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(C^C*)-cyclometalated platinum(II) imidazo[1,5-*a*]pyridine NHC complexes – Synthesis and characterization

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ABSTRACT

Imidazo[1,5-*a*]pyridines have been used as monodentate ligands in late transition-metal *N*-heterocyclic carbene (NHC) complexes, but the *N*-aryl substituted heterocyclic ligands also allow for the formation of C^C* cyclometalated complexes, which has previously only been shown for iridium(III) complexes. Here we present the first C^C* platinum(II) NHC complexes of this class. A monoanionic bidentate ligand L – acetylacetonato (acac) or dipivaloylmethanato (dpm) – was used to generate heteroleptic compounds of the general formula [(C^C*-NHC)Pt(L)]. Seven mononuclear complexes and one binuclear complex are presented. The square-planar coordination of the C^C* cyclometalated species was confirmed by spectroscopy and additionally by three solid-state structures. The complexes have been fully characterized including ^{195}Pt NMR and extensive 2D NMR studies (COSY, HSQC, HMBC, NOESY). From the experimental data we exclusively see the formation of five-membered metallacycles to the aryl substituent and no interaction with the pyridine part of the ligand, in good agreement with density functional theory calculations (B3LYP/6-31G(d)), which show that the five-membered metallacycles are significantly favoured over the four-membered metallacycles.

Introduction

Over the last decades *N*-heterocyclic carbenes (NHCs) have been found to be a unique and important class of ligands in transition-metal chemistry [1–8]. One of the current research interests in academia as well as in industry is the improvement of the properties of these ligands and their respective metal complexes for applications in various fields. Important features of NHCs are their strong σ-donating capabilities, minor dissociation tendency and the possibility to fine-tune the properties by modification of their electronic structure and sterics.

Platinum(II) complexes with NHC ligands have been investigated in detail because of their promising properties. Their catalytic activity was further enhanced by modifying the chosen carbene ligands [9–11]. Imidazo[1,5-*a*]pyridine NHCs are a class of unsymmetrical ligands (Scheme 1) that have been well studied as part of transition-metal complexes in homogeneous catalysis [12–20] but have not received much attention in platinum chemistry so far.

Herein, we report the synthesis of several imidazopyridinium salts and their coordination to platinum(II) as bidentate monoanionic NHC ligands. In the resulting square-planar complexes the π-system of the carbene ligand and any substituents therein are placed in the same plane as the metallacycle, allowing for direct manipulation of the electronic situation at the metal centre and thus the complex properties.

Experimental section

General considerations

Solvents of at least 99.5% purity were used throughout this study. 1,4-Dioxane and DMF were dried using standard techniques and stored under an argon atmosphere over molecular sieve (3 Å). Dichloro(1,5-cyclooctadiene)platinum(II) (Pt(COD)Cl_2) [23] was prepared following a modified literature procedure [24]. Potassium tetrachloroplatinate(II) (≥99.9% trace metal basis) and all other chemicals were obtained from common suppliers and used without further purification. ^{1}H, ^{13}C, ^{19}F and ^{195}Pt NMR spectra were recorded on a Bruker 300 MHz, 500 MHz and 600 MHz NMR spectrometer at room temperature. ^{1}H and ^{13}C NMR spectra were referenced internally using the resonances of the solvent (^{1}H: 7.26, ^{13}C: 77.0 for $CDCl_3$; ^{1}H: 2.50, ^{13}C: 39.43 for DMSO-d_6). ^{19}F NMR spectra were referenced externally against trifluoromethylbenzene ($F_3C–C_6H_5$). ^{195}Pt NMR spectra were referenced externally using

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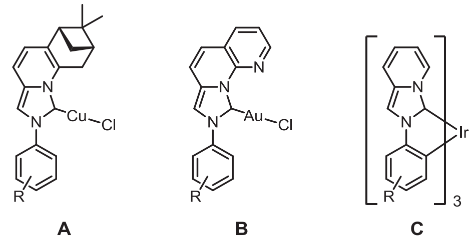

Scheme 1. Some known examples of Imidazo[1,5-*a*]pyridine complexes [20–22].

potassium tetrachloroplatinate(II) in D_2O (−1617.2 ($PtCl_4^{2-}$), −2654.1 ($PtCl_2$)). Shifts are given in ppm, coupling constants J in Hz. Elemental analyses were performed by the microanalytical laboratory of our institute on a Hekatech elemental analyser. Melting points have been determined using a Wagner and Munz Poly Therm A system and are not corrected.

