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## The first aryldiazenido complex of platinum(IV): an NMR study on the addition of aryldiazonium to platinum(II)†

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*para*-Methoxybenzenediazonium cation oxidatively adds to a platinum(II) complex, 4,4'-di-*tert*-butyl-2,2'-bipyridine-chelated 9,10-dihydroplatinaanthracene, resulting in the first directly observed aryldiazenido complex of platinum(IV). Multinuclear nuclear magnetic resonance (NMR) data (including  $^{15}\text{N}$  via  $^{15}\text{N}$ - $^1\text{H}$  gHMBC) are reported.

**Keywords:** Platinum; NMR spectroscopy;  $^{15}\text{N}$ -NMR; Aryldiazonium; Aryldiazenido

### 1. Introduction

Aryldiazonium cations,  $\text{ArN}_2^+$  (Ar = aryl), are tremendously useful synthetic intermediates in organic synthesis. Their interaction with organic substrates often involves initial formation of a  $\pi$ -complex [1]. Actual synthetic transformations occur mostly under  $\text{N}_2$  release, and typically involve transfer of an aryl cation, either to a halide or to a complex organic substrate; the latter reactions are often metal-catalyzed [2, 3]. The reactivity of aryldiazonium cations with metals is thus of great interest, and this reactivity is very diverse. The coordination of an aryldiazonium cation to a metal center can occur in various coordination modes (linear, singly bent, side-on, and doubly bent, see figure 1) [4–6]. These adducts can be stable, may be amenable to further functionalization (such as hydrogenation of nitrogen [7, 8]), or they may eliminate  $\text{N}_2$  effecting oxidative addition of  $\text{Ar}^+$  to the metal center [9]. It is relevant that redox chemistry can occur before  $\text{N}_2$  elimination. Particularly, if doubly-bent geometry is observed, the coordinated ligand is typically considered a monoanionic aryldiazenido ligand (formally a deprotonated aryldiazene), and since it has formed from a cationic aryldiazonium ion, the oxidation state of the metal has increased by two units (oxidative addition) [5, 6, 10, 11].

Platinum is one of the metals that has received significant attention in the context of aryldiazonium chemistry. Existing research has prepared platinum(II) products. The synthesis of bridged, dinuclear platinum(II) aryldiazenido complexes involves

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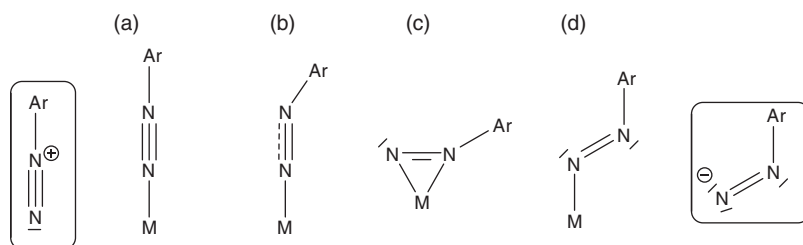


Figure 1. Coordination modes of  $\text{ArN}_2$  to metal centers, linear (a), singly bent (b), side-on (c), doubly bent (d), along with Lewis structures of aryldiazonium cation (left) and aryldiazenido anion (right).

diazonium addition to “A-frame” Pt(I)–Pt(I) dinuclear complexes [12, 13]. The synthesis of mononuclear platinum(II) aryldiazenido complexes involves either a platinum(0) precursor or a platinum(0) equivalent. Isolated platinum(0) complexes have been used directly in reactions with aryldiazonium cations to form complexes of platinum(II) that contain an anionic aryldiazenido ligand  $\text{ArN}_2^-$  [7, 8, 14, 15]. Alternatively, as a platinum(0) equivalent, platinum(II) hydrides in the presence of base (external or internal) have been used as well, since deprotonation of a hydride reduces the oxidation state of the metal by two units [16–19]. For the latter reactions, there exists kinetic evidence that deprotonation of the metal-bound hydride can occur after the addition of diazonium cation to the metal [18]. An intermediate on the reaction pathway may thus be a platinum(IV) aryldiazenido complex. However, no platinum(IV) aryldiazenido complex has been directly observed. Irrespective of whether a platinum(0) complex or a platinum(0) equivalent (Pt(II) hydride) was used, addition products observed were platinum(II) complexes with a coordinated aryldiazenido ligand  $\text{ArN}_2^-$  or (if the ligand acts as an internal base) [16] coordinated  $\text{ArN}_2\text{H}$ . Some complexes subsequently eliminated  $\text{N}_2$  to form the corresponding platinum(II) aryl complexes [14, 15]. Thus, while the oxidation of platinum(0) to platinum(II) *via* the addition of diazonium cations is well known, the analogous platinum(II)/(IV) chemistry has not been synthetically explored. We report here on the first stable platinum(IV) aryldiazenido complex, characterized by nuclear magnetic resonance (NMR) spectroscopy.

## 2. Experimental

### 2.1. General techniques

All manipulations involving organometallic compounds were carried out under inert-atmosphere conditions (vacuum line/glove box) using oven-dried glassware. NMR spectra ( $\text{CD}_3\text{CN}$  solution,  $-20^\circ\text{C}$  unless otherwise noted) were obtained on a Varian Unity/Inova 500 MHz spectrometer. Standard VNMR pulse sequences for correlation spectroscopy (gCOSY), nuclear overhauser effect spectroscopy (NOESY), heteronuclear single quantum coherence (gHSQC), and heteronuclear multiple bond correlation (gHMBC) were used. Thermolysis experiments were recorded on a Bruker Avance III 400 MHz spectrometer. Solvent proton and carbon peaks were used

as reference:  $^1\text{H}$  ( $\text{CD}_3\text{CN}$ ,  $\delta$  1.93 ppm),  $^{13}\text{C}$  ( $\text{CD}_3\text{CN}$ ,  $\delta$  1.3 ppm).  $\text{CD}_3\text{CN}$  was obtained from Cambridge Isotopes and was dried over  $\text{CaH}_2$  and vacuum transferred, and stored over molecular sieves for at least 2 days. *p*-Methoxybenzenediazonium tetrafluoroborate ( $\text{PMBD-BF}_4$ , 98%) was obtained from Sigma–Aldrich. Compound **1** was prepared as described previously [20].

## 2.2. Synthesis of **2-BF<sub>4</sub>**

$\text{PMBD-BF}_4$  (5.4 mg, 0.0243 mmol) was added to a suspension of **1** (13.7 mg, 0.0217 mmol), in 600  $\mu\text{L}$  of acetonitrile- $d_3$  (dried over  $\text{CaH}_2$  under reflux for 12 h and then stored for at least 2 days on activated molecular sieves) in a Wilmad J. Young-valved NMR tube. The mixture was shaken vigorously and exposed to an ultrasound bath for 45 s. The initial yellow insoluble precipitate went into the solution to form a deep orange solution. The solution was then cooled (or frozen with liquid nitrogen) until needed for NMR analysis. Attempts to obtain crystalline material yielded only oily/glassy material. Conversion is quantitative and free of side products as judged by NMR spectroscopy. However, within hours/days, decomposition occurs at room temperature. *m/z* [matrix assisted laser desorption ionization time-of-flight mass spectrometry, alpha-cyano-4-hydroxy cinnamic acid (MALDI-TOF-MS, CHCA) matrix] from all-protio sample, 764.3 ( $2^+$  with solv = empty;  $\text{C}_{38}\text{H}_{41}\text{N}_4\text{O}_1\text{Pt}^+$ ; isotope pattern: 764.3 (100%), 763.3 (70%), 765.3 (90%), 766.3 (30%), 767.3 (*ca* 20%)), 804.3 (small,  $2^+$ -minus-H with solv =  $\text{CH}_3\text{CN}$ ), 629.3 ( $1^+$ ), and 735.3 ( $2^+$ -minus-H-minus- $\text{N}_2$ ). NMR data for **2-BF<sub>4</sub>** are reported in table 1.

## 2.3. $^{15}\text{N}$ -NMR spectroscopy of **2-BF<sub>4</sub>**

$^{15}\text{N}$ - $^1\text{H}$  gHMBC spectra were recorded to indirectly detect  $^{15}\text{N}$  signals for those nitrogens (the  $\alpha$ -nitrogen on the  $\text{MeO-C}_6\text{H}_4$  fragment and the two non-equivalent nitrogens of *tert*-butyl-bipyridine) that show significant coupling to  $^1\text{H}$ . The experiment was optimized for an average  $^3J_{\text{NH}}$  coupling of 2 Hz.  $^{15}\text{N}$  shifts are referenced relative to external nitromethane contained in a coaxial capillary ( $\delta$  0.0 ppm) (see figures 4, 5, and 6 for spectra and table 1 for summary of resonances).

## 2.4. IR-spectroscopy of **2-BF<sub>4</sub>**

Room temperature spectra were obtained from a KBr pellet using a Nicolet Avatar 360 FT-IR instrument. Relevant absorbances ( $\text{cm}^{-1}$ ): 2244, m,  $\nu_{\text{CN}}$  of  $\text{MeCN}$ ; 1615, 1528, s,  $\nu_{\text{NN}}$  of aryldiazenido coupled to  $\delta_{\text{CH}}$  of arene.

## 2.5. Thermolysis of **2-BF<sub>4</sub>**

A  $\text{CD}_3\text{CN}$  solution of **2-BF<sub>4</sub>** (as prepared above) left standing at room temperature for many hours or days shows significant decomposition/conversion to other platinum(IV)-based products. The process can be accelerated if the solution is heated in a 50°C water bath, as monitored by  $^1\text{H}$ -NMR spectroscopy. Within 45 min of heating, approximately 85% of **2-BF<sub>4</sub>** was converted to a complex reaction mixture, where the main product,

Table 1. NMR data (CD<sub>3</sub>CN, 253 K) for 2<sup>+</sup>.

Label	A	A'	B	B'	C	C'	D	D'	E
$\delta$ ( <sup>1</sup> H)	8.21, d, $J_{HH} =$ 6.0 Hz, $J_{PH} \approx 14$ Hz, NOE to L	8.89, d, $J_{HH} =$ 5.8 Hz, $J_{PH}$ (nr), NOE to L', Q	7.60, dd, $J_{HH} =$ 6.0 Hz, 2.0 Hz	7.99, dd, $J_{HH} =$ 5.9 Hz, 1.9 Hz	–	–	8.52, d, $J_{HH} =$ 2.0 Hz	8.56, d, $J_{HH} =$ 1.9 Hz	–
$\delta$ ( <sup>13</sup> C) or $\delta$ ( <sup>15</sup> N)	150.8	147.3	125.4	125.6	167.1	167.4	123.4	123.1	154.2
Label	E'	F	F'	G	G'	H	H'	I, I'	J
$\delta$ ( <sup>1</sup> H)	–	–	–	–	–	1.39, s, NOE to B, D	1.48, s, NOE to B', D'	3.88 (acci- dently degener- ate AB- system), NOE to A, O, O'	–
$\delta$ ( <sup>13</sup> C) or $\delta$ ( <sup>15</sup> N)	154.7	–151.4	–135.8	36.5	36.6	30.0	30.1	46.7	140.1
Label	J'	K	K'	L	L'	M	M'	N	N'
$\delta$ ( <sup>1</sup> H)	–	–	–	7.84, dd, $J_{HH} =$ 7.7 Hz, 1.3 Hz, $J_{PH} \approx$ 39 Hz	6.49, dd, $J_{HH} =$ 8.1 Hz, 1.2 Hz, $J_{PH} \approx$ 48 Hz	7.13, dd d, $J_{HH} =$ 7.7 Hz, 7.1 Hz, 2.0 Hz	6.55, dd d, $J_{HH} =$ 8.1 Hz, 7.2 Hz, 1.7 Hz	7.18, dd d, $J_{HH} =$ 7.2 Hz, 7.1 Hz, 1.2 Hz	6.82, dd d, $J_{HH} =$ 7.3 Hz, 7.2 Hz, 1.2 Hz
$\delta$ ( <sup>13</sup> C) or $\delta$ ( <sup>15</sup> N)	141.0	134.4, $J_{PIC} =$ 906 Hz	124.7, $J_{PIC} =$ 970 Hz	136.1, $J_{PIC} \approx 22$ Hz	131.9, $J_{PIC}$ (nr).	127.1, $J_{PIC} \approx 36$ Hz	126.1, $J_{PIC} \approx 45$ Hz	126.5	126.3
Label	O	O'	P	Q	R	S	T	$\alpha$ -N	
$\delta$ ( <sup>1</sup> H)	$\delta$ 7.21, d d, $J_{HH} =$ 7.2 Hz, 1.7 Hz	$\delta$ 6.94, d d, $J_{HH} =$ 7.3 Hz, 1.7 Hz	–	7.49, d, $J_{HH} =$ 9.0 Hz	6.97, d, $J_{HH} =$ 9.0 Hz	–	3.80, s, NOE to R	–	
$\delta$ ( <sup>13</sup> C) or $\delta$ ( <sup>15</sup> N)	128.7, $J_{PIC} \approx 36$ Hz	128.3, $J_{PIC} \approx 45$ Hz	143.5, $J_{PIC} =$ 173 Hz	124.0, $J_{PIC} \approx 32$ Hz	114.9	162.0	56.1	128.5	

