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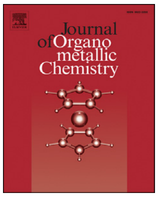

Platinum(IV) complexes of primary amines *via* oxidative addition

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ABSTRACT

Oxidative addition allows to synthesize the first cycloplatinated primary amines in which the platinum adopts oxidation state +IV: Square planar organoplatinum(II) complexes can be converted with elementary diiodine and dibromine to the corresponding pseudo-octahedral Pt(IV) derivatives. The reaction may be monitored with the help of NMR spectroscopy and five of the target products have been characterized by single crystal X-ray diffraction. Two of these Pt(IV) complexes provide structural evidence for *cis* addition of the halogen and for the pronounced *trans* effect of the Pt–C bond. The latter is also reflected in a substitution reaction promoted by $AgBF_4$: The halide substituent *trans* to the C in the coordination sphere can be selectively replaced by the pseudohalide cyanate. In the absence of a suitable silver salt, the pseudo-octahedral Pt(IV) complexes are inert in substitution reactions.

1. Introduction

Cope and Friedrich initiated the orthometallation of activated benzyl amines with palladium and platinum in the late 1960ies [1]. In contrast to advances in the field of cyclo**palladation**, only little progress had been made for the cyclo**platination** of primary amines (Scheme 1) until 2007 [2]. In 2008, our group reported the first convenient cycloplatination of primary amines based on a mixed-valent platinum iodide precursor [3].

The good yields thus achieved enabled us to address a series of square planar Pt(II) derivatives *via* substitution: Phosphanes or pyridines may act as alternative donor ligands; an intermediate aqua complex allows to exchange X (originally iodide, Scheme 1) for other (pseudo)halides, including a radiomarker [4]; chelating ligands such as ethylenediamine may displace both L and X and will result in cationic complexes [5].

Powder diffraction has shown [3] that our successful cycloplatination of primary amines requires the concomitant presence of K_2PtI_4 and K_2PtI_5 [6]; the latter contains both divalent and tetravalent platinum. In the context of our work on cycloplatinations, we also isolated trace amounts of Pt(IV) complexes in which primary amines act as cycloplatinated ligands. The yield of such products could, however, not be increased by a higher Pt(IV) content in the precursor, and we therefore can neither provide a rational synthesis nor a complete characterization for these potentially attractive target compounds. Interest in organoplatinum complexes in this oxidation state goes beyond mere scientific curiosity: In view of their pronounced inertness, such derivatives might be suitable candidates for orally administered prodrugs, similar to Satraplatin [7]. In our present contribution, we do not aim at the direct reaction of tetravalent platinum with primary amines but rather focus on an alternative route, namely oxidative addition. Earlier examples for oxidative addition in related organoplatinum complexes shall shortly be reviewed: The group of van Koten reported the first oxidative addition with a tertiary cycloplatinated amine in 1980 [8] and the first such reaction with elementary halogen in 1983 [9]; for the latter reaction, they found evidence for *trans* addition [10]. For cycloplatinated imines, the groups of Crespo [11] and Biswas [12] successfully performed oxidative addition not only with halogen but also with methyl iodide. To date, only a few structurally characterized secondary [13] and no primary cycloplatinated amines of tetravalent platinum have been documented in the Cambridge Structural Database [14]. We here communicate the first examples of this class of compounds. Our results concerning their synthesis, reactivity and structure have been summarized in Scheme 2.

2. Experimental section

2.1. Chemicals and instrumentation

$AgBF_4$ (Aldrich, 98%), bromine (Merck), iodine (KMF-Laborchemie, 99,5%), K_2PtCl_4 (Alfa Aesar), R-1-Phenylethylamine (Merck), S-1-4-Fluoro-phenylethylamine (BASF), sodiumcyanate (Aldrich),

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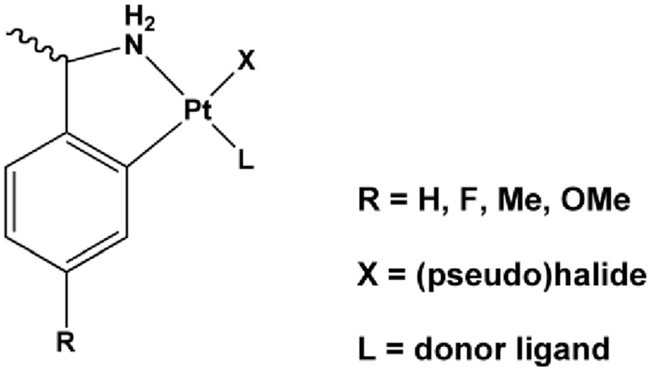


Scheme 1. Cycloplatinated primary amines.

triphenylphosphine (Aldrich, 99%) and hydroiodic acid (57%)(Merck) were used without further purification. The Pt(II) complexes **1** and **2** were synthesized as published [3].

