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Palladacycle Chemistry on the Edge of Naphthalene and Triphenylene: Alkyne Cycloadditions and Autocatalytic Coupling

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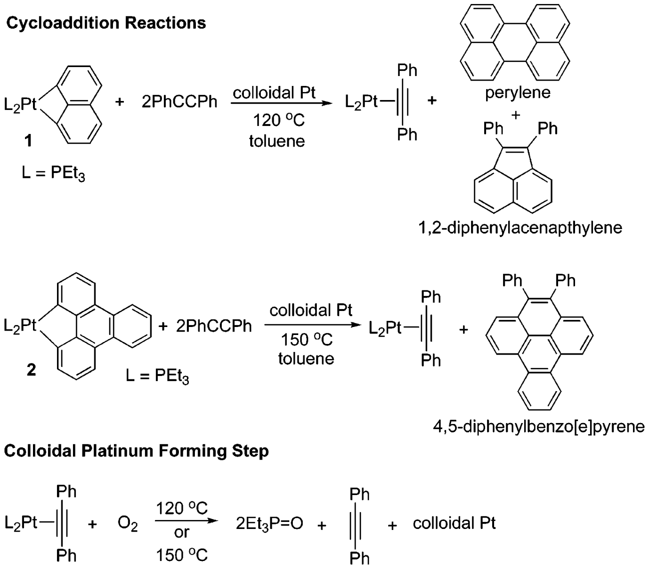
The four-membered palladacycle Pd(PEt_3)$_2$(1,8-naphthalenediyl) (**3**) and the five-membered palladacycle Pd(PEt_3)$_2$(1,12-triphenylenediyl) (**4**) were prepared from Pd(PEt_3)$_2$$Cl_2$ and the appropriate dilithio reagent. Both palladacycles are thermally unstable, decomposing autocatalytically at 100 °C to palladium black, Pd(PEt_3)$_3$, and perylene (for **3**) or dinaphtho[*def,pqr*]tetraphenylene (for **4**). In the presence of PhCCPh, the decomposition is slowed and the cycloaddition products 1,2-diphenylacenapthylene (for **3**) and 4,5-diphenylbenzo[*e*]pyrene (for **4**) are formed, along with the decomposition products. Kinetic data again indicate autocatalytic behavior. The decomposition and cycloaddition reactions are faster in the presence of dioxygen but are arrested by the addition of PEt_3 or mercury, consistent with colloidal palladium (detected by TEM) catalysis. Further reactions of the previously reported platinum analogue of **3** are also reported. The thermally stable platinacycle Pt(PEt_3)$_2$(1,8-naphthalenediyl) (**1**) decomposes at 120 °C in the presence of colloidal platinum, yielding perylene, platinum black, and platinum(0) phosphine complexes. Complex **1** also decomposes in wet toluene, and the colloidal platinum catalyzed cycloaddition reaction of **1** with PhCCPh is promoted by water. Interestingly, colloidal platinum also appears to catalyze the decomposition and alkyne cycloaddition reactions of palladacycle **3**. Finally, heating alkyne complex Pt(PEt_3)$_2$(η^2-PhCCPh) with O_2 and PhCCPh gives Pt(η^2-PhCCPh)$_2$ in good yield.

Introduction

Cycloaddition reactions with metallacyclic complexes are critical steps in many stoichiometric and catalytic reactions.[1−11] These reactions are generally assumed to occur on mononuclear metal centers in solution. Recently, we reported the synthesis and alkyne cycloaddition chemistry of platinacycles **1** and **2** (Scheme 1).[12] A full study of these reactions, including TEM and kinetic investigations, provided strong evidence that these cycloaddition reactions do not occur on a mononuclear center but rather on the surface of a small amount of colloidal Pt generated in the reactions. The exceptionality of these reactions was first indicated by their accelerating rate, indicative of an autocatalytic reaction[13,14] where a product of the reaction is a catalyst or a catalyst precursor for the reaction. (Similar kinetic behavior is also displayed in colloidal metal catalyzed organic reactions, where the colloid is formed during the reaction by autocatalytic nucleation and growth processes.[15,16]) Generation of the colloidal platinum catalyst was traced to the reaction of the product alkyne complex Pt(η^2-PhCCPh)(Et_3P)$_2$ with dioxygen (Scheme 1).

