ARTICLE IN PRESS

Journal of Organometallic Chemistry xxx (2016) 1–6

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Neutral platinum(II) N-heterocyclic carbene complexes with tetrazolide-tethered imidazolin-2-ylidene ligands

Mario Tenne, Thomas Strassner*

Physikalische Organische Chemie, Technische Universität Dresden, Bergstrasse 66, 01062 Dresden, Germany

ARTICLE INFO

Article history:
Received 4 February 2016
Received in revised form
18 April 2016
Accepted 20 April 2016
Available online xxx

Dedicated to Prof. Dr. Heinrich Lang on the occasion of his 60th birthday.

Keywords:
Tetrazole
Carbene
NHC
Platinum
Solid state structure

ABSTRACT

Neutral platinum(II) complexes with two bidentate 1-((tetrazolid-5-yl)methyl)-3-alkylimidazolin-2-ylidene ligands (alkyl = methyl, *n*-butyl) have been synthesized and characterized to investigate the electronic and steric effects of tetrazolidyl NHC ligands. Solid state structures of the complexes as well as of a ligand precursor are presented.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

During the last decade the chemistry of palladium and platinum complexes with chelating NHC ligands [1] and their catalytic and photophysical properties has seen further developments [2–32]; applications of these homogenous catalysts include palladium catalyzed CH-activation chemistry, cross coupling reactions and platinum catalyzed hydrosilylation reactions. The NHC ligands are conveniently accessible by various synthetic routes and show in general enhanced catalytic performance compared to the organophosphanes, especially by being more robust against traces of water or air. This has contributed to the success of the NHC ligands in the field of homogeneous catalysis [33–39]. Transition metal complexes with chelating NHC ligands are often even more stable as they exploit a combination of two positive effects, the chelation and the strong σ-donor character of the carbene unit, which leads to a strong metal-carbene bond in the complexes [40]. We recently found that chelating NHC ligands are also of interest for photophysical applications as emitters in organic light emitting devices (OLEDs) [41–43]. Efficient iridium(III) and platinum(II) emitters benefit from the strong ligand-field of NHC ligands, which may help to suppress non-radiative quenching and to increase the HOMO-LUMO energy gap leading to blue emissions [44–47].

The first platinum(II) complexes with a chelating (bis(3-alkylimidazolin-2-ylidene-1-yl)dihydroborate) NHC ligand have been reported in 2001 [48]. Further reports concerning chelated platinum complexes with bidentate and tetradentate carbene ligands followed [2,49–56]. In 2009, we reported a series of emissive homoleptic and heteroleptic platinum(II) tetracarbene complexes containing bis(imidazolin-2-ylidene) ligands **I** [41] and bis(4,5-dihydro-1*H*-triazol-5-ylidene) ligands **II** [42] (Fig. 1). These complexes turned out to be strongly phosphorescent at room temperature with emission wavelengths in the near-UV (**I**: 386–387 nm) and blue region (**II**: 432–465 nm) of the spectrum. Unfortunately, those charged emitters can only be spin-coated and can not be processed by a vacuum deposition process. Therefore we developed neutral complexes which integrate the strongly donating carbenes into chelating ligands carrying one anionic charge per ligand. Herein we report the synthesis of two neutral complexes with the overall structure **III** containing two tetrazolide-tethered imidazolin-2-ylidene ligands (R = methyl, *n*-butyl).

2. Experimental details

The AG 1-X8 anion exchange resin was purchased from BioRad

---

* Corresponding author.
E-mail address: thomas.strassner@chemie.tu-dresden.de (T. Strassner).

http://dx.doi.org/10.1016/j.jorganchem.2016.04.027
0022-328X/© 2016 Elsevier B.V. All rights reserved.

Please cite this article in press as: M. Tenne, T. Strassner, Journal of Organometallic Chemistry (2016), http://dx.doi.org/10.1016/j.jorganchem.2016.04.027

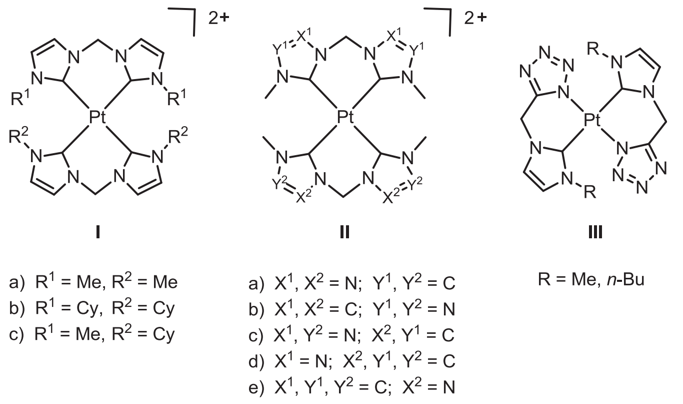

Fig. 1. General structure of imidazole- and triazole-based platinum(II) tetracarbene complexes (**I** and **II**) and the tetrazolide-tethered platinum(II) dicarbene complexes (**III**).

