



Promoting C–C Bond Coupling of Benzyne and Methyl Ligands in Electron-Deficient (triphos)Pt–CH₃⁺ Complexes

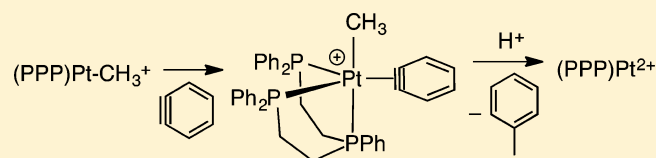
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S Supporting Information

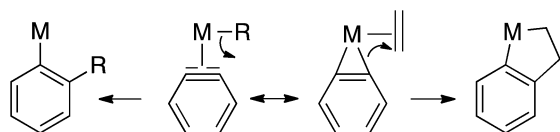
ABSTRACT: In situ generated benzyne reacts at room temperature with (triphos)Pt–CH₃⁺ to form a five-coordinate π -complex (**2**) that is isolable and stable in solution. Thermolysis of **2** at 60 °C generates (triphos)Pt(o-tolyl)⁺ (**3**), which is the product of formal migratory insertion of CH₃[–] onto the coordinated benzyne. The reaction of **2** with the acid Ph₂NH₂⁺ yields toluene at room temperature over the course of 8 h, while the same reaction with **3** only proceeds to 40% conversion over 2 days. These data indicate that the protonolysis of **2** does not proceed by CH₃ migration onto benzyne to form **3** followed by protodemetalation. Instead, the data suggest either that protonation of **2** is first and is followed by H migration to yield a Pt^{IV}Ph(Me) dication or that this latter species is generated by direct protonolysis of coordinated benzyne prior to reductive elimination of toluene.



INTRODUCTION

The organometallic chemistry of benzyne is a fascinating one,¹ as it simultaneously stabilizes the reactive intermediate and guides its subsequent reactivity in catalysis/synthesis.^{2–4} Its coordination chemistry is best described by contributions from the π -L and X₂ formulations, each of which can be invoked to explain its migratory insertion characteristics (Scheme 1).² In

Scheme 1

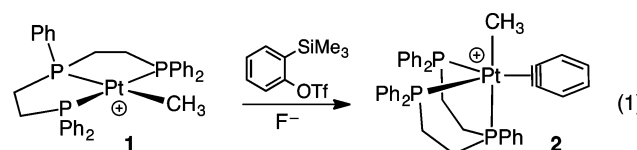


the neutral π -donor formulation it can couple with X ligands, while the X₂ formulation helps to rationalize its coupling with other π -donors.^{3,4} Broadly speaking, the majority of isolable π -benzyne complexes either are zerovalent (e.g., Ni⁰)⁵ or have readily available $n + 2$ oxidation states (e.g., Nb(III)).^{1,2}

In the context of a project whose goals are to utilize the unique electrophilic character of P₃Pt²⁺ complexes⁶ for electrophilic cascade cyclizations,^{7–9} we sought to explore the reactivity of (triphos)Pt–CH₃⁺ with arynes, in the hope that they might couple in a way that revealed novel turnover mechanisms. In this contribution we describe the synthesis and characterization of an isolable benzyne adduct of (triphos)Pt–CH₃⁺, describe its thermolysis with an eye to CH₃/benzyne coupling, delineate its reactivity toward mild acid sources, and analyze the mechanistic implications thereof.

RESULTS AND DISCUSSION

The reaction of (triphos)Pt–CH₃⁺ (**1**) with in situ generated benzyne (*o*-trimethylsilylphenyl triflate/CsF)¹⁰ in CH₃CN cleanly yields an air-stable yellow complex, **2**, that analyzes for a 1:1 adduct of benzyne and **1** (eq 1).¹¹ Complex **2** is stable



in chloroform solutions for several hours at room temperature, which enabled full characterization by multinuclear (¹H, ³¹P, and ¹³C) NMR spectroscopy and mass spectrometry (HRMS). The ³¹P NMR spectrum of **2** indicated a significant change in structure, as each resonance shifted to higher field relative to **1** (³¹P: 41.3 ppm, 1P, ¹J_{PtP} = 2737 Hz; 96.3 ppm, 2P, ¹J_{PtP} = 1527 Hz), and the corresponding Pt–P coupling constants dropped relative to those of typical square-planar [(triphos)Pt(R)][BF₄] complexes (R = alkyl, aryl).^{12,13} In **2**, the terminal P atoms are equivalent and appear as a singlet at 20.3 ppm with platinum satellites ¹J_{PtP} = 2223 Hz, while the central P is also a singlet at 49.8 ppm with Pt satellites (¹J_{PtP} = 1182 Hz). The equivalency of the terminal P atoms together with the Pt satellites show that triphos still acts as a pincer ligand in **2**. The ¹H NMR spectrum was similarly informative with the ¹⁹⁵Pt satellites in the methyl ligand (δ 0.74, ²J_{PtH} = 55 Hz; cf. 61.6 Hz in **1**) also indicating that the Pt–Me remains. Heating **2** to 40 °C for 30 min causes partial loss (~35%) of benzyne and re-formation of **1**.

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The spectroscopic data are consistent with benzyne binding **1** in a fashion that maintains the connectivity of the (triphos)Pt-CH₃⁺ fragment. The upfield shift of the central P ligand (loss of angle strain)¹⁴ and the decreased Pt-P coupling constants additionally suggest that triphos has shifted from a square-planar P₃Pt arrangement to a facial geometry where the three Ps are no longer coplanar with Pt. Amine-coordinated trigonal-bipyramidal (tbp) Pt(II) alkene models¹⁵ suggest a similar geometry for **2**.

Although crystals suitable for X-ray diffraction could not be obtained, DFT calculations on a model replacing the P-Ph groups in triphos for P-H groups indicated that the Gibbs free energy for coordinating free benzyne to **1** was favored by nearly 9 kcal/mol ($\Delta H = -22$ kcal/mol).¹⁷ This structure converged to a distorted tbp with the benzyne and the methyl group occupying equatorial and axial positions, respectively (Figure 1). In L₂PtX₂(η^2 -alkene) and L₃PtX(η^2 -alkene)⁺ complexes, the

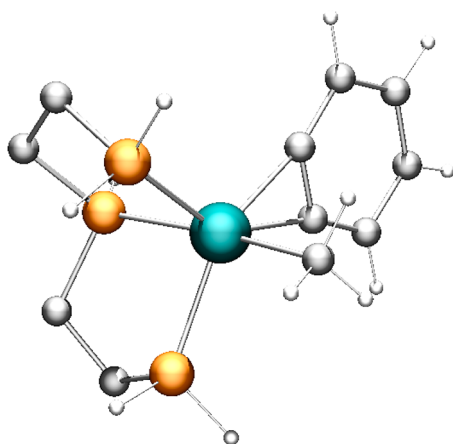
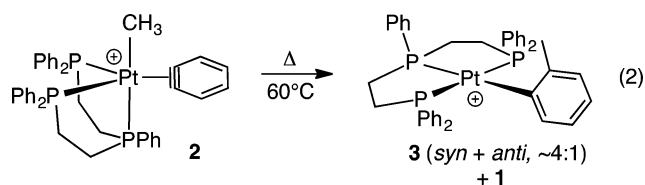


Figure 1. Geometry optimized DFT structure of **2**, substituting P-Ph for P-H (i.e., **comp2**). See the Supporting Information for computational details.

alkene is strongly biased to equatorial coordination.^{15,16} Consistent with this trend, the isomer that exchanges the benzyne and methyl positions lies 9.0 kcal/mol higher in energy (DFT).

Thermolysis of **2** occurs smoothly at 60 °C in chlorobenzene over 3 days to yield two isomers of a new species (**3**) along with a minor quantity of **1** from benzyne loss (2.4:1, eq 2). The

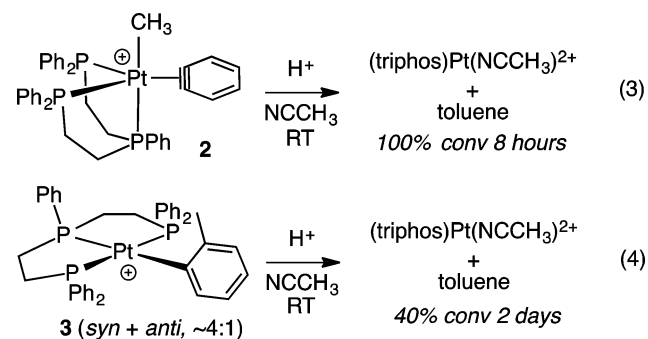


downfield shift of the central P in the ³¹P NMR spectrum suggests that **3** has returned to the square-planar geometry. It was characterized by a set of singlets at δ 36.0/36.7 (¹J_{PtP} = 2760/2706 Hz) and 92.3/91.0 ppm (¹J_{PtP} = 1491/1490 Hz) for the major/minor isomers, respectively. (triphos)Pt-*o*-tolyl⁺ was independently synthesized,¹³ to test for the possibility of a benzyne-methyl coupling.^{18–20} As synthesized, this complex exists as a ~4:1 mixture of syn and anti rotamers due to hindered rotation about the Pt-aryl bond and was spectroscopically identical with the thermolysis product **3**. The major isomer was assigned the syn orientation (to the

central P-Ph) on the basis of its similarity to known asymmetrically substituted Pt-aryl complexes.⁸

This reactivity thus demonstrates the feasibility of Pt-Me migratory insertion onto a coordinated benzyne to yield a Pt-aryl complex in an electron-deficient environment. Frequency corrected DFT calculations show the ΔG value for the insertion in eq 2 to be -62 kcal/mol (see the Supporting Information for details).

