

# Synthesis and characterization of pyridine- and thiophene-based platinacyclines

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## Abstract

Seven heterocyclic macrocycles, including the first platinacycles with pyridine and thiophene rings incorporated into the cycline system, are reported. Pt-acetylide cyclines were assembled via tin transmetalation or amine-mediated oxidative addition with stoichiometric  $\text{PtCl}_2(\text{PEt}_3)_2$  and  $\text{CuI}$ . The organometallic cyclines exhibited enhanced electronic properties compared to previously described platinabenzocyclines.

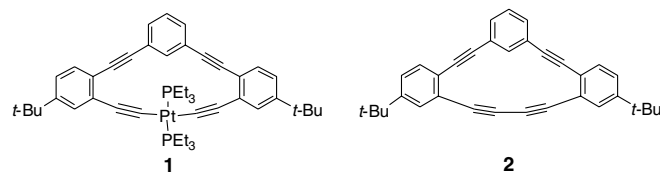
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**Keywords:** Platinum(II); Acetylide; Metallacycle; Benzocycline; Heterocycle

## 1. Introduction

The last 30 years has seen a noteworthy evolution from simple, acyclic Pt-acetylide complexes [1] to a diverse array of Pt-acetylide assemblies including macrocycles [2], dendrimers [3], oligomeric scaffolds [4], and polymers [5]. The defined directionality of the square planar platinum atom, the ethynyl group's rigid linearity, and the well-established, straightforward chemistry of platinum and alkyne functionalities have made Pt-acetylide complexes ideal in the construction of these multifaceted systems. Pt-acetylide complexes have shown further utility as an efficient means of introducing stereocenters into metallacycles through ligand exchange [6], facilitating intermolecular cyclization of  $\alpha,\omega$ -diethynyl monomers through reductive elimination of Pt-bisacetylide intermediates [7], as well as mediating self-assembly for host complexes and chiral platinacyclophanes capable of asymmetric catalysis [8]. Most recently, highly conjugated Pt-acetylide polymers have

been thoroughly investigated for use in organic photocells, light-emitting diodes, and models for triplet manifold studies of conjugated polymers [4d,5,9].



We recently reported selective metallacyclization of several *cis*- and *trans*-Pt-acetylide macrocycles as well as production of the non-organometallic parent benzocyclines [10]. A notable deficiency of the benzo[15]cycline systems (**1**, **2**) was limited electronic delocalization resultant from cross-conjugation of the central phenyl ring and further compounded by introduction of platinum into the cycle backbone. Based on recent successful production and evaluation of several new heterocyclic macrocycles [2d,2e,7,11], replacement of phenyl moieties in **1** and **2** with heterocycles was subsequently investigated to enhance electronic

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properties through intramolecular charge transfer via  $\pi$ -backbonding and/or donor–acceptor relationships between the metal, heteroatoms, and  $\pi$ -conjugated network. We herein describe the synthesis and characterization of four new platinacycles and three new macrocycles with heterocycles incorporated into the cycle backbone and discuss the electronic delocalization via comparison of UV–Vis spectra.

