) dibromide (*2*)

200 mg (0.38 mmol) of 3,3′-Bis-(3-methoxyphenyl)-1,1′-methylene-diimidazolium-dibromide (**6**) and 80 mg (0.36 mmol) $[Pd(OAc)_2]$ were heated in 5 mL DMSO from ambient temperature to 60 °C for 18 h. After 2 h the formation of a white precipitate was observed. At the end of the reaction the solvent was removed under reduced pressure and the resulting white solid was washed twice with 2 mL of MeOH, THF and CH_2Cl_2. Volatiles were removed in vacuo to yield an off-white solid (0.20 g, 85% based on $[Pd(OAc)_2]$).

^1H NMR (500.13 MHz, DMSO-d_6, $T = 323$ K): δ 7.91–7.69 (m, 4H, NC*H*); 7.66–7.23 (m, 6H, Ar); 7.06 (s, 2H, Ar); 6.53 (s, 2H, NCH_2N); 3.93 (s, 6H, CH_3) ppm. ^{13}C NMR (150.91 MHz, DMSO-d_6, 300 K): δ 159.02 (i-*C* of Ar); 140.12 (i-*C* of Ar); 129.04 (*C*H of Ar); 122.43 (N*C*H), 121.87 (N*C*H), 116.64 (*C*H of Ar); 113.54 (*C*H of Ar); 110.83 (*C*H of Ar); 62.96 (CH_2); 55.11 (CH_3) ppm; carbene carbon signal not detected due to poor solubility. Mp. > 300 °C. MS (ESI): $m/z = 525.1$ $[PdL(OAc)]^+$. *Anal.* Calc. for $C_{21}H_{20}N_4Br_2O_2Pd\cdot0.35$ DMSO: C, 39.85; H, 3.41; N, 8.57; S, 1.72. Found: C, 39.56; H, 3.09; N, 8.56; S, 1.68%.

2.3. Synthesis of imidazolium salts

2.3.1. 3,3′-Bis(2-methoxyphenyl)-[(1,1′-diimidazolium)methane] dibromide (*6*)

1.30 g (7.5 mmol) 1-(2-Methoxyphenyl)-imidazole (**4**) and 0.28 mL (0.70 g, 4.0 mmol) dibromomethane were dissolved in 5 mL of THF. The reaction mixture was heated in a pressure tube at 130 °C for 48 h. The brown precipitate was filtrated and washed with 10 mL of cold THF. The resulting brown solid was stirred for six days in 20 mL of EtOAc. The remaining crude product was filtrated and washed with THF until it was colorless. The resulting hygroscopic solid was dried in vacuo (0.70 g, 36% based on **4**).

^1H NMR (300.13 MHz, DMSO-d_6, $T = 295$ K): δ 10.12 (s, 2H, NC*H*N); 8.39 (s, 2H, NC*H*); 8.23 (s, 2H, NC*H*); 7.68 (*d*, $J = 7.4$ Hz, 2H, Ar); 7.63 (t, $J = 8.2$ Hz, 2H, Ar); 7.42 (d, $J = 8.2$ Hz, 2H, C*H* of Ar); 7.22 (t, 2H, $J = 7.4$ Hz, C*H* of Ar); 6.97 (*s*, 2H, NCH_2N); 3.92 (s, 6H, CH_3) ppm. ^{13}C NMR (74.475 MHz, DMSO-d_6, $T = 295$ K): δ 151.74 (i-*C* of Ar); 138.73 (N*C*H); 131.89 (*C*H of Ar); 125.03 (*C*H of Ar); 124.06 (*C*H of Ar); 122.96 (i-*C* of Ar); 121.92 (*C*H of Ar); 113.37 (*C*H of Ar); 107.97 (*C*H of Ar); 58.37 (CH_2), 56.40 (CH_3) ppm. Mp. 235.9 °C (decomp.). *Anal.* Calc. for $C_{21}H_{20}N_4O_2$: C, 48.30; H, 4.25; N, 10.73. Found: C, 48.06; H, 4.04; N, 10.67%.

2.3.2. 3,3′-Bis(3-methoxyphenyl)-[(1,1′-diimidazolium)methane] dibromide (*7*)

1.80 g (10.3 mmol) of 1-(3-Methoxyphenyl)-imidazole (**5**) were dissolved in 5 mL THF containing 0.36 mL (0.89 g, 5.2 mmol) dibromomethane. The reaction mixture was heated in a pressure tube at 130 °C for 24 h. A white precipitate was formed. The crude product was filtrated, washed with 10 mL of THF and the remaining solvent was removed in vacuo to yield a colorless hygroscopic solid (1.9 g, 71% based on **5**).

^{1}H NMR (300.13 MHz, DMSO-d_6, T = 295 K): δ 10.28 (s, 2H, NC*H*N); 8.46 (t, J = 2.0 Hz,2H, C*H* of Ar); 8.33 (*s*, 2H, NC*H*); 7.62 (t, 2H, J = 8.3 Hz, C*H* of Ar); 7.44 (*s*, 1H, NC*H*); 7.38 (*d*, 2H J = 8.3 Hz, C*H* of Ar); 7.21 (*dd*, 2H, J_1 = 8.3 Hz, J_2 = 2.0 Hz, C*H* of Ar); 6.85 (s, 2H, NCH_2N); 3.88 (s, 6H, CH_3) ppm. ^{13}C NMR (74.475 MHz, DMSO-d_6, T = 295 K): δ 160.37 (i-*C* of Ar, 8); 137.40 (N*C*HN, 1); 135.42 (i-*C* of Ar); 131.36 (C of Ar); 122.96 (N*C*H); 121.66 (N*C*H); 115.70 (*C*H of Ar); 113.71 (*C*H of Ar); 107.97 (*C*H of Ar); 55.94 (*C*H_2), 49.23 (*C*H_3) ppm. Mp. 323.2 °C (decomp.). *Anal.* Calc. for $C_{21}H_{20}N_4O_2$: C, 48.30; H, 4.25; N, 10.73. Found: C, 48.66; H, 4.07; N, 10.91%.

2.4. Synthesis of complexes with hexafluorophosphate counterions

2.4.1. 3,3′-Bis(2-methoxyphenyl)-[(1,1′-diimidazolin-2,2′-diylidene) methane](bis-acetonitrile) palladium(II) hexafluorophosphate (*8*)

60 mg (0.10 mmol) of 3,3′-Bis(2-methoxyphenyl)-[(1,1′-diimidazolin-2,2′-diylidene)methane] palladium(II) dibromide (**1**) and 53 mg of [AgPF_6] (0.21 mmol) were suspended in 2 mL of MeCN and stirred at 60 °C for 9 h. The solution was filtrated over Celite and the solvent was removed subsequently. The crude product was washed twice with 2 mL H_2O, dried in vacuo, recrystallized by condensing Et_2O into a saturated solution in MeCN and filtrated. Volatiles were removed in vacuo to yield a colorless crystalline solid (35 mg, 44% based on **1**).

^{1}H NMR (300.15 MHz, DMSO-d_6, T = 295 K): δ 7.89 (d, J = 1.9 Hz, 2H, NC*H*); 7.88 (d, J = 7.6 Hz 2H, Ar); 7.72 (d, J = 1.9 Hz, 2H, NC*H*); 7.60 (t, J = 7.6 Hz, 2H, Ar); 7.36 (d, J = 7.6 Hz, 2H, Ar); 7.25 (t, J = 7.6 Hz, 2H, Ar); 6.61 (d, J = 26.6 Hz, 2H, NCH_2N); 3.89 (s, 6H, CH_3); 2.07 (s, 6H, NCCH_3) ppm. ^{13}C NMR (74.475 MHz, DMSO-d_6, T = 295 K): δ 153.15 (i-*C* of Ar, 12); 147.35 (i-*C*, Carbene); 130.92 (*C*H of Ar); 128.06 (*C*H of Ar); 126.57 (i-*C* of Ar); 125.12 (N*C*H); 122.29 (N*C*H); 120.52 (*C*H of Ar); 117.99 (CH_3*C*N); 112.73 (*C*H of Ar); 56.01 (*C*H_3); 1.06 (*C*H_3CN) ppm. ^{19}F NMR (282.40 MHz, DMSO-d_6, T = 295 K): δ −70.14 (d, J = 711.2 Hz) ppm. Mp. 155.3 °C (decomp.). MS (ESI): m/z = 525.1 [PdL(OAc)]$^+$. *Anal.* Calc. for $C_{25}H_{26}F_{12}N_6O_2P_2Pd$: C, 35.79; H, 3.12; N, 10.02. Found: C, 35.84; H, 2.91; N, 9.66%.