Scheme 1



In contrast, the much less stable and more reactive nickel analogues of **1** and **2**[17−19] as well as related nickelacycles[10,20,21]

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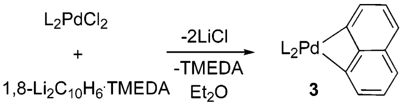
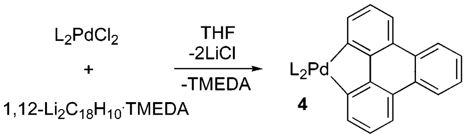
appear to undergo alkyne cycloaddition reactions via mononuclear or perhaps dinuclear solution-phase complexes. With the importance of palladium in many catalytic reactions and the involvement of colloidal palladium,[22] we became interested in the palladium analogues of **1** and **2** and if they behave like the nickel complexes undergoing alkyne cycloaddition through solution species or more like the platinum complexes with colloidal metal catalysis. As presented below, we find that the palladacycle chemistry resembles more closely that of **1** and **2**, but with additional features resulting from the lower stability of the palladium complexes. We also report additional chemistry of platinacycle **1** and a remarkably effective synthesis of the binary alkyne complex $Pt(\eta^2\text{-PhCCPh})_2$[23,24] by oxidative deligation of $Pt(\eta^2\text{-PhCCPh})(PEt_3)_2$ in the presence of excess alkyne at 120 °C.

Results

Palladacycles. The palladacycles **3** and **4**, prepared analogously to the previously reported platinum analogues **1** and **2**,[12] are isolated in ~80% yield from the reaction of L_2PdCl_2 (L = PEt_3) with the TMEDA ($Me_2NCH_2CH_2NMe_2$) adducts of 1,8-dilithionaphthalenediyl or 1,12-dilithiotriphenylenediyl (eqs 1 and 2). (Biphenyl analogues of **4** have been reported.[25−29]) NMR spectroscopic data for the yellow crystalline complexes match closely with those for the analogous platinum complexes **1** and **2** and are consistent with the expected structures.



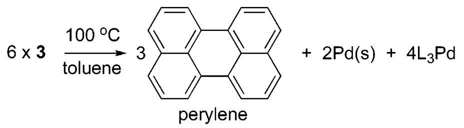
(1)



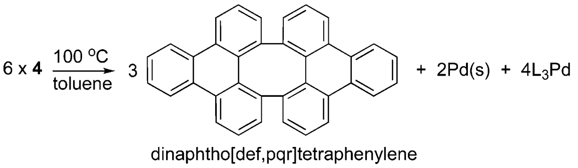
(2)

In contrast to **1** and **2**, which are thermally very robust and withstand heating in toluene at more than 150 °C for hours, **3** and **4** are thermally sensitive and decompose at 100 °C in toluene. The decomposition products are palladium black, PdL_3,[30] and the coupled organic products perylene for **3** and dinaphtho[*def,pqr*]tetraphenylene for **4** with the assumed stoichiometries given in eqs 3 and 4.

The decompositions are sensitive to the presence of dioxygen and display autocatalytic behavior. Plots of the disappearance of **4** under various conditions are shown in Figure 1. Plots of the disappearance of palladacycle **3** are provided in the Supporting Information and are similar to those in Figure 1, but with a somewhat shorter reaction time frame (~60%), consistent with the lower stability of the smaller four-membered palladacycle **3**.



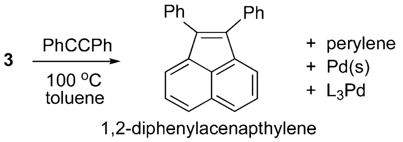
(3)



(4)

The accelerating rate displayed in these plots is indicative of an autocatalytic reaction where a product of the reaction is a catalyst or catalyst precursor for the reaction. Previous work has shown that Pt alkyl complexes are subject to autocatalytic decomposition by colloidal platinum.[31] Examination of the decomposition reaction solutions of **3** and **4** by TEM (see the Supporting Information) reveals colloidal Pd particles ranging from a few (under N_2) to several hundred nanometers (added O_2) that we believe are responsible for the autocatalytic decomposition of **3** and **4** (see below).

Alkyne Cycloadditions. As previously reported, the platinacycles **1** and **2** undergo autocatalytic cycloadditions with alkynes at 120−150 °C (Scheme 1).[12] Palladacyles **3** and **4** also undergo cycloadditions with PhCCPh, but at temperatures where decomposition also occurