The First Aryldiazenido Complex of Platinum(IV):
An NMR-Study on the Addition of Aryldiazonium to Platinum(II)

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

Keywords: Platinum, NMR spectroscopy, $^{15}$N-NMR, aryldiazenium, aryldiazenido

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1. Introduction

Aryldiazonium cations, ArN$_2^+$ (Ar = aryl), are known as tremendously useful synthetic intermediates in organic synthesis. Their interaction with organic substrates often involves initial formation of a π-complex. [1] Actual synthetic transformations occur mostly under 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. Coordination of an aryldiazonium cation to a metal center can occur in various coordination modes (linear, singly bent, side-on, doubly bent, see Figure 1). [4,5,6] These adducts can be stable, may be amenable to further functionalization (such as hydrogenation of nitrogen [7,8]), or they may eliminate N$_2$ effecting oxidative addition of Ar$^+$ to the metal center. [9] It is relevant that redox chemistry can occur before 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]

![Figure 1](image-url)

**Figure 1.** Coordination modes of 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).
Platinum is one of the metals that have received significant attention in the context of aryl diazonium chemistry. Existing research has prepared platinum(II) products. Synthesis of bridged, dinuclear platinum(II) aryl diazenido complexes involves diazonium addition to ‘A-frame’ Pt(I)-Pt(I) dinuclear complexes. [12,13] Synthesis of mononuclear platinum(II) aryl diazenido complexes involves either a platinum(0) precursor or a platinum(0) equivalent. Isolated platinum(0) complexes have been used directly in reactions with aryl diazonium cations to form complexes of platinum(II) that contain an anionic aryl diazenido ligand 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. [16,17,18,19] For the latter reactions, there exists kinetic evidence that deprotonation of the metal-bound hydride can occur after addition of diazonium cation to the metal. [18] An intermediate on the reaction pathway may thus be a platinum(IV) aryl diazenido complex. However, no platinum(IV) aryl diazenido complex has been directly observed so far. 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 aryl diazenido ligand ArN$_2^-$ or (if the ligand acts as an internal base) [16] coordinated ArN$_2$H. Some complexes subsequently eliminated N$_2$ to form the corresponding platinum(II) aryl complexes.[14,15] Thus, while oxidation of platinum(0) to platinum(II) via 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) aryl diazenido complex, characterized by NMR spectroscopy.
2. 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]

![Diagram of compound 1](image)

**Figure 2.** A 9,10-dihydroplatinaanthracene containing 4,4’-di-tert-butyl-2,2’-bipyridine (compound 1). Due to the pucker in the metallacyclic ring, the methylene hydrogens are not equivalent, and the symmetry of the molecule is $C_3$ (not $C_{2v}$). [20]

Oxidative addition of electrophiles is often a good method to oxidize platinum(II) to platinum(IV). Classic examples are $\text{H}^+ [21,22,23,24]$ 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, $p$-MeO-C$_6$H$_4$-N$_2$\(^{+}\) (PMBD\(^{+}\), as its BF$_4^{-}$-salt). We observed rapid formation of a new species (2\(^{+}\)) that was assigned as a platinum(IV) aryldiazenido complex using multinuclear NMR spectroscopy, as will be described in the following section.