## 2. Results and discussion

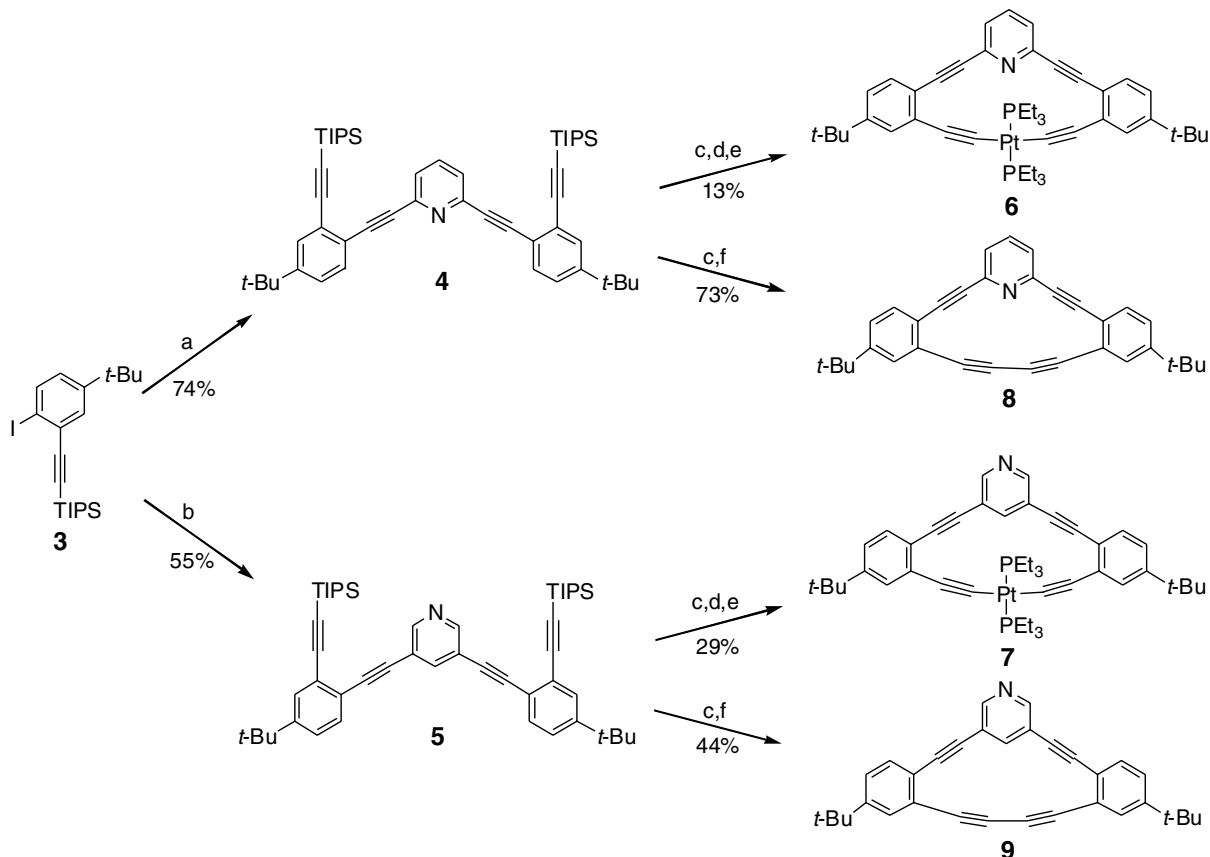
### 2.1. Synthesis of pyridocyclines

Production of pyridine analogs of cycles **1** and **2** began with Pd-catalyzed cross-coupling of 2,6- and 3,5-diethynylpyridine [2d,12] with previously reported ethynylarene **3** [13] to afford isomeric  $\alpha,\omega$ -polyynes **4** and **5** in 74% and 55% yields, respectively (Scheme 1). Platinacycles **6** and **7** were obtained from their corresponding isomeric precursor in low yield, the result of competing oligomerization, by a three-step metallacyclization procedure [10] consisting of desilylation with  $\text{Bu}_4\text{NF}$  [14], treatment with  $\text{Me}_3\text{SnNMe}_2$  [15], and final transmetalation with *trans*- $\text{PtCl}_2(\text{PEt}_3)_2$  and  $\text{CuI}$  [16]. Oxidative alkyne homocoupling of desilylated

$\alpha,\omega$ -polyynes **4** and **5** with  $\text{CuCl}$  and pyridine [17] provided cyclines **8** and **9** in 73% and 44% yields, respectively.

The  $^{31}\text{P}$  NMR spectra of platinacycles **6** ( $\delta$  11.13,  $J = 2381$  Hz) and **7** ( $\delta$  10.60,  $J = 2316$  Hz) showed characteristic *trans*  $J_{\text{P-Pt}}$  values [2b,4b,10] with both resonances shifted downfield in contrast to **1** ( $\delta$  10.49). The interior proton resonances of cycles **7** ( $\delta$  9.09) and **9** ( $\delta$  8.90) also showed enhanced electron deficiency in  $^1\text{H}$  NMR when compared to benzocycline **1** ( $\delta$  7.74). The significant downfield shift in  $^1\text{H}$  NMR ( $>1$  ppm) can be rationalized by the electron deficiency of the 4-pyridine position [18] further compounding the deshielding effects of ethynyl anisotropy and close proximity of the platinum atom ( $\sim 3$  Å) [19].

Crystals of **6** suitable for single-crystal X-ray diffraction were obtained by diffusion of hexanes into a concentrated THF solution (Fig. 1). Ethynyl distortion was most significant in the acetylene linker  $\sigma$ -bonded to the platinum (C1 11.5°, C2 14.7°) in comparison to the monoynes bridging phenyl rings (C9 5.7°, C10 2.6°) (Table 1). Similar to **1**, insertion of platinum into the cycline resulted in a significant distortion of the carbon-rich backbone with the alkylated phenyl rings twisted in relation to each other (Fig. 1b). The platinum atom exhibited  $\sim 10^\circ$  distortion from square planar with the  $\text{PEt}_3$  ligands bent away from the cycle core. The



Scheme 1. Synthesis of cycles **6–9**. Conditions: (a) 2,6-diethynylpyridine,  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{CuI}$ , *i*- $\text{Pr}_2\text{NH}$ , THF, 50 °C; (b) 3,5-diethynylpyridine,  $\text{Pd}(\text{PPh}_3)_4$ ,  $\text{CuI}$ , *i*- $\text{Pr}_2\text{NH}$ , THF, 50 °C; (c)  $\text{Bu}_4\text{NF}$ , THF, MeOH; (d)  $\text{Me}_3\text{SnNMe}_2$ , THF; (e) *trans*- $\text{PtCl}_2(\text{PEt}_3)_2$ ,  $\text{CuI}$ , THF; and (f)  $\text{CuCl}$ , pyridine, MeOH, 50 °C.

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