See figure 3 for labeling scheme.

assigned as the product resulting from aryl transfer (scheme 1), forms in approximately 65% NMR yield. For this major complex, a partial  $^1\text{H}$  spectrum ( $-20^\circ\text{C}$ ,  $\text{CD}_3\text{CN}$ , 500 MHz) is described. The *tert*-butyl peaks appear at 1.49 (s, 9H) and 1.43 (s, 9H) ppm, the diastereotopic methylene protons of the metallacycle appear at 3.22 (d, 1H,  $J_{\text{HH}}=16.7\text{ Hz}$ ,  $^4J_{\text{PtH}}$  of 13.6 Hz) and 3.53 (d, 1H,  $J_{\text{HH}}=16.7\text{ Hz}$ ,  $^4J_{\text{PtH}}=\text{broad}$ , unresolved), and the methyl peak of the methoxy group at 3.71 (s, 3H). The aromatic region, however, is complex. An *ortho* proton at 6.21 (d, 1H,  $J_{\text{HH}}=8.1\text{ Hz}$ ,  $^3J_{\text{PtH}}=54.7\text{ Hz}$ ) is clearly identified. A combination of gCOSY and NOESY assigns it as belonging to a Pt-bound  $\text{C}_6\text{H}_4\text{-OMe}$  unit. After 24 h,  $\mathbf{2}\text{-BF}_4$  has essentially decomposed completely.

### 3. Results and discussion

We recently synthesized a dihydroplatinaanthracene chelated by 4,4'-di-*tert*-butyl-2,2'-bipyridine, the platinum(II) complex **1** shown in figure 2 [20]. Oxidative addition of electrophiles is often a good method to oxidize platinum(II) to platinum(IV). Classic examples are  $\text{H}^+$  [21–24] or carbocation equivalents [25, 26]. Intrigued by the apparently untapped potential of aryldiazonium cations as electrophiles to generate platinum(IV) from platinum(II), we decided to react **1** with *p*-methoxybenzenediazonium cation,  $p\text{-MeO-C}_6\text{H}_4\text{-N}_2^+$  (PMBD $^+$ , as its  $\text{BF}_4$ -salt). We observed the rapid formation of a new species ( $\mathbf{2}^+$ ) that was assigned as a platinum(IV) aryldiazenido complex using multinuclear NMR spectroscopy, as will be described in the following section.

#### 3.1. General observations and $^1\text{H}$ -NMR spectroscopy

Compound **1** is sparingly soluble in acetonitrile. A slurry of **1** in  $\text{MeCN-d}_3$  was prepared as a pale yellow solution containing suspended yellow microcrystalline powder. The addition of 1.1 eq of PMBD- $\text{BF}_4$  under rapid shaking/sonication immediately led to a

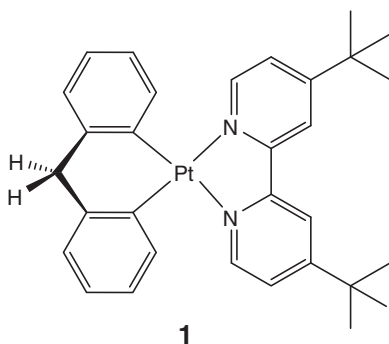
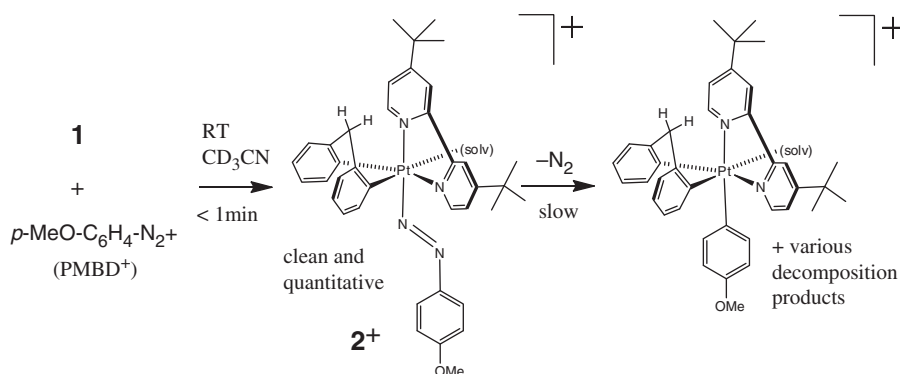


