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Autocatalytic Alkyne Cycloadditions: Evidence for Colloidal Pt Catalysis

Rowshan Ara Begum, Nripen Chanda, T. V. V. Ramakrishna, and Paul R. Sharp*

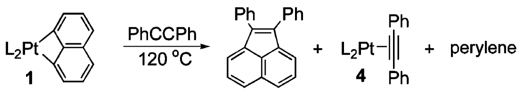
Department of Chemistry, University of Missouri, 125 Chemistry Building, Columbia, Missouri 65211

Received July 20, 2005; E-mail: SharpP@missouri.edu

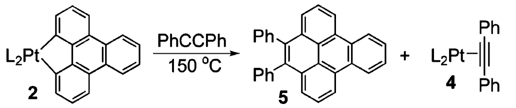
Metal-mediated cycloadditions are important chemical reactions.[1−6] Metallacycles, intermediates in many of these reactions, have been intensively investigated over the years and shown to give cycloaddition products with alkynes.[7−11] Herein, we report alkyne cycloaddition reactions of two members of a little-studied metallacycle class, where the metallacycles are fused to the edge of polycyclic aromatic carbon compounds (PAC's).

The two platinacycles **1** and **2** are readily synthesized from L_2PtCl_2 (L = PEt_3) and the dilithio PAC's (Scheme 1).[12] Complex **1**, a rare four-membered example of this class of metallacycles,[13−15] may also be prepared by Na/Hg reduction of **3** or, as previously reported, from L_2PtCl_2 and $[Mg(1,8\text{-naphthalendiyl})]_4$.[13] Both **1** and **2** are thermally robust and withstand heating in toluene solution to more than 150 °C for hours with no observable decomposition.

Part of our interest in this class of metallacycles is for the synthesis of larger, more complex PAC's through coupling and cycloaddition reactions.[16] We, therefore, studied the reactions of **1** and **2** with alkynes under N_2. At 25 °C, there is no reaction between **1** and PhCCPh in toluene solution. However, heating the mixture to 120 °C gives, after several hours, a clear yellow solution containing the cycloaddition product 1,2-diphenylacenaphthylene[17] (64% isolated yield), perylene (18%), and alkyne complex **4**[18] (quantitative yield by NMR) (eq 1). Similar reactions with the alkynes RCCR (R = Et, CO_2Me, CO_2Et) give the expected acenaphthylenes. An analogous reaction of **2** and PhCCPh at 150 °C yields cycloaddition product 4,5-diphenylbenzo[*e*]pyrene **5** (86% isolated yield) and **4** (eq 2).



(1)

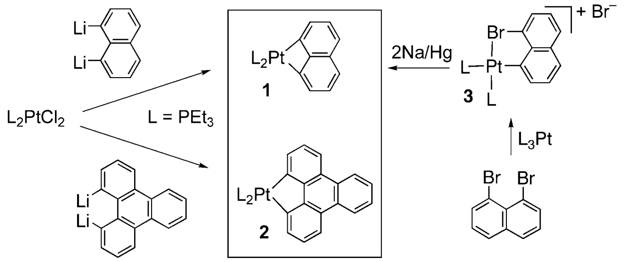


(2)

As the reaction in eq 1 is the first example of an alkyne cycloaddition reaction of a four-membered PAC metallacycle,[14,15] we investigated the kinetics of the reaction. Plots of the concentration of **1** versus time for the reaction of **1** with 2 equiv of PhCCPh under different atmospheric conditions are given in Figure 1. There are two notable features: (1) each set of data cannot be fit to any simple order rate law with the unusual downward curvatures of the plots indicating an accelerating reaction rate, and (2) the reaction is sensitive to O_2 with the slowest reaction in a vacuum-sealed tube (blue circles), the fastest with added O_2 (red squares), and intermediate in a dinitrogen atmosphere (green triangles).

Accelerating reaction rates are encountered in autocatalytic reactions,[19,20] where a product is a catalyst for the reaction, and in colloidal metal-catalyzed organic reactions, where the colloid is produced during the reaction by an autocatalytic nucleation and growth process.[21,22]

Scheme 1



Consistent with the generation of a catalyst during the reaction, re-addition of **1** and alkyne to a completed N_2 reaction mixture results in a rapid initial reaction rate without the downward curvature of Figure 1. This could result if the product alkyne complex **4** is a catalyst, and indeed, when independently prepared **4** is added to a fresh reaction mixture, a rapid initial reaction rate is observed. However, while **4** must be a catalyst precursor under the reaction conditions, it is not itself a catalyst as **4** does not react with **1** in the absence of alkyne.

The O_2 sensitivity of the cycloaddition reaction suggests that O_2 is involved in catalyst generation.[23] To explore this, separate solutions of **1** and **4** were heated for 1 h with 0.2 equiv of O_2. By ^{31}P NMR spectroscopy, there is no observed change in **1**, but **4** showed the formation of a small amount of Et_3PO. These solutions were then degassed and used to prepare cycloaddition reactions under N_2. The reaction prepared from the treated solution of **1** followed the same reaction curve as an untreated sample. In contrast, the reaction prepared from the treated solution of **4** gave a greatly enhanced reaction rate over a similar untreated sample and was comparable to the fastest rate observed in the reaction conducted