Synthesis of ligands

*2-Phenyl-2H-imidazo[1,5-a]pyridinium tetrafluoroborate (**1**)*

The general synthesis starts with the slow addition of excess concentrated hydrochloric acid to aniline (4.66 g, 4.6 mL, 50.0 mmol) dissolved in a small amount of methylene chloride under rigorous stirring. A solid immediately formed, which was collected, washed with diethyl ether and dried at 40 °C at $<$10 mbar for two hours. Then the hydrochloride salt was dissolved in 100 mL ethanol, and 37 wt% aqueous formaldehyde solution (2.25 g, 2.1 mL, 75.0 mmol) as well as 2-pyridinecarboxyaldehyde (5.36 g, 4.8 mL, 50.0 mmol) were added. Afterwards the reaction mixture was stirred for 24 h at room temperature. The formed precipitate was filtered off, washed with diethyl ether and dried *in vacuo*. To obtain the tetrafluoroborate compound the chloride salt was completely dissolved in a methanol/water mixture and 50 wt% aqueous tetrafluoroboric acid was added in one step. Again a solid formed which was filtered off, washed with diethyl ether and dried *in vacuo* to give the product in 21% yield (2.91 g, 10.3 mmol).

An alternative synthetic route starts by dissolving the aniline (0.93 g, 0.9 mL, 10 mmol) in a small amount of diethyl ether followed by addition of 50 wt% aqueous tetrafluoroboric acid (4.23 g, 24 mmol). After stirring the solution for one hour the solid was collected, washed with diethyl ether and dried. The salt was dissolved in 50 mL ethanol, and 37 wt% aqueous formaldehyde solution (1.22 g, 0.4 mL, 15.0 mmol) as well as 2-pyridinecarboxyaldehyde (1.07 g, 0.9 mL, 10.0 mmol) were added at room temperature. The reaction mixture was stirred overnight, the precipitate collected, washed with ether and dried *in vacuo* (Yield: 34%). ^{1}H NMR (600 MHz, DMSO-d_6): δ 10.30 (d, J = 1.1 Hz, 1H, NC*H*N), 8.75 (s, 1H, CH_{arom}), 8.58 (dd, J = 0.8 Hz, J = 7.2 Hz, 1H, CH_{arom}), 7.95–7.88 (m, 3H, CH_{arom}), 7.77–7.72 (m, 2H, CH_{arom}), 7.70–7.66 (m, 1H, CH_{arom}), 7.36 (dd, J = 6.8 Hz, J = 9.4 Hz, 1H, CH_{arom}), 7.29–7.25 (m, 1H, CH_{arom}) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ 135.0 (C_i), 130.4 (CH_{arom}), 130.3 (CH_{arom}), 129.7 (N*C*HN), 125.8 (C_i), 125.2 (CH_{arom}), 124.1 (CH_{arom}), 122.8 (CH_{arom}), 118.2 (CH_{arom}), 118.1 (CH_{arom}), 112.2 (CH_{arom}) ppm. ^{19}F NMR (282 MHz, DMSO-d_6): δ −148.9 ppm. M.p.: 145–147 °C. Anal. calcd for $C_{13}H_{11}BF_4N_2$: C 55.36, H 3.93, N 9.93; found: C 55.23, H 3.83, N 9.64%.

*2-(3,5-Bis(trifluormethyl)phenyl)-2H-imidazo[1,5-a]pyridinium tetrafluoroborate (**2**)*

The synthesis followed the general procedure as given for **1**. 3,5-Bis(trifluoromethyl)aniline (11.46 g, 50.0 mmol) was used as amine. Yield: 62% (13.0 g, 31.1 mmol). ^{1}H NMR (600 MHz, DMSO-d_6): δ 10.52 (d, J = 1.1 Hz, 1H, NC*H*N), 8.96 (s, 1H, CH_{arom}), 8.73 (s, 2H, CH_{arom}), 8.65 (d, J = 7.2 Hz, 1H, CH_{arom}), 8.52 (s, 1H, CH_{arom}), 7.99 (d, J = 9.4 Hz, 1H, CH_{arom}), 7.39 (dd, J = 6.6 Hz, J = 9.2 Hz, 1H, CH_{arom}), 7.35–7.29 (m, 1H, CH_{arom}) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ 136.5 (C_i), 131.8 (CF_3), 129.5 (C_i), 126.9 (N*C*HN), 125.5 (CH_{arom}), 124.9 (CH_{arom}), 124.3 (CH_{arom}), 124.1 (CH_{arom}), 121.7 (C_i), 118.7 (CH_{arom}), 118.4 (CH_{arom}), 112.9 (CH_{arom}) ppm. ^{19}F NMR (282 MHz, DMSO-d_6): δ −61.9 (CF_3), −148.9 (BF_4) ppm. M.p.: 163–165 °C. Anal. calcd for $C_{15}H_9BF_{10}N_2$: C 43.10, H 2.17, N 6.70; found: C 42.84, H 2.06, N 6.59%.