**General Observations and $^{1}{H}$-NMR spectroscopy**

Compound 1 is sparingly soluble in acetonitrile. A slurry of 1 in MeCN-d$_3$ was prepared, as a pale yellow solution containing suspended yellow microcrystalline powder. Addition of 1.1 eq of PMBD-BF$_4$ under rapid shaking/sonication immediately led to a 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 will decay if left at ambient temperature in solution over an extended period of time (see below). NMR characterization was done at –20 °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 Experimental Section) confirms that a diazonium adduct of 1 has formed, and solution-based NMR spectroscopy allows for determination of the solution structure. A $^1$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$_6$H$_4$-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 the product, complex 2$^+$ (see below). All arene hydrogens in the metallacyclic unit and in the bis-tert-butyl-bipyridine are non-equivalent in 2$^+$. Two tert-butyl resonances (each 9 H) 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$_2$ 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$_6$H$_4$-N=N fragment are straightforwardly assigned by virtue of being 2 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 NOE between the OMe and the arene proton ortho to oxygen. No platinum coupling is observed for any the aromatic hydrogen resonances of this $p$-MeO-C$_6$H$_4$-N=N fragment. This conclusively rules out that an aryl cation has added to platinum (via N$_2$ loss) and strongly suggests that a diazenido ligand has formed. Taking the lack of symmetry in 2$^+$ 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 $^1$H nor by $^{15}$N (see below) NMR. A coordinated acetonitrile-d$_3$ molecule would be, of course, invisible in the $^1$H-NMR spectrum and, since it is deuterated, invisible in the $^{15}$N-$^1$H gHMBC spectrum (see below) as well. No
bound CD₃CN is observed in the $^{13}$C NMR spectrum. Since the last ten years have seen several examples of stable five-coordinate platinum(IV) species, [27,28,29,30,31,32,33] the alternative possibility should be mentioned that $2^+$ may be truly five-coordinate. Mass spectrometry ($2^+$ from protio-acetonitrile for MALDI-TOF) shows a clear large signal (with expected isotope pattern) for a species $2^+$ with solv = empty (highest intensity peak at m/z = 764.3) and a very small signal for what may be a species $2^+$-minus-H with solv = CH₃CN (highest intensity peak at m/z = 804.3). Two more major signals correspond to $1^+$ (m/z = 629.3) and $2^+$-minus-H-minus-N₂ (m/z = 735.3), indicating that loss of aryldiazonium or loss of N₂, respectively, are viable fragmentation pathways under mass spectrometry conditions. $2^+$ 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 °C speeds up the decomposition reaction. In the mixture of products, we have been able to identify a species (ca. 65% NMR yield) where N₂ 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-C₆H₄ unit in the new species (Scheme 1). Fluorene, the expected product of reductive elimination from a 9,10-dihydroplatinaanthracene [35], was not observed, supporting the proposal that Pt remains in the +IV oxidation state. The intriguing compound $2^+$ deserves detailed study of the nitrogen environment, and multinuclear (including $^{15}$N via $^{15}$N-$^1$H gHMBC) NMR data have been obtained.

**Scheme 1**
**Detailed NMR spectroscopy, including $^{15}$N-NMR via $^{15}$N-$^1$H gHMBC**

The low natural abundance and low sensitivity of $^{15}$N prompted us to detect $^{15}$N via $^1$H in a 2D experiment ($^{15}$N-$^1$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 again the low symmetry of the complex (cis-addition). Most importantly, the C-bound nitrogen of the aryl diazenido unit is observed. The aryl hydrogen *ortho* to N (in the $p$-MeO-$C_6H_4$-NN fragment) couples sufficiently strongly to $^{15}$N to allow for 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 aryl diazenidos 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 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] $^{15}$N-NMR thus allows us to firmly conclude not only that nitrogen is retained in $2^+$ but also that $2^+$ contains a monoanionic (reduced) aryl diazenido, such that the oxidation state of platinum is clearly Pt(IV). The most common coordination mode of reduced ArN$_2$ (aryl diazenido) is doubly bent (d in Figure 1). The side-on coordination mode [6,37] (c in Figure 1) would also imply reduced ArN$_2$ but is quite rare. $^{15}$N data for side-on aryl diazenido have not been reported yet. Some evidence against side-on coordination in $2^+$ is arguably the still fairly ‘normal’ (for doubly bent diazenido) N-N stretch of $2^+$ in the IR spectrum (1615 cm$^{-1}$, see Experimental Section). Lower frequencies were noted for side-on diazenido coordinated to nickel(II) [6] and titanium(IV) [37] (1602 cm$^{-1}$ and 1550 cm$^{-1}$, respectively), although the well-known coupling [38] between $\nu$(NN) and $\delta$(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 complex $2^+$, as determined by a combination of $^1$H and $^{13}$C spectra, including gCOSY and NOESY spectra, as well as $^{15}$N-$^1$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 due to showing NOEs to their respective t-butyl group. The MeO-C₆H₄-N=N unit rotates freely about the N-C bond, and the protons ortho to N are clearly distinguished from the protons meta to N due to their coupling to ¹⁵N. A combination of gCOSY and NOESY spectra allows for assignment of all metallacycle resonances. The doubly-bent geometry of the aryldiazenido naturally leads to the 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 ArN₂ 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. ¹H-NMR, ¹⁵N-¹H gHMBC and NOESY spectra are shown in Figures 4, 5, and 6, respectively.
**Figure 3.** Labeling scheme for $2^+$. See Table 1 for NMR data and Figures 4, 5 and 6 for NMR spectra.
Table 1. NMR data (CD$_3$CN, 253 K) for $2^+$. See Figure 3 for labeling scheme.

<table>
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<th>Label</th>
<th>A</th>
<th>A'</th>
<th>B</th>
<th>B'</th>
<th>C</th>
<th>C'</th>
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<td>$\delta$ ($^1$H)</td>
<td>8.21, d, $\delta_{HH} = 6.0$ Hz, $\delta_{PH} \approx 14$ Hz, NOE to L.</td>
<td>8.89, d, $\delta_{HH} = 5.8$ Hz, $\delta_{PH}$ (nr), NOE to L', Q.</td>
<td>7.60, dd, $\delta_{HH} = 5.9$ Hz, NOE to L.</td>
<td>8.52, d, $\delta_{HH} = 2.0$ Hz.</td>
<td>8.56, d, $\delta_{HH} = 1.9$ Hz.</td>
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<td>$\delta$ ($^{13}$C) or $\delta$ ($^{15}$N)</td>
<td>150.8</td>
<td>147.3</td>
<td>125.4</td>
<td>125.6</td>
<td>167.1</td>
<td>167.4</td>
<td>123.4</td>
<td>123.1</td>
<td>154.2</td>
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<th>G</th>
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<th>L</th>
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<td>-</td>
<td>-</td>
<td>-</td>
<td>7.84, dd, $\delta_{HH} = 7.7$ Hz, $\delta_{PH} \approx 13$ Hz</td>
<td>6.49, dd, $\delta_{HH} = 8.1$ Hz, $\delta_{PH} = 1.2$ Hz</td>
<td>7.13, dd, $\delta_{HH} = 7.1$ Hz, $\delta_{PH} = 2.0$ Hz.</td>
<td>6.55, dd, $\delta_{HH} = 7.2$ Hz, $\delta_{PH} = 1.7$ Hz.</td>
<td>7.18, dd, $\delta_{HH} = 7.3$ Hz, $\delta_{PH} = 1.2$ Hz.</td>
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<td>$\delta$ ($^{13}$C) or $\delta$ ($^{15}$N)</td>
<td>141.0</td>
<td>134.4, $\delta_{PC} = 906$ Hz.</td>
<td>124.7, $\delta_{PC} = 970$ Hz.</td>
<td>136.1, $\delta_{PC} \approx 22$ Hz.</td>
<td>131.9, $\delta_{PC}$ (nr).</td>
<td>127.1, $\delta_{PC} \approx 36$ Hz.</td>
<td>126.1, $\delta_{PC} \approx 45$ Hz.</td>
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<th>S</th>
<th>T</th>
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<td>$\delta_{7.21, d}$, $\delta_{6.94, d}$, $\delta_{6.97, d}$, $\delta_{6.97, d}$, $\delta_{9.0, Hz}$, $\delta_{9.0, Hz}$, $\delta_{3.80, s}$, NOE to R.</td>
<td>-</td>
<td>7.49, d, $\delta_{HH} = 9.0$ Hz.</td>
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<td>-</td>
<td>3.80, s, NOE to R.</td>
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<tr>
<td>$\delta$ ($^{13}$C) or $\delta$ ($^{15}$N)</td>
<td>128.7, $\delta_{PC} \approx 36$ Hz.</td>
<td>128.3, $\delta_{PC} \approx 45$ Hz.</td>
<td>143.5, $\delta_{PC} \approx 32$ Hz.</td>
<td>124.0, $\delta_{PC} \approx 173$ Hz.</td>
<td>114.9</td>
<td>162.0</td>
<td>56.1</td>
<td>128.5</td>
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Figure 4. $^1$H-NMR spectrum (500 MHz) of the aromatic region of $2^+$ (CD$_3$CN, 253 K). See Figure 3 for labeling scheme. "*" denotes excess diazonium, PMBD$^+$. 

Figure 5. $^{15}$N-$^1$H gHMBC spectrum of $2^+$ (CD$_3$CN, 253 K). See Figure 3 for labeling scheme. "*" denotes excess diazonium, PMBD$^+$. 
Figure 6. NOESY spectrum of $2^+$ (CD$_3$CN, 253 K). See Figure 3 for labeling scheme and Figure 4 for an enlarged $^1$H-NMR spectrum.
3. 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 $^{15}$N-NMR spectroscopy. The new species slowly decomposed, 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) is a promising method for Pt-N bond (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.