An ORTEP plot of **8** in the solid state is shown in the Supplementary material (together with the corresponding crystallographic details). Thermal ellipsoids are drawn at 50% probability level showing two independent molecules of **8** in the asymmetric unit.

2.4.2. 3,3′-Bis(3-methoxyphenyl)-[(1,1′-diimidazolin-2,2′-diylidene) methane] (bis-acetonitrile) palladium(II) hexafluorophosphate (*9*)

100 mg (0.16 mmol) 3,3′-Bis(3-methoxyphenyl)-[(1,1′-diimidazolin-2,2′-diylidene)methane] palladium(II) dibromide (**2**) and 89 mg [AgPF_6] (0.35 mmol) were suspended in 3 mL MeCN and stirred at 60 °C for 9 h. The solution was filtrated over Celite and the solvent was removed subsequently. The crude product was washed twice with 2 mL H_2O, dried in vacuo, recrystallized by condensing Et_2O into a saturated solution in MeCN and filtrated. Volatiles were removed in vacuo to yield a colorless crystalline solid (45 mg, 34% based on **2**).

^{1}H NMR (300.15 MHz, DMSO-d_6, T = 295 K): δ 7.99 (d, J = 2.0 Hz, NC*H*); 7.92 (d, J = 2.0 Hz, 2H, NC*H*); 7.72 (t, J = 1.9 Hz, 2H, Ar); 7.57 (t, J = 7.9 Hz, 2H, Ar); 7.50 (d, J = 7.9 Hz, 2H, Ar); 7.20 (dd, J = 1.9, J = 7.9 Hz, 2H, Ar); 6.66 (dd, J = 13.0, J = 46.6 Hz, 2H, NCH_2N); 3.96 (s, 6H, CH_3); 2.07 (s, 6H, NCCH_3) ppm. ^{13}C NMR (74.475 MHz, DMSO-d_6, T = 295 K): δ 159.80 (i-*C* of Ar); 146.56 (i-*C*, Carbene); 138.96 (i-*C* of Ar, 5); 130.34 (*C*H of Ar); 123.64 (N*C*H); 123.15 (N*C*H); 118.06 (*C*H of Ar); 116.68 (*C*H of Ar); 114.98 (CH_3*C*N); 110.95 (*C*H of Ar); 62.68 (*C*H_2); 55.74 (*C*H_3); 1.10 (*C*H_3CN) ppm. ^{19}F NMR (282.40 MHz, DMSO-d_6, T = 295 K): δ −70.14 (d, J = 711.2 Hz) ppm. Mp. 229.6 °C (decomp.). MS (ESI): m/z = 525.1 [PdL(OAc)]$^+$. *Anal.* Calc. for $C_{25}H_{26}F_{12}N_6O_2P_2Pd$: C, 35.79; H, 3.12; N, 10.02. Found: C, 35.60; H, 2.96; N, 9.94%.

2.4.3. 3,3′-Bis(4-methoxyphenyl)-[(1,1′-diimidazolin-2,2′-diylidene) methane] (bis-acetonitrile) palladium(II) hexafluorophosphate (*10*)

80 mg (0.12 mmol) 3,3′-Bis(4-methoxyphenyl)-[(1,1′-diimidazolin-2,2′-diylidene)methane] palladium(II) dibromide (**3**) and 71 mg [AgPF_6] (0.28 mmol) were suspended in 3 mL MeCN and stirred at 60 °C for 9 h. The solution was filtrated over Celite and the solvent was removed subsequently. The crude product was washed twice with 2 mL H_2O, dried in vacuo, recrystallized by condensing Et_2O into a saturated solution in MeCN and filtrated. Volatiles were removed in vacuo to yield a colorless crystalline solid (25 mg, 23% based on **3**).