Laboratories Inc., and platinum(II) acetylacetonate was obtained from Degussa. All other chemicals were obtained from common suppliers and used without further purifications. Melting Points were determined with a Wagner & Munz Polytherm A System. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature at a Bruker NMR spectrometer. Signals are referenced internally using the resonances of the solvents (^{1}H: 7.24, ^{13}C: 77.2 for $CDCl_3$, ^{1}H: 2.50, ^{13}C: 39.5 for DMSO-d_6). Shifts are given in ppm; coupling constants *J* in Hz. Elemental analyses were performed by the analytical laboratory of the department using a Eurovektor Hekatech EA-3000 analyzer.

2.1. Synthesis of 1-cyanomethyl-3-methylimidazolium chloride 2a

In a round-bottom flask, 1-methylimidazole **1a** (6.87 g, 84 mmol) was dissolved in 85 mL of THF. Chloroacetonitrile (5.73 g, 76 mmol) was added to the solution and the mixture was refluxed for 16.5 h. After cooling to room temperature, the obtained precipitate was filtered, washed twice with THF and dried *in vacuo* to yield a white powder (6.37 g, 53%). Mp: 132 °C. ^{1}H NMR (DMSO-d_6, 500.13 MHz): δ 9.30 (s, 1 H, NC*H*N); 7.91 (s, 1 H, NC*H*CHN); 7.80 (s, 1 H, NCHC*H*N); 5.63 (s, 2 H, C*H*$_2$); 3.89 (s, 3 H, C*H*$_3$) ppm. ^{13}C NMR (DMSO-d_6, 125.77 MHz): δ 137.8 (N*C*HN); 124.4 (NCH*C*HN); 122.6 (N*C*HCHN); 114.8 (CH_2*C*N); 36.8 (*C*H_2CN); 36.2 (*C*H_3) ppm. Anal. Calcd for $C_6H_8ClN_3$: C 45.73%; H 5.12%; N 26.66%; found: C 45.75%; H 5.27%; N 26.74%.

2.2. Synthesis of 1-butyl-3-cyanomethylimidazolium chloride 2b

In a round-bottom flask, freshly destilled 1-butylimidazole **1b** (10.00 g, 80 mmol) was dissolved in 70 mL of THF. Chloroacetonitrile (5.29 g, 70 mmol) was added and the mixture was refluxed for 24 h. After cooling to room temperature the THF phase was decanted. The remaining oil was dissolved in 100 mL water and washed four times with 100 mL of dichloromethane each. The water of the aqueous solution was removed under reduced pressure and the residue was dried *in vacuo* to obtain a brown oil (13.28 g, 95%). The product was used without further purification. ^{1}H NMR (DMSO-d_6, 300.13 MHz): δ 9.48 (s, 1 H, NC*H*N); 7.96 (s, 1 H, NC*H*CHN); 7.92 (s, 1 H, NCHC*H*N); 5.67 (s, 2 H, C*H*$_2$CN); 4.23 (t, $^3J_{HH} = 7.2$ Hz, 2 H, NC*H*$_2$CH$_2$); 1.77 (m, 2 H, NCH$_2$C*H*$_2$); 1.26 (m, 2 H, C*H*$_2$CH$_3$); 0.90 (t, $^3J_{HH} = 7.4$ Hz, 3 H, C*H*$_3$) ppm. ^{13}C NMR (DMSO-d_6, 125.77 MHz): δ 137.3 (N*C*HN); 123.1 (NCH*C*HN); 122.8 (N*C*HCHN); 114.8 (CH$_2$*C*N); 49.0 (N*C*H$_2$CH$_2$); 36.9 (*C*H$_2$CN); 31.2 (NCH$_2$*C*H$_2$); 18.8 (*C*H$_2$CH$_3$); 13.3 (CH$_2$*C*H$_3$) ppm.

2.3. Synthesis of 1-cyanomethyl-3-(4-methoxyphenyl)imidazolium chloride 2c

In a round-bottom flask, 1-(4-methoxyphenyl)imidazole **1c** (505 mg, 2.9 mmol) was dissolved in 10 mL THF. Chloroacetonitrile (199 mg, 2.6 mmol) was added and the mixture was refluxed for 24 h. After cooling to room temperature, the resulting precipitate was filtered and washed with THF. After recrystallization from ethanol, the product was dried *in vacuo* to yield a white powder (76 mg, 12%). Mp: 129 °C. ^{1}H NMR (DMSO-d_6, 300.13 MHz): δ 9.95 (s, 1 H, NC*H*N); 8.32 (s, 1 H, NC*H*CHN); 8.16 (s, 1 H, NCHC*H*N); 7.72 (d, 2 H, $^3J_{HH} = 9.0$ Hz, C2*H*$_{arom}$, C6*H*$_{arom}$); 7.21 (d, 2 H, $^3J_{HH} = 9.0$ Hz, C3*H*$_{arom}$, C5*H*$_{arom}$); 5.70 (s, 2 H, C*H*$_2$CN); 3.85 (s, 3 H, OC*H*$_3$) ppm. ^{13}C NMR (DMSO-d_6, 75.48 MHz): δ 160.2 (*C*4$_{arom}$); 136.7 (N*C*HN); 127.6 (*C*1$_{arom}$); 123.8 (*C*2$_{arom}$, *C*6$_{arom}$); 123.2 (NCH*C*HN); 122.3 (N*C*HCHN); 115.2 (*C*3$_{arom}$, *C*5$_{arom}$); 114.5 (CH$_2$*C*N); 55.8 (O*C*H$_3$); 37.0 (*C*H$_2$CN) ppm. Anal. Calcd for $C_{12}H_{12}ClN_3O$: C 57.72%; H 4.84%; N 16.83%; found: C 57.46%; H 4.75%; N 16.52%.