*2-(4-Methoxyphenyl)-2H-imidazo[1,5-a]pyridinium chloride monohydrate (**3**)*

The synthesis followed the general procedure as given for **1** but without salt metathesis to the corresponding tetrafluoroborate salt. 4-Methoxyaniline (6.16 g, 50.0 mmol) was used as amine. Yield: 60% (8.3 g, 29.8 mmol). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.33 (s, 1H, NC*H*N), 8.69 (s, 1H, CH_{arom}), 8.59 (s, 1H, CH_{arom}), 7.90 (d, J = 9.1 Hz, 1H, CH_{arom}), 7.84 (d, J = 8.8 Hz, 2H, CH_{arom}), 7.34 (dd, J = 6.3 Hz, J = 9.8 Hz, 1H, CH_{arom}), 7.29–7.21 (m, 3H, CH_{arom}), 3.33 (s, 3H, CH_3) ppm. ^{13}C NMR (125 MHz, DMSO-d_6): δ 160.5 (C_i), 129.5 (C_i), 128.0 (C_i), 125.6 (CH_{arom}), 125.1 (CH_{arom}), 124.3 (CH_{arom}), 124.1 (CH_{arom}), 118.2 (CH_{arom}), 118.0 (CH_{arom}), 115.3 (CH_{arom}), 112.3 (CH_{arom}), 55.8 (CH_3) ppm. M.p.: 206–208 °C. Anal. calcd for $C_{14}H_{13}ClN_2O \cdot H_2O$: C 60.33, H 5.42, N 10.05; found: C 60.31, H 5.44, N 10.04%.

*2-(4-Bromophenyl)-2H-imidazo[1,5-a]pyridinium chloride hydrate (**4**)*

The synthesis followed the general procedure as given for **1** but without salt metathesis to the corresponding tetrafluoroborate salt. 4-Bromoaniline (3.55 g, 20.0 mmol) was used as amine. Yield: 88% (5.78 g, 17.5 mmol). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.46 (s, 1H, NC*H*N), 8.77 (s, 1H, CH_{arom}), 8.62 (d, J = 7.0 Hz, 1H, CH_{arom}), 8.02–7.84 (m, 5H, CH_{arom}), 7.41–7.32 (m, 1H, CH_{arom}), 7.31–7.23 (m, 1H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 134.3 (C_i), 133.1 (CH_{arom}), 129.6 (C_i), 126.0 (CH_{arom}), 125.2 (CH_{arom}), 124.9 (CH_{arom}), 124.1 (CH_{arom}), 123.5 (C_i), 118.2 (2xCH_{arom}), 112.2 (CH_{arom}) ppm. M.p.: 255–260 °C. Anal. calcd for $C_{13}H_{10}BrClN_2 \cdot 1.2H_2O$: C 47.14, H 3.77, N 8.46; found: C 46.90, H 3.68, N 8.47%.

*2-(4-Cyanophenyl)-2H-imidazo[1,5-a]pyridinium chloride monohydrate (**5**)*

The synthesis followed the general procedure as given for **1** but without salt metathesis to the corresponding tetrafluoroborate salt. 4-Aminobenzonitrile (6.03 g, 50.0 mmol) was used as amine. Yield: 54% (7.44 g, 27.2 mmol). ^{1}H NMR (300 MHz, DMSO-d_6): δ 10.63 (s, 1H, NC*H*N), 8.87 (s, 1H, CH_{arom}), 8.65 (d, J = 7.0 Hz, 1H, CH_{arom}), 8.32–8.24 (m, 2H, CH_{arom}), 8.21–8.13 (m, 2H, CH_{arom}), 7.95 (d, J = 9.3 Hz, 1H, CH_{arom}), 7.41–7.33 (m, 1H, CH_{arom}), 7.32–7.26 (m, 1H, CH_{arom}) ppm. ^{13}C NMR (75 MHz, DMSO-d_6): δ 138.2 (C_i), 134.4 (CH_{arom}), 129.7 (C_i), 126.4 (CH_{arom}), 125.4 (CH_{arom}), 124.2 (CH_{arom}), 123.8 (CH_{arom}), 118.5 (CH_{arom}), 118.3 (CH_{arom}), 117.6 (C_i), 113.0 (C_i), 112.1 (CH_{arom}) ppm. M.p.: 288–290 °C. Anal. calcd for $C_{14}H_{10}ClN_3 \cdot H_2O$: C 61.43, H 4.42, N 15.35; found: C 61.23, H 4.23, N 15.41%.

*2-(4-Methoxyphenyl)-1-phenyl-2H-imidazo[1,5-a]pyridinium tetrafluoroborate (**6**)*

The synthesis followed the general procedure as given for **1**. 4-Methoxyaniline (6.16 g, 50.0 mmol) was used as amine and 2-benzoylpyridine (9.25 g, 50.0 mmol) as carbonyl compound. Yield: 88% (16.98 g, 43.7 mmol). ^{1}H NMR (600 MHz, DMSO-d_6): δ 10.11 (s, 1H, NC*H*N), 8.63 (d, J = 6.8 Hz, 1H, CH_{arom}), 7.80 (d, J = 9.0 Hz, 1H, CH_{arom}), 7.48 (m, 5H, CH_{arom}), 7.40–7.29 (m, 4H, CH_{arom}), 7.12 (d, J = 8.7 Hz, 2H, CH_{arom}), 3.81 (s, 3H, CH_3) ppm. ^{13}C NMR (150 MHz, DMSO-d_6): δ 160.4 (C_i), 130.1 (CH_{arom}), 129.7 (CH_{arom}), 129.0