^{1}H NMR (300.15 MHz, DMSO-d_6, T = 295 K): δ 7.95 (d, J = 2.0 Hz, 2H, NC*H*); 7.89 (d, J = 8.8 Hz, 4H, Ar); 7.85 (d, J = 2.0 Hz, 2H, NC*H*); 7.28 (d, J = 8.8 Hz, 4H, Ar); 6.62 (dd, J = 12.9 Hz, J = 50.4 Hz, 2H, NCH_2N); 3.88 (s, 6H, CH_3); 2.07 (s, 6H, NCCH_3) ppm. ^{13}C NMR (74.475 MHz, DMSO-d_6, T = 295 K): δ 159.71 (i-*C* of Ar); 146.32 (i-*C*, Carbene); 130.91 (i-*C* of Ar); 126.11 (*C*H of Ar); 123.73 (N*C*H); 123.03 (N*C*H); 118.02 (CH_3*C*N); 114.61 (*C*H of Ar); 62.56 (*C*H_2); 55.74 (*C*H_3); 1.10 (*C*H_3CN) ppm. ^{19}F NMR (282.40 MHz, DMSO-d_6, T = 295 K): δ −70.12 (d, J = 711.7 Hz) ppm. Mp. 223.9 °C (decomp.). MS (ESI): m/z = 525.1 [PdL(OAc)]$^+$. *Anal.* Calc. for $C_{25}H_{26}F_{12}N_6O_2P_2Pd$: C, 35.79; H, 3.12; N, 10.02. Found: C, 36.07; H, 3.05; N, 10.09%.

An ORTEP plot of **10** in the solid state is shown in the Supplementary material (together with the corresponding crystallographic details). Thermal ellipsoids are drawn at 30% probability level showing two independent molecules of **10** in the asymmetric unit.

2.5. Structure determination of compound *9* (*8*, *10* see Supp. material)

For solid state structure analysis preliminary examination and data collection were carried out on a NONIUS κ-CCD device with an Oxford Cryosystems cooling system at the window of a sealed fine-focus X-ray tube with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The reflections were integrated, raw data were corrected for Lorentz and polarization effects and, arising from the scaling procedure, for latent decay. An absorption correction was applied using SADABS [37]. After merging, the independent reflections were all used to refine the structure. The structure was solved by a combination of direct methods [38] and difference Fourier synthesis [39]. All non-hydrogen atom positions were refined with anisotropic displacement parameters. All hydrogen atoms were placed in calculated positions and afterwards refined using the SHELXL-97 riding model. Full-matrix least-squares refinements were carried out by minimizing $\Sigma w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/err <0.001. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography [40]. All calculations were performed with the programs COLLECT [41], DIRAX [42], EVALCCD [43], SIR97 [38], SADABS [37], the SHELXL-97 package [39,44] and ORTEP-III [45]. The crystallografic details are given in Table 1.

2.6. Computational details

All optimizations have been performed with the GAUSSIAN 03 program package [46]. They were carried out using the BP86 gradient corrected density functional [47,48] and the 6-31G(d) basis set [49,50] for all non-metal atoms. The BP86 functional was chosen as it is known to reproduce experimental vibrational

Table 1
Crystallographic details.

Complex	**9**
Formula	$C_{25}H_{26}F_{12}N_6O_2P_2Pd$
a (Å)	8.6060(13)
b (Å)	18.876(3)
c (Å)	20.4680(15)
α (°)	90.000
β (°)	106.675(8)
γ (°)	90.000
V (Å^3)	3185.1(7)
Z	4
Formula weight	838.86
Space group (No.)	$P\,2_1/c$(14)
T (°C)	−75(2)
λ (Å)	0.71073
D_{calcd} (g cm^{-3})	1.75
µ (mm^{-1})	0.789
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0378, wR_2 = 0.0882
R indices (all data)	R_1 = 0.0537 wR_2 = 0.0968

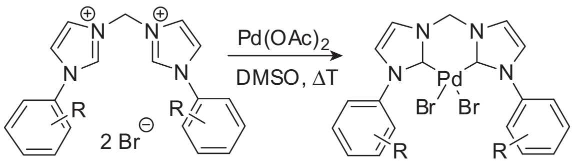
frequencies very well [51]. All structures were fully optimized without constraints. Harmonic force constants were calculated for all geometries in order to verify them as ground states. In all cases palladium was described using a decontracted Hay-Wadt($n+1$) ECP and basis set [52,53].