Figure 2. A 9,10-dihydroplatinaanthracene containing 4,4'-di-*tert*-butyl-2,2'-bipyridine (**1**). Due to the pucker in the metallacyclic ring, the methylene hydrogens are not equivalent, and the symmetry of the molecule is  $C_s$  (not  $C_{2v}$ ) [20].

reaction; the reaction mixture became clear and homogeneous and assumed an intense orange color. No gas bubbles were observed. The newly formed product is stable at room temperature for a couple of hours but decays if left at ambient temperature in solution over an extended period of time (see below). NMR characterization was done at  $-20^{\circ}\text{C}$ . If solvent is removed, the product is obtained as viscous oil that becomes glassy under vacuum. While we have not been able to obtain crystalline material, mass spectrometry (see below and section 2) confirms that a diazonium adduct of **1** has formed, and solution-based NMR spectroscopy allows for the determination of the solution structure. A  $^1\text{H}$ -NMR spectrum revealed that the newly formed complex has retained both the metallacyclic ring and the 4,4'-di-*tert*-butyl-2,2'-bipyridine and also has added the *p*-MeO-C<sub>6</sub>H<sub>4</sub>-N=N containing fragment. The addition has reduced the symmetry of the complex. While **1** contains a mirror plane, this plane of symmetry is lost in **2**<sup>+</sup> (see below). All arene hydrogens in the metallacyclic unit and in the bis-*tert*-butyl-bipyridine are non-equivalent in **2**<sup>+</sup>. Two *tert*-butyl resonances (each 9H) are observed. The question remains as to whether the metal coordination sphere contains a newly formed aryldiazenido ligand or a newly formed aryl ligand (implying N<sub>2</sub> loss). A Pt-bound aryl would be clearly discernible *via* Pt-coupling on the aryl hydrogens *ortho* to platinum. The arene hydrogens in the *p*-MeO-C<sub>6</sub>H<sub>4</sub>-N=N fragment are straightforwardly assigned by virtue of being two signals (superficially resembling doublets but actually AA'XX' spin systems, at 7.49 and 6.97 ppm) integrating to two protons each (free rotation of this dangling aryl). This assignment was confirmed with a NOESY experiment showing nuclear overhauser effect (NOE) between the OMe and the arene proton *ortho* to oxygen. No platinum coupling is observed for any aromatic hydrogen resonances of this *p*-MeO-C<sub>6</sub>H<sub>4</sub>-N=N fragment, conclusively ruling out that an aryl cation has added to platinum (*via* N<sub>2</sub> loss) and strongly suggesting that a diazenido ligand has formed. Taking the lack of symmetry in **2**<sup>+</sup> into account, the octahedral platinum(IV) structure shown in scheme 1 is assigned, which involves a doubly-bent diazenido ligand. NMR spectroscopy on nitrogen (see below) has been used to corroborate this assignment. While we formulate the structure in scheme 1 as six-coordinate, we have not observed a bound solvent molecule directly, neither by  $^1\text{H}$  nor by  $^{15}\text{N}$  (see below) NMR. A coordinated acetonitrile-*d*<sub>3</sub> molecule would be,



Scheme 1. Reaction of Pt(II) metallacycle **1** with aryldiazonium PMBD<sup>+</sup> to give Pt(IV).



of course, invisible in the  $^1\text{H}$ -NMR spectrum and, since it is deuterated, invisible in the  $^{15}\text{N}$ - $^1\text{H}$  gHMBC spectrum (see below) as well. No bound  $\text{CD}_3\text{CN}$  is observed in the  $^{13}\text{C}$ -NMR spectrum. Because the last 10 years have seen several examples of stable five-coordinate platinum(IV) species [27–33], the alternative possibility should be mentioned that  $\mathbf{2}^+$  may be truly five-coordinate. Mass spectrometry ( $\mathbf{2}^+$  from protioacetonitrile for MALDI-TOF) shows a clear large signal (with expected isotope pattern) for a species  $\mathbf{2}^+$  with solv = empty (highest intensity peak at  $m/z = 764.3$ ) and a very small signal for what may be a species  $\mathbf{2}^+$ -minus-H with solv =  $\text{CH}_3\text{CN}$  (highest intensity peak at  $m/z = 804.3$ ). Two more major signals correspond to  $\mathbf{1}^+$  ( $m/z = 629.3$ ) and  $\mathbf{2}^+$ -minus-H-minus- $\text{N}_2$  ( $m/z = 735.3$ ), indicating that loss of aryldiazonium or loss of  $\text{N}_2$ , respectively, are viable fragmentation pathways under mass spectrometry conditions.  $\mathbf{2}^+$  is stable at room temperature for a few hours, but slow decomposition occurs over a period of days. Heating the reaction mixture for several hours to  $50^\circ\text{C}$  speeds up the decomposition. In the mixture of products, we have been able to identify a species (*ca* 65% NMR yield) where  $\text{N}_2$  elimination has occurred, to attach the aryl to platinum, as indicated by the large platinum coupling (54.7 Hz, consistent with a platinum(IV) aryl [34]) to the *ortho* protons of the *p*-MeO- $\text{C}_6\text{H}_4$  unit in the new species (scheme 1). Fluorene, the expected product of reductive elimination from a 9,10-dihydroplatinanthracene [35], was not observed, supporting the proposal that Pt remains in the +IV oxidation state. The intriguing compound  $\mathbf{2}^+$  deserves detailed study of the nitrogen environment, and multinuclear (including  $^{15}\text{N}$  via  $^{15}\text{N}$ - $^1\text{H}$  gHMBC) NMR data have been obtained.

### 3.2. Detailed NMR spectroscopy, including $^{15}\text{N}$ -NMR via $^{15}\text{N}$ - $^1\text{H}$ gHMBC

The low natural abundance and low sensitivity of  $^{15}\text{N}$  prompted us to detect  $^{15}\text{N}$  via  $^1\text{H}$  in a 2-D experiment ( $^{15}\text{N}$ - $^1\text{H}$  gHMBC method). Two bipyridyl nitrogens are detected, each coupling to three hydrogens in their pyridyl ring. The observation of two distinct bipyridyl nitrogens confirms the low symmetry of the complex (*cis*-addition). Most importantly, the C-bound nitrogen of the aryldiazenido unit is observed. The aryl hydrogen *ortho* to N (in the *p*-MeO- $\text{C}_6\text{H}_4$ -NN fragment) couples sufficiently strongly to  $^{15}\text{N}$  to allow for the detection of a nitrogen NMR signal for the C-bound nitrogen (referred to as “ $\alpha$ -nitrogen” here). The  $\beta$ -nitrogen (Pt-bound) is, expectedly, invisible with this technique. The  $\alpha$ -nitrogen resonance is observed at  $\delta = +128.5$  ppm (relative to nitromethane). This chemical shift has excellent diagnostic value: it is known that  $\alpha$ -nitrogens of doubly-bent aryldiazenidos occur in the range from +40 to +165 ppm, with most examples between *ca* +130 and +165 ppm [5, 36]. Quite in contrast,  $\alpha$ -nitrogens of almost linear or singly-bent  $\text{Ar-N}_2$  units occur in a separate region, in the range from  $-250$  to +5 ppm, where most values range from  $-250$  to  $-190$  ppm [5, 36].  $^{15}\text{N}$ -NMR, thus, allows us to firmly conclude not only that nitrogen is retained in  $\mathbf{2}^+$ , but also that  $\mathbf{2}^+$  contains a monoanionic (reduced) aryldiazenido, such that the oxidation state of platinum is clearly Pt(IV). The most common coordination mode of reduced  $\text{ArN}_2$  (aryldiazenido) is doubly bent (in figure 1d). The side-on coordination mode [6, 37] (in figure 1c) would also imply reduced  $\text{ArN}_2$  but is quite rare.  $^{15}\text{N}$  data for side-on aryldiazenido have not been reported yet. Some evidence against side-on coordination in  $\mathbf{2}^+$  is arguably the still fairly “normal” (for doubly-bent diazenido) N–N stretch of  $\mathbf{2}^+$  in the infrared (IR)