2.4. Synthesis of 1-cyanomethyl-3-(2,4,6-trimethylphenyl) imidazolium chloride 2d

In a round-bottom flask, 1-(2,4,6-trimethylphenyl)imidazole **1d** (3.01 g, 16.2 mmol) was dissolved in 30 mL THF. Chloroacetonitrile (1.11 g, 14.7 mmol) was added and the mixture was refluxed for three days. After cooling to room temperature, the resulting precipitate was filtered, washed three times with water and dried *in vacuo* to yield a white powder (1.40 g. 36%). Mp: 136 °C. ^{1}H NMR (DMSO-d_6, 300.13 MHz): δ 9.72 (s, 1H, NC*H*N); 8.26 (s, 1 H, NC*H*CHN); 8.04 (s, 1 H, NCHC*H*N); 7.15 (s, 2 H, C3*H*$_{arom}$, C5*H*$_{arom}$); 5.75 (s, 2 H, C*H*$_2$CN); 2.33 (s, 3 H, *p*-C*H*$_3$); 2.03 (s, 6 H, *o*-C*H*$_3$) ppm. ^{13}C NMR (DMSO-d_6, 75.48 MHz): δ 140.5 (*C*4$_{arom}$); 138.8 (N*C*H); 134.3 (*C*2$_{arom}$, *C*6$_{arom}$); 131.0 (*C*1$_{arom}$); 129.3 (*C*3H$_{arom}$, *C*5H$_{arom}$); 124.5 (NCH*C*HN); 123.4 (N*C*HCHN); 114.7 (CH$_2$*C*N); 37.5 (*C*H$_2$CN); 20.6 (*p*-*C*H$_3$); 16.9 (*o*-*C*H$_3$) ppm. Anal. Calcd for $C_{14}H_{16}ClN_3$: C 64.24%; H 6.16%; N 16.05%; found: C 64.08%; H 6.26%; N 15.87%.

2.5. Synthesis of 1-methyl-3-((tetrazol-5-yl)methyl)imidazolium bromide 3a

Compound **2a** (4.00 g, 25 mmol) and sodium azide (1.81 g, 28 mmol) were dissolved in 30 mL water in a round-bottom flask. Zinc bromide (6.29 g, 28 mmol) was added to the solution, and the mixture was stirred for three hours at 100 °C. The resulting precipitate was filtered, washed with water and dried *in vacuo*, leaving 6.89 g of a white solid. 709 mg of the solid were dissolved in 10 mL of a 9 N hydrochloric acid. A glass column (400 mm length, 10 mm inner diameter, wool plug) was washed with deionized water, and filled with 23 g of anion exchange resin (chloride form) suspended in deionized water and covered by a sand plug. The column was covered with a wool plug and rinsed with 90 mL of a 9 N hydrochloric acid. The zinc containing imidazolium solution was introduced to the column and eluted with 9 N hydrochloric acid. The first 45 mL of the eluted solution were collected and the solvent was removed under reduced pressure. The remaining solid was washed with an acetone/diethyl ether mixture (20 mL, 1:1), filtered and dried *in vacuo* to obtain the product as a white powder (474 mg, 74% over two steps). Mp: 148 °C. ^{1}H NMR (DMSO-d_6, 500.13 MHz): δ 9.31 (s, 1 H, NC*H*N), 7.84 (s, 1 H, NC*H*CHN), 7.79 (s, 1 H, NCHC*H*N), 5.93 (s, 2 H, C*H*$_2$CN), 3.91 (s, 3 H, C*H*$_3$) ppm. ^{13}C NMR (DMSO-d_6, 125.77 MHz): δ 153.9 (CH$_2$*C*N), 137.6 (N*C*HN); 124.0 (NCH*C*HN); 123.2 (N*C*HCHN); 42.5 (*C*H$_2$CN); 36.1 (*C*H$_3$) ppm. Anal. Calcd for $C_6H_9BrN_6$: C 29.40%; H 3.70%; N 34.29%; found: C 29.49%; H 3.54%;

Please cite this article in press as: M. Tenne, T. Strassner, Journal of Organometallic Chemistry (2016), http://dx.doi.org/10.1016/j.jorganchem.2016.04.027

Download English Version:

https://daneshyari.com/en/article/5153281

Download Persian Version:

https://daneshyari.com/article/5153281

Daneshyari.com