4. Experimental Section

General techniques

All manipulations involving organometallic compounds were carried out under inert-atmosphere conditions (vacuum line/glove box) using oven-dried glassware. NMR spectra (CD$_3$CN solution, -20 °C unless otherwise noted) were obtained on a Varian Unity/Inova 500 MHz spectrometer. Standard VNMR pulse sequences for gCOSY, NOESY, gHSQC and gHMBC were used. Thermolysis experiments were recorded on a Bruker Avance III 400 MHz spectrometer. Residual proton and carbon peaks were used as reference: $^1$H (CD$_3$CN, δ 1.93 ppm), $^{13}$C (CD$_3$CN, δ 1.3 ppm). CD$_3$CN was obtained from Cambridge Isotopes and was dried over CaH$_2$ and vacuum-transferred, stored over molecular sieves for at least 2 days. $p$-Methoxybenzenediazoniumentetrafluoroborate
(PMBD-BF\textsubscript{4}, 98\%) was obtained from Sigma-Aldrich. Compound \textbf{1} was prepared as previously described. [20]

\textit{Synthesis of 2-BF\textsubscript{4}}

\textit{para}-methoxybenzenediazoniumtetrafluoroborate, PMBD-BF\textsubscript{4}, (5.4 mg, 0.0243 mmol) was added to a suspension of \textbf{1} (13.7 mg, 0.0217 mmol), in 600 \textmu L of acetonitrile-\textit{d}\textsubscript{3} (dried over CaH\textsubscript{2} under reflux for 12 hours and then 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 seconds. The initially yellow insoluble precipitate went into 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 [MALDI-TOF-MS, CHCA matrix] from all-protoio sample, 764.3 (2\textsuperscript{+} with solv = empty; C\textsubscript{38}H\textsubscript{41}N\textsubscript{4}O\textsubscript{1}Pt\textsuperscript{1}+; isotope pattern: 764.3 (100 \%), 763.3 (70 \%), 765.3 (90 \%), 766.3 (30 \%), 767.3 (ca. 20 \%)), 804.3 (small, 2\textsuperscript{+}-minus-H with solv = CH\textsubscript{3}CN), 629.3 (1\textsuperscript{+}), 735.3 (2\textsuperscript{+}-minus-H-minus-N\textsubscript{2}). NMR data for 2-BF\textsubscript{4} are reported in Table 1.

\textit{\textsuperscript{15}N-NMR spectroscopy of 2-BF\textsubscript{4}}

\textit{\textsuperscript{15}N-\textsuperscript{1}H gHMBC} spectra were recorded to indirectly detect \textit{\textsuperscript{15}N} signals for those nitrogens (the \textit{\alpha}-nitrogen on the MeO-C\textsubscript{6}H\textsubscript{4} fragment and the two non-equivalent nitrogens of \textit{tert}-butyl-bipyridine) that show significant coupling to \textsuperscript{1}H. The experiment was optimized for an average \textsuperscript{3}J\textsubscript{NH} coupling of 2 Hz. \textit{\textsuperscript{15}N} shifts are referenced relative to external nitromethane contained in a coaxial capillary (\textdelta 0.0 ppm). See Figure 5 for spectrum and Table 1 for summary of resonances.
**IR-spectroscopy of 2-BF₄**

Room temperature spectra were obtained from a KBr pellet using a Nicolet Avatar 360 FT-IR instrument. Relevant absorbances (cm⁻¹): 2244, m, ν₉CN of MeCN; 1615, 1528, s, νNN of aryldiazenido coupled to δCH of arene.

**Thermolysis of 2-BF₄**

A CD₃CN solution of 2-BF₄ (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 ¹H NMR spectroscopy. Within 45 min of heating, approximately 85% of 2-BF₄, was converted to a complex reaction mixture, where the main product, assigned as the product resulting from aryl transfer (see Scheme 1), forms in approximately 65% NMR yield. For this major complex, a partial ¹H spectrum (-20 °C, CD₃CN, 500 MHz) is described. The tert-butyl peaks appear at 1.49 (s, 9H) and 1.43 (s, 9H) ppm, the diasterotopic methylene protons of the metallacycle appear at 3.22 (d, 1H, JHH = 16.7 Hz, JPH of 13.6 Hz), and 3.53 (d, 1H, JHH = 16.7 Hz, JPH = 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, JHH = 8.1 Hz, JPH = 54.7 Hz) is clearly identified. A combination of gCOSY and NOESY assigns it as belonging to a Pt-bound C₆H₄-OMe unit. After 24 hours, 2-BF₄ has essentially completely decomposed.

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