spectrum ( $1615\text{cm}^{-1}$ , see section 2). Lower frequencies were noted for side-on diazenido coordinated to nickel(II) [6] and titanium(IV) [37] ( $1602$  and  $1550\text{cm}^{-1}$ , respectively), although the well-known coupling [38] between  $\nu(\text{NN})$  and  $\delta(\text{CH})$  makes a direct comparison difficult. Furthermore, NOESY data are more consistent with doubly bent than with side-on diazenido (see below). The structure of  $\mathbf{2}^+$ , as determined by a combination of  $^1\text{H}$  and  $^{13}\text{C}$  spectra, including gCOSY and NOESY spectra, as well as  $^{15}\text{N}$ - $^1\text{H}$  gHMBC experiments, is shown in figure 3, along with its labeling scheme. The methylene linker (I, I' in figure 3) of the metallacycle (appearing as an AB pattern that closely approximates a singlet due to nearly degenerate chemical shifts) shows NOE to the pyridyl *ortho*-proton appearing at 8.21 ppm. The protons of each pyridyl ring are assigned based on NOEs to their respective *t*-butyl group. The  $\text{MeO}-\text{C}_6\text{H}_4-\text{N}=\text{N}$  unit rotates freely about the  $\text{N}-\text{C}$  bond, and the protons *ortho* to  $\text{N}$  are clearly distinguished from the protons *meta* to  $\text{N}$  due to their coupling to  $^{15}\text{N}$ . A combination of gCOSY and NOESY spectra allows for the assignment of all metallacycle resonances. The doubly-bent geometry of the aryldiazenido naturally leads to close proximity of arene protons Q and bipyridine protons A' (NOE observed), whereas side-on coordination of aryldiazenido likely would put Q into proximity of L – no such NOE is observed. While the data appear more consistent with doubly-bent, end-on coordination of aryldiazenido rather than with side-on coordination, the assignment of redox state is independent of this detail; both doubly-bent and side-on  $\text{ArN}_2$  are reduced, such that the firm conclusion can be made that a platinum(IV) complex with a reduced aryldiazenido ligand is observed. Complete assignment of all nuclei observed is contained in table 1, referring to the labeling scheme in figure 3.  $^1\text{H}$ -NMR,  $^{15}\text{N}$ - $^1\text{H}$  gHMBC, and NOESY spectra are shown in figures 4, 5, and 6, respectively.

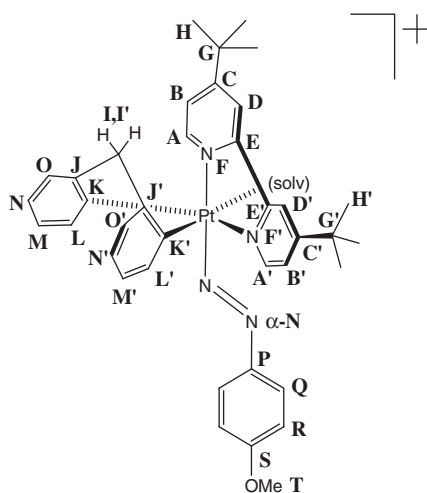


Figure 3. Labeling scheme for  $\mathbf{2}^+$  (see table 1 for NMR data and figures 4, 5, and 6 for NMR spectra).

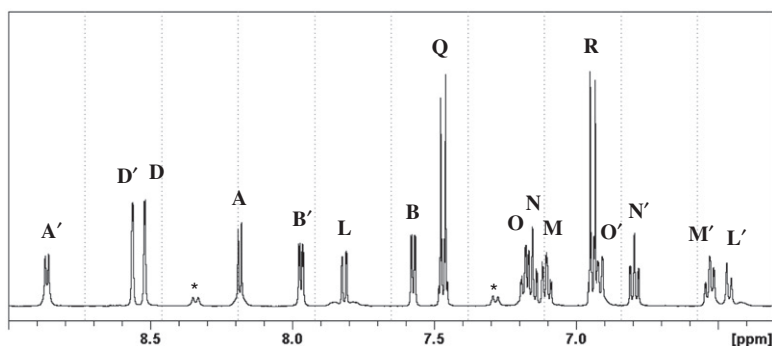


Figure 4.  $^1\text{H}$ -NMR spectrum (500 MHz) of the aromatic region of  $2^+$  ( $\text{CD}_3\text{CN}$ , 253 K) (see figure 3 for labeling scheme. “\*” denotes excess diazonium,  $\text{PMBD}^+$ ).

