



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,*}

^aPhysikalische Organische Chemie, Technische Universität Dresden, Bergstrasse 66, 01062 Dresden, Germany

^bInstitut für Chemie, Professur Anorganische Chemie, Technische Universität Chemnitz, Straße der Nationen 62, 09111 Chemnitz, Germany

^cAnorganische 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 cyclovolttammetry, 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.

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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 imidazole-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.

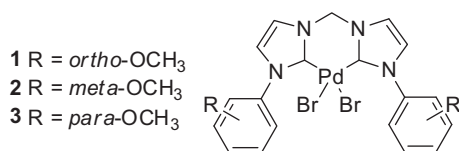
The *para* methoxy substituted complex **3** was found to be a considerably more efficient catalyst than other *para* functionalized aryl substituted bis-NHC palladium complexes (i.e., the analogous *para* bromophenyl or *para* nitrophenyl complexes) in the Heck reaction of aryl halogenides with styrene [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

* Corresponding author. Tel.: +4935146338571.

E-mail address: thomas.strassner@chemie.tu-dresden.de (T. Straßner).

¹ X-ray analysis.



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 $25\text{ }^\circ\text{C}$ 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-PF₆ was employed as the solvent. The solvent and TBA-PF₆ were carefully dried prior to use. All organometallic compounds were added to achieve a concentration of $c = 0.1\text{ mmol}$. 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 NH₄OAc 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'-methylenediimidazolium-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 $60\text{ }^\circ\text{C}$ 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 CH₂Cl₂. 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, $T = 323\text{ K}$): δ 7.78 (s, 2H, NCH); 7.68–7.42 (m, 6H, Ar and NCH); 7.33–7.08 (m, 4H, Ar); 6.50 (s, 2H, NCH₂N); 3.83 (s, 6H, CH₃) ppm. ^{13}C NMR (125.77 MHz, DMSO-*d*₆, $T = 353\text{ K}$): δ 153.25 (i-C of Ar); 129.71 (CH); 128.06 (CH); 124.37 (CH); 120.70 (CH); 119.71 (CH); 112.68 (CH); 62.59 (CH₂); 54.83 (CH₃) ppm; carbene carbon atom signal not detected due to poor solubility. Mp. > $300\text{ }^\circ\text{C}$. MS (ESI): $m/z = 525.1$ [PdL(OAc)]⁺, 547.0 [PdLBr]⁺. Anal. Calc. for C₂₁H₂₀N₄Br₂O₂Pd·0.8 C₂H₆SO: 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'-methylenediimidazolium-dibromide (**6**) and 80 mg (0.36 mmol) [Pd(OAc)₂] were heated in 5 mL DMSO from ambient temperature to $60\text{ }^\circ\text{C}$ 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 CH₂Cl₂. 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, $T = 323\text{ K}$): δ 7.91–7.69 (m, 4H, NCH); 7.66–7.23 (m, 6H, Ar); 7.06 (s, 2H, Ar); 6.53 (s, 2H, NCH₂N); 3.93 (s, 6H, CH₃) 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 (CH of Ar); 122.43 (NCH), 121.87 (NCH), 116.64 (CH of Ar); 113.54 (CH of Ar); 110.83 (CH of Ar); 62.96 (CH₂); 55.11 (CH₃) ppm; carbene carbon signal not detected due to poor solubility. Mp. > $300\text{ }^\circ\text{C}$. MS (ESI): $m/z = 525.1$ [PdL(OAc)]⁺. Anal. Calc. for C₂₁H₂₀N₄Br₂O₂Pd·0.35 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 $130\text{ }^\circ\text{C}$ 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, $T = 295\text{ K}$): δ 10.12 (s, 2H, NCHN); 8.39 (s, 2H, NCH); 8.23 (s, 2H, NCH); 7.68 (d, $J = 7.4\text{ Hz}$, 2H, Ar); 7.63 (t, $J = 8.2\text{ Hz}$, 2H, Ar); 7.42 (d, $J = 8.2\text{ Hz}$, 2H, CH of Ar); 7.22 (t, $J = 7.4\text{ Hz}$, CH of Ar); 6.97 (s, 2H, NCH₂N); 3.92 (s, 6H, CH₃) ppm. ^{13}C NMR (74.475 MHz, DMSO-*d*₆, $T = 295\text{ K}$): δ 151.74 (i-C of Ar); 138.73 (NCH); 131.89 (CH of Ar); 125.03 (CH of Ar); 124.06 (CH of Ar); 122.96 (i-C of Ar); 121.92 (CH of Ar); 113.37 (CH of Ar); 107.97 (CH of Ar); 58.37 (CH₂), 56.40 (CH₃) ppm. Mp. $235.9\text{ }^\circ\text{C}$ (decomp.). Anal. Calc. for C₂₁H₂₀N₄O₂: 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)

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