3. Results and discussion

3.1. Synthesis of the complexes with bromide counterions

The *para* methoxy substituted complex **3** was prepared according to literature procedures [25], whereas the new complexes **1** and **2** have been synthesized as described in Schemes 2 and 3. The arylimidazoles **4** and **5** were prepared by an Ullmann type coupling of imidazole and methoxyphenyl iodide in the presence of catalytic amounts of copper(I) oxide and phenanthroline. Copper(I) catalyzed arylhalogenide–*N*-heterocycle couplings have found widespread use in organic synthesis, as they provide straightforward access to *N*-arylated imidazoles in usually high yields [54,55]. Phenanthroline and Cu_2O are a frequently employed ligand/copper(I) precatalyst combination [56,57]. The bisimidazolium salts **6** and **7** could be obtained in moderate yields by heating two equivalents of the corresponding methoxyphenyl imidazoles **4** and **5** in THF with one equivalent of CH_2Br_2 in an ACE pressure tube (Scheme 2) following standard procedures [25].

Palladium complexes **1** and **2** were prepared in good yields from the corresponding bisimidazolium bromide salts **6** and **7** using [$Pd(OAc)_2$] as metal precursor in wet DMSO using an optimized temperature program (Scheme 3).



6, 7

1 R = *ortho*-OCH_3 (69%)
2 R = *meta*-OCH_3 (85%)

Scheme 3. Synthesis of complexes **1** and **2**.

During the preparation of complexes **1**–**3** the crude product readily precipitated from hot DMSO as a colorless solid. The very low solubility of **1**–**3** in all examined organic solvents may be a limiting factor for the catalytic performance in the Heck reaction [25] and is an obstacle for the spectroscopic analysis, but is has also been reported for similar bis-NHC ligands incorporating aryl rings [21]. To get ^{13}C and ^{1}H NMR spectra of **1**–**3** with a decent signal/noise ratio we had to heat the probe to 70 °C. Therefore we decided that for the evaluation of the donor properties we needed to "design" better soluble species – the dicationic acetonitrile complexes. Cationic palladium complexes have very recently drawn considerable attention, as they have often been shown to lead to significantly milder reaction conditions than complexes with stronger coordinating counterions like halogenides or trifluoroacetates. Examples include the Suzuki-Miyaura coupling or CH-activation strategies [58,59].

3.2. Syntheses of the complexes with hexafluorophosphate counterions

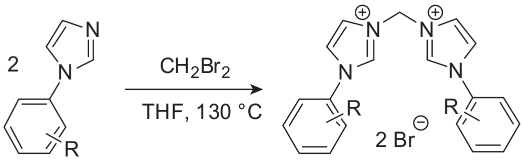
The dicationic acetonitrile complexes with hexafluorophosphate counteranions (**8**–**10**) (Scheme 4) were synthesized by silver mediated counterion exchange starting from **1**–**3**. By heating them with [$AgPF_6$] in acetonitrile the bromides could be replaced by the non-coordinating PF_6^- ions.

These complexes were purified by filtration of their acetonitrile solution over Celite, washed with water and subsequently recrystallized from acetonitrile/diethyl ether, thereby removing the remaining silver salts. This halogen exchange reaction follows a slightly modified previously established procedure [60].

Unlike complexes **1**–**3** the dicationic species **8**–**10** can easily be dissolved in polar aprotic solvents, like acetonitrile or DMSO. In addition, the C≡N vibrations of the coordinated acetonitrile, which are isolobal [61] to the C≡O vibrations normally used to measure the TEP, can be unambiguously identified in their IR spectra.

The non-coordinating counterion PF_6^- can be used as part of the auxiliary electrolyte in cyclovoltammetry. It also has a favorable electrochemical window and was previously used for CV studies of palladium NHC complexes [62].

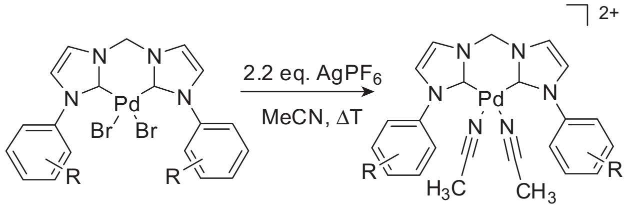
Single crystals suitable for the determination of the solid state structures of complexes **8**–**10** were obtained by slow diffusion of



4 , 5 **6 , 7**

4 R = *ortho*-OCH_3 (**6**: 36%)
5 R = *meta*-OCH_3 (**7**: 71%)

Scheme 2. Synthesis of the new bisimidazolium salts **6** and **7**.



8 R = *ortho*-OCH_3
9 R = *meta*-OCH_3
10 R = *para*-OCH_3

2 $PF_6^{\ominus}$

Scheme 4. Synthesis of the dicationic complexes **8**–**10**.

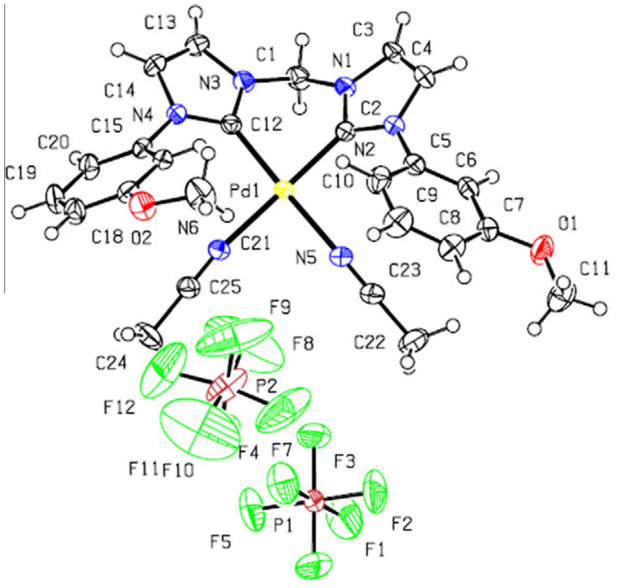


Fig. 1. ORTEP plot of **9** in the solid state, thermal ellipsoids drawn at 50% probability level. Selected distances (Å) and angles (°): Pd1–C2 1.970(3); Pd1–C12 1.977(3); Pd1–N5 2.052(3); Pd1–N6 2.058(3); N6–C25 1.122(4); N5–C23 1.128(5); C2–Pd1–N6 179.49(13); C12–Pd1–N5 174.43(13); N5–Pd1–N6 87.29 (11); Pd1–C2–N1–C1 −0.2(4); Pd1–C12–N3–C1 −2.2(4); C2–N2–C5–C10 −53.8(5); C12–N4–C15–C16 55.8(4).

diethyl ether into a saturated solution of the respective complexes in acetonitrile. However, only the data set obtained from a single crystal of **9** (Fig. 1) was of suitable quality for the deposition (see Supp. material).

3.3. Conformational behavior of complexes *1–3* and *8–10*

The solid state structure reveals the characteristic boat conformation of the 6-membered metallacycle (Pd–C–N–CH_2–N–C), which previously also had been reported for **3** [25]. ^1H NMR spectroscopy indicates a change of the molecular conformation, which can be observed as it is relatively slow on the NMR timescale. The ambient temperature ^1H NMR spectra of the dicationic complexes **8–10** show an AB spin system for the diastereotopic hydrogen atoms of the bridging methylene group. NMR spectra at higher temperatures reveal that the system converges into a singlet, corresponding to a ring flip of the central 6-membered metallacycle. This ring flip has already been studied in detail by us and others with related methylene bridged biscarbene complexes [25,63].

Quantum chemical calculations (BP86/6-31G(d)) were performed on the three cationic complexes and the results were compared with data from the solid state structures **8–10**. Bond lengths and angles calculated by gas phase DFT calculations are in good agreement with the values derived from the diffraction data. Only for the bonds of the weakly coordinated acetonitrile ligands, a maximum deviation of 0.04 Å was found. The methoxy groups at the phenyl ring point away from the central metallacycle in the solid state structures (Fig. 1) as well as in the gas phase calculations. The observation of two independent molecules in the unit cell of **8** and **9**, differing slightly in the dihedral angle between the phenyl rings and the heterocycle indicate a certain conformational flexibility. The BP86 calculated minimum structures of complexes **8–10** exhibit an overall difference for that dihedral angle of up to 9° (complex **8**: 51°, **9**: 60°, **10**: 56°). This small difference will not influence the electronic communication between the rings significantly.

3.4. Cyclovoltammetry

As cyclovoltammetric experiments by Amatore and Jutand have shown for chelated phosphine complexes [64] and monodentate NHC complexes [29], CV can be a valuable tool for mechanistic investigations of catalytic cycles. Plenio used CV in order to study the electronic properties of *para* phenyl substituted monodentate NHC complexes [65–68]. He reasoned that through space π-interactions might be important in certain cases and furthermore obtained an excellent correlation of *para* Hammett substituent constants and reduction potentials. We very recently became also aware of two other electrochemical studies involving chelated bis-NHC palladium(II) complexes [31,32].

This study focuses on the examination of position-dependent (*ortho*, *meta*, *para*) electronic effects of methoxyphenyl substituted bis-NHC ligands. By the direct preparation of the dicationic complexes **8–10** and by using [*n*-Bu_4N][PF_6] as supporting electrolyte we eliminated the problem of having different counterions which might have different effects on the reaction.

A reduction peak was found for complexes **8–10** as shown in Fig. 2. It corresponds to an irreversible two electron reduction of palladium(II) to palladium(0) according to the results obtained by Jutand et al. [29,70], van Huynh's group [62] and Tubaro [31]. We were able to find a significant difference in the reduction potentials for the three complexes (Table 2).

The reduction potentials clearly show that the *para* substituted bis-NHC complex **10** (Table 2) needs a stronger negative potential to be reduced than **8** and **9**, which corresponds to a more electron-rich palladium center. As the observed reduction potentials are irreversible they clearly involve follow-up processes besides the transfer of electrons to the metal and π-system.

In order to put into perspective the overall donor properties of the chelated methoxyaryl biscarbene palladium complexes they were compared to the corresponding halogenide substituted complex [$PdCl_2(MeCN)_2$]. For [$PdCl_2(MeCN)_2$] a reduction potential of −0.71 V was obtained.

3.5. NMR spectroscopy

A characteristic resonance is the carbene carbon signal in the ^{13}C NMR spectra, which has successfully been used to characterize

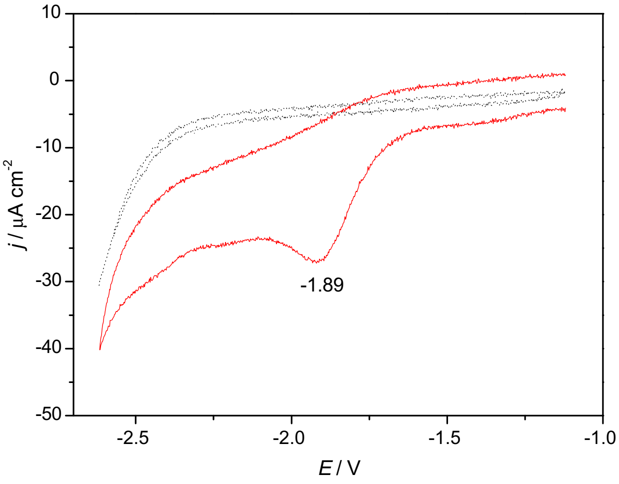


Fig. 2. Cyclovoltammogram of **10** in acetonitrile in the presence of [*n*-Bu_4N][PF_6] (*c* = 0.10 M) at 25 °C under argon at a scan rate of 100 mV s^{-1}. Potentials are referenced to the $FeCp_2/FeCp_2^+$ redox couple as internal standard ($FeCp_2 = Fe(\eta^5\text{-}C_5H_5)_2$, $E_0 = 0.00$ V)[69]. The 1st scan is shown in red, the dotted line shows the control experiment, the supporting electrolyte solution only. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Reduction potentials of complexes **8–10.** Values are given in Volt.