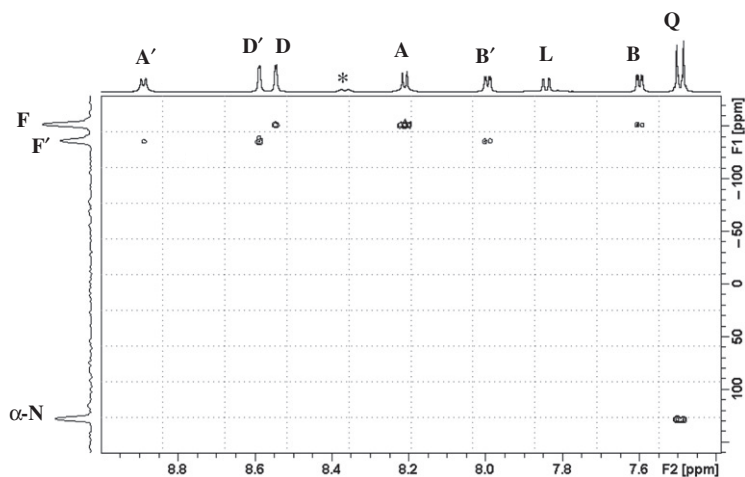


Figure 5.  $^{15}\text{N}$ - $^1\text{H}$  gHMBC spectrum of  $2^+$  ( $\text{CD}_3\text{CN}$ , 253 K) (see figure 3 for labeling scheme. “\*” denotes excess diazonium,  $\text{PMBD}^+$ ).

#### 4. Conclusion and outlook

We conclude that *para*-methoxybenzenediazonium cation oxidatively adds to 4,4'-di-*tert*-butyl-2,2'-bipyridine-chelated 9,10-dihydroplatinaanthracene to form an observable (stable for hours) aryldiazenido complex of platinum(IV). Experimental evidence for the reduced form of the nitrogen moiety was directly obtained from  $^{15}\text{N}$ -NMR spectroscopy. The new species decomposed slowly, in part by aryl cation transfer to platinum. While our interest in metallacycles has led us to perform the current investigation with a 9,10-dihydroplatinaanthracene, it should be very interesting in the future to study the behavior of conventional platinum(II) diaryls and dialkyls with diazonium cations. The study of diazonium addition to platinum(0) has led to fairly rich chemistry in the past. The addition of aryldiazonium to platinum(II), observed here, may suggest that oxidative addition of diazonium cations to platinum(II)

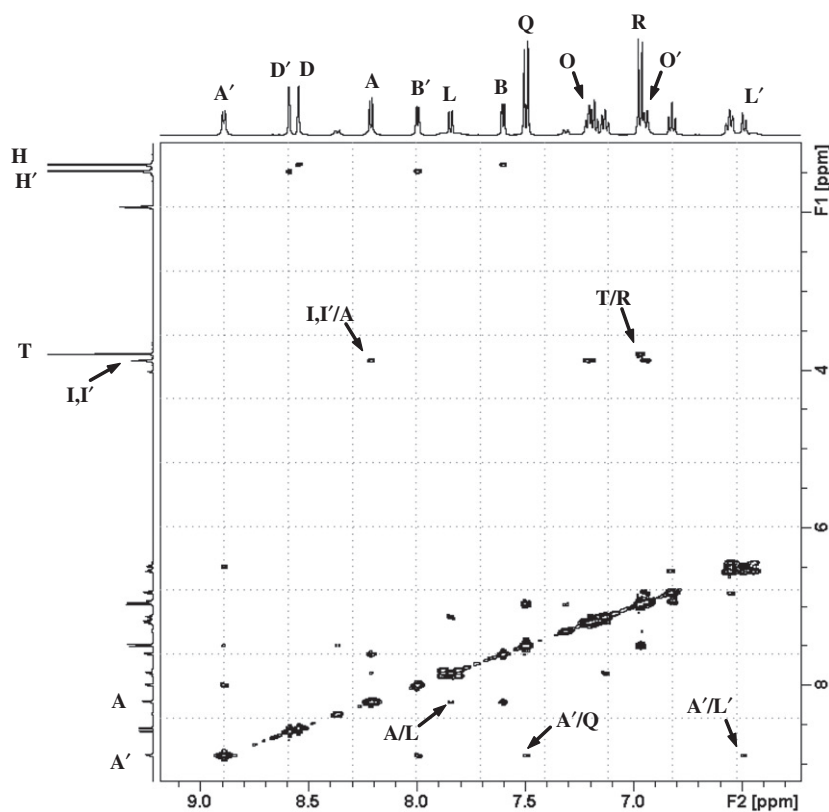


Figure 6. NOESY spectrum of  $2^+$  ( $\text{CD}_3\text{CN}$ , 253 K) (see figure 3 for labeling scheme and figure 4 for an enlarged  $^1\text{H-NMR}$  spectrum).

is a promising method for Pt-N (and potentially Pt-C) bond formation. Given the similarity between palladium and platinum, it may be speculated here that palladium(IV) species could be involved in Pd-catalyzed coupling reactions [39] involving aryldiazonium cations.

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