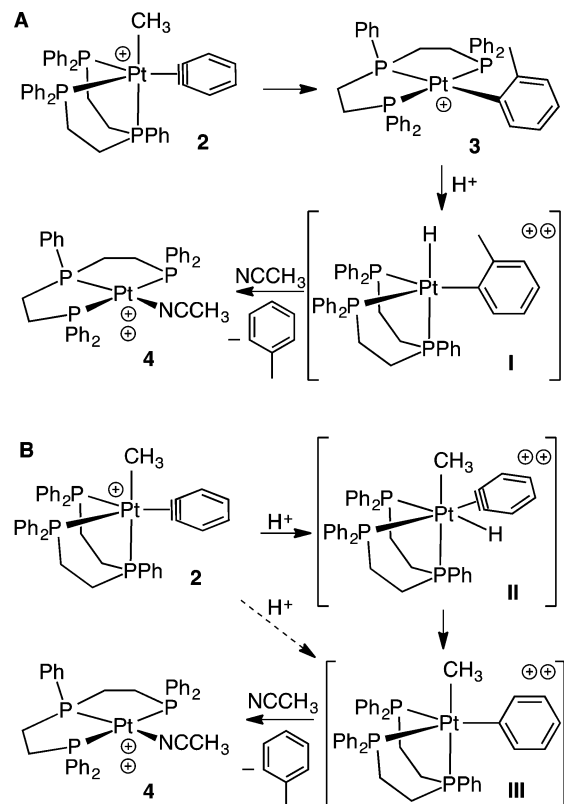
The comparative protonolysis behavior of **2** and **3** was examined next. Reacting **2** with a 10-fold excess of [Ph₂NH₂]-[BF₄] in CH₃CN at room temperature ($pK_a \approx 0.8$)²¹ led to rapid consumption of starting material and generation of toluene and (triphos)Pt(NCCH₃)²⁺ (**4**) (100% conversion in 8 h, eq 3).²² In contrast, protonolysis of the aryl complex **3** only



reached 40% conversion to toluene over 2 days under the same conditions (eq 4). The formation of toluene was monitored and quantified by GC.

Two mechanisms for toluene production were considered (Scheme 2). The first was thermally induced migratory

Scheme 2



insertion of the methyl group onto the coordinated benzyne to give the tolyl complex **3**, followed by Pt–Ar bond protonolysis through intermediate **I**²³ (Scheme 2A). The bicyclo angle strain inherent to the square-planar geometry has previously been shown to facilitate the addition of electrophiles (X = H⁺, F⁺) to (triphos)Pt–CH₃⁺ as the strain is relieved in the five-coordinate Pt^{IV}–methyl(X) intermediate that precedes X–C reductive elimination (i.e., ground-state destabilization).^{12,13,24} The slow kinetics of the elementary steps in this mechanism (eqs 2 and 4), however, indicate that it is not competitive.

A second possibility initiates with protonolysis of **2** to yield the octahedral intermediate **II** (Scheme 2B), followed by H-migratory insertion to **III** and C–C reductive elimination to the observed products.²³ An alternative mechanism that avoids invoking a Pt^{IV}–benzyne complex has the protonolysis occurring directly at the benzyne ligand to yield **III**.^{25–28} Both mechanisms combine benzyne and H⁺ on the coordination sphere of the metal to yield the product of a formal addition of Ph⁺ to **1** (**III**). Experimentally, we have been unable to successfully add Ph⁺ sources to (triphos)Pt–R⁺ complexes or Me⁺ to (triphos)Pt–Ar⁺ complexes to achieve such a coupling. The inner-sphere coupling of benzyne and H⁺ thus provides an alternative approach to achieving productive C–C couplings.

Giving credence to the benzyne protonolysis possibility were efforts to computationally characterize **II**. All attempts were unsuccessful, as the various starting geometries either did not converge onto chemically meaningful structures or they minimized along reaction trajectories that eliminated methane or formed the tolyl hydride structure (Me migration).

Attempts to react benzyne with other (triphos)Pt–X⁺ compounds (X = Ph, 2-PhAr, 2,4-Me₂Ar, I) were not successful (i.e., no reaction), nor were reactions of **1** with nonstrained alkynes such as PhCCH and 3-hexyne.¹⁷

In conclusion, we have successfully demonstrated that (triphos)Pt–CH₃⁺ can expand its coordination sphere to the t_{bp} geometry, provided that the reacting alkyne is sufficiently strained/reactive. Moreover, the resulting 18-electron complex was susceptible to protonolysis with mild acid and led to a net Ph⁺/CH₃[–] coupling to give toluene. A mechanism that initiates by H migration or direct protonolysis of coordinated benzyne to generate a dicationic Pt^{IV}Ph(Me) complex prior to reductive elimination of toluene is implicated.

■ ASSOCIATED CONTENT

Supporting Information

Text, figures, and an XYZ file giving synthetic and characterization data, computational procedures, and optimized structures. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00121.

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Notes

The authors declare no competing financial interest.

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