NMR spectra were recorded on a Bruker Avance II Ultrashield^{TM} plus 400 (^{1}H NMR: 400 MHz; ^{13}C NMR: 100.6 MHz; ^{19}F NMR: 376.5 MHz; ^{31}P NMR 162.0 MHz; ^{195}Pt-NMR: 86 MHz); ^{1}H and ^{13}C resonances are referenced to TMS, and ^{195}Pt to H_2PtCl_4. Powder diffraction experiments were performed at room temperature on flat samples with a Stoe&Cie STADI P diffractometer equipped with an imageplate detector with constant ω-angle of 55° using Germanium-monochromated Cu-Kα1 radiation ($\lambda = 1.54051$ Å). CHN microanalyses were obtained from the Institute of Organic Chemistry, RWTH Aachen University, using a HERAEUS CHNO-Rapid, and from Institute of Inorganic Chemistry, Düsseldorf University, with a Hekatech Euro EA 3000 elemental analyser. UV–Vis spectra were measured on WPA S1200 Spectrawave Visible Spectrophotometer von Biochrom. Infrared spectra were recorded on KBr pellets with an Avatar 360 FTIR spectrometer from Nicolet.

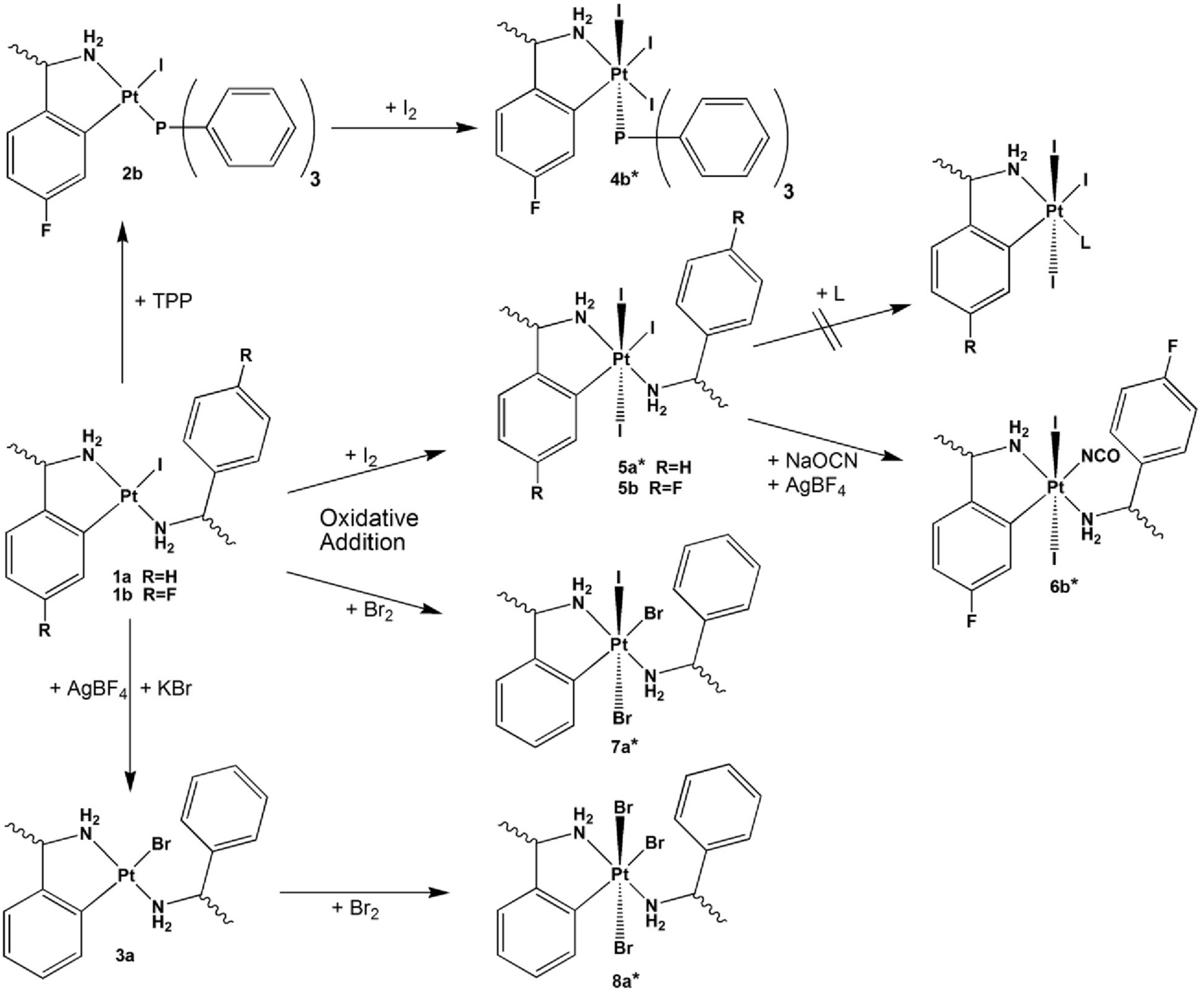
2.2. General comments

The new complexes reported in this article do not melt but decompose when heated.

For easier comparison, all NMR spectra were registered in C_6D_6 (see Scheme 3 for assignment).

2.2.1. Synthesis of the complex **3a**

57 mg (0.1 mmol) of **1a** were dissolved in 7 ml of methanol. An equimolar amount of $AgBF_4$ was added, and the yellow precipitate of AgI was removed by centrifugation. 12 mg (0.1 mmol) of KBr



Scheme 2. Overview of the reaction pathway (compounds marked with an * have been structurally characterized).