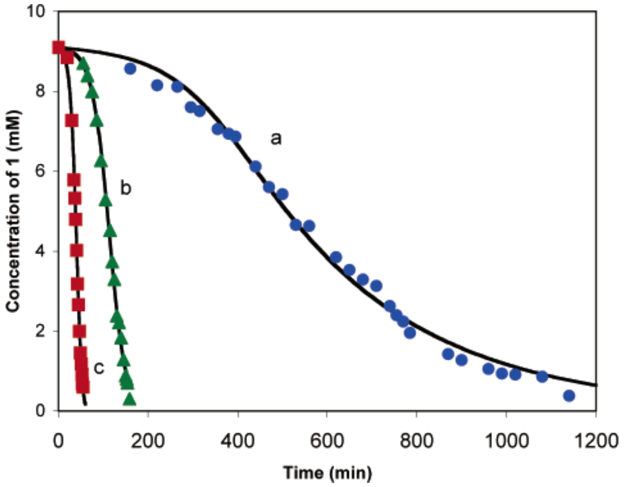


Figure 1. Plot of the concentration of **1** versus time for the reaction in eq 1 (2 equiv of PhCCPh, 120 °C): (a) blue dots, vacuum-sealed; (b) green triangles, under N_2; (c) red squares, 30 μL of O_2 (0.2 equiv). Line traces represent fitted curves (see text).

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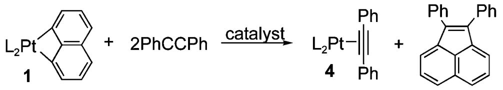
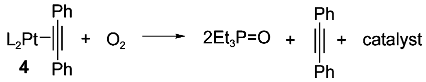
with added O_2. We conclude that the reaction of **4** with O_2 yields the catalyst. Taking these observations together, we propose the reaction sequence of eqs 3 and 4.



(3)



(4)

A simplified mechanism based on this scheme is given in eqs 5 and 6 and was used to fit the data in Figure 1 (solid lines). First, the kinetics of reaction 6 (i.e., reaction 4) were determined by monitoring the reaction of **4** with various amounts of excess O_2. The reaction proceeds as indicated and is first order in **4** and O_2 with $k_2 = 0.0052(3)$ mM^{-1} min^{-1} at 120 °C. This k_2 and the known $[O_2]$ for the O_2-added cycloaddition reaction were fitted to the data in Figure 1 (red squares) solving for the initial catalyst concentration and k_1. The resulting k_1 (20(1) mM^{-1} min^{-1}) and the previously determined k_2 were then used to fit the vacuum (blue circles) and N_2 (green triangles) data in Figure 1 solving for the initial catalyst and O_2 concentrations. The fit of all three data sets is remarkably good considering the simple two-step mechanism of eqs 5 and 6. Initial catalyst concentrations range from 4.8×10^{-6} to 8×10^{-5} mM and presumably result from impurities or slight decomposition of **1**. Variations in the rates from sample to sample of **1** are observed where data fitting suggests this is principally due to differences in initial catalyst concentrations.

$$\mathbf{1} + \text{catalyst} \xrightarrow{k_1} \mathbf{4} + \text{catalyst} \tag{5}$$

$$\mathbf{4} + O_2 \xrightarrow{k_2} \text{catalyst} \tag{6}$$

The question remains as to the identity of the catalyst. The stoichiometry of eq 4 suggests Pt metal. Generally, Pt metal is not observed in the cycloaddition reactions but could be present as a colloid. TEM examination of the final reaction mixtures reveals the presence of Pt particles (50−100 nm) in apparent correlation to the cycloaddition reaction rate. The O_2 reaction shows the greatest density with fewer but larger particles in the N_2 reaction. Pt particles are not detected in the very slow vacuum reaction. Similarly, the O_2-treated sample of **4** shows an abundance of particles, whereas none are detected in the O_2-treated sample of **1**. Finally, particles are not detected in samples of **1** or **4**, eliminating TEM beam decomposition of these complexes as the source of the observed particles.[24,25]

Further evidence for colloidal Pt as the catalyst is the observation that the cycloaddition reactions are completely suppressed by Hg(l) or small amounts of PEt_3 (0.2 mol % of **1**). Both are assumed to inhibit the reaction by blocking sites on the colloid surface, Hg(l) by amalgamation[22,26] and PEt_3 by strong coordination.[27] We have also observed mild inhibition (slowed reactions) with excess alkyne, suggesting that the alkyne and **1** compete for sites on the Pt colloid.

Although **1** was our main focus, the cycloaddition kinetics of **2** with diphenylacetylene similarly show autocatalysis, suggesting that colloidal Pt also catalyzes the cycloaddition reactions of **2**. In addition to being rare examples of heterogeneous catalysis of organometallic reactions,[26,28] these are also rare examples of cycloaddition chemistry catalyzed by colloidal metal.[29−32]

In conclusion, evidence is presented that the cycloaddition reactions of the PAC platinacycles **1** and **2** with diphenylacetylene are catalyzed by colloidal Pt generated by the oxidative de-ligation of product $L_2Pt(\eta^2\text{-PhCCPh})$ by traces of O_2. These results should be considered in the mechanisms of other organometallic reactions, including those that are steps in catalytic cycles in metal-catalyzed organic reactions. In addition, the formation of colloidal metal from a metal complex and ubiquitous O_2 is in contrast to the more usual reductive colloid synthesis[29] and suggests that colloid formation under oxidative conditions may be common for noble metal complexes.

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Supporting Information Available: Experimental procedures, compound characterization, TEM images, and kinetic data and fitting procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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