Complex	E_{red} (V)
8 (*ortho*)	−1.69
9 (*meta*)	−1.72
10 (*para*)	−1.89

the donor strength of different monodentate NHC ligands [71]. We were able to obtain ^{13}C NMR spectra of dicationic complexes **8–10** in DMSO at ambient temperature and could assign ^{13}C shifts for the carbene carbon atoms (Table 3).

The *para* methoxy substituted complex **10** has the lowest chemical shift δ. Although the differences in the ^{13}C chemical shift values are rather low, our results agree well with results recently published by Tubaro et al. [31], who also obtained an upfield shift for electron-rich methylene bridged palladium(II) bisimidazolinylidene complexes compared to those with less electron density. The observed ordering of the three complexes **8–10** predicts the *para* substituted biscarbene complex **10** in accordance to the CV results to be the most electron-rich bis-NHC complex.

3.6. IR spectroscopy

Donor effects of ligands are often quantified by Tolman's Electronic Parameter (TEP) [36], which is the IR absorption band corresponding to the carbonyl $C\equiv O$ vibration of complexes of the type $Ni(CO)_3L$ (L = monodentate 2-electron ligand) and has been transferred to CO complexes of the same coordination geometry [9]. As the $R{-}C\equiv N$ fragment can be described as an isolobal analogon [61] to the $C\equiv O$ bond of carbon monoxide, we expected additional information about the donor effects by the IR vibrations of the $C\equiv N$ bonds of the coordinated acetonitrile molecules [72,73]. Therefore, the solid state ATR-FTIR spectra of **8–10** were measured and compared to the calculated (BP86/6-31G(d)) harmonic IR spectra (Table 4). The resonances corresponding to the IR vibration of the CN groups can be clearly identified in the spectra, as there are no other resonances of significant intensity close to the region around 2300 cm^{-1}. We therefore could assign them to the symmetric and asymmetric bond stretch vibrations of the CN functionality as predicted by DFT (Table 4).

The measured vibrational frequencies show only small differences, but as lower frequencies correspond to stronger donor properties, *para* substituted **10** shows the highest donor strength among the methoxyphenyl substituted complexes, indicating an electronic effect on complexes **8–10**. These results confirm our expectation and together with results of the CV and ^{13}C NMR studies we could show that a methoxy substituent in *meta* position will have a negative effect on the donor properties, while the *para* substituted complex **10** is the most electron-rich complex.

Table 3
^{13}C NMR shifts of the carbene carbon atoms, measured in DMSO-d_6. Values are given in ppm.

Complex	^{13}C Carbene
8 (*ortho*)	147.35
9 (*meta*)	146.56
10 (*para*)	146.32

Table 4
Observed and calculated acetonitrile vibrational frequencies of complexes **8–10**. Values given in cm^{-1}.

Complex	ν_{CN} (ATR-IR)	ν_{CN} (BP86/6-31G(d))
8 (*ortho*)	2329, 2304	2319, 2312
9 (*meta*)	2331, 2305	2318, 2312
10 (*para*)	2328, 2301	2317, 2311

4. Conclusion

Five new 3,3′-bis(methoxyphenyl)-[(1,1′-diimidazolin-2,2′-diylidene)methane] palladium(II) complexes have been prepared and characterized. Due to their better solubility the *ortho*, *meta* and *para* substituted isomers with hexafluorophosphate counterions were used to investigate electronic effects of substituents at the aromatic ring. They extend our work on aryl substituted bis-NHC ligands, which previously had been limited to substitution in *para* position of the aryl ring. The effect of the position of methoxy substitution on the electronic properties has been investigated by cyclovoltammetry, IR, and NMR spectroscopy. The results indicate that a variation of the position of the methoxy substituent has a considerable electronic effect on the metal. The *para* substituted complex was found by all characterization methods applied to have the strongest donor properties. These results have also been confirmed by DFT calculations.

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Appendix A. Supplementary material

Supplementary crystallographic data and 3D-plots of **8** and **10**, IR spectra of **8–10**, experimental details for the synthesis of imidazoles **4** and **5** as well as detailed computational results are available free of charge via the Internet. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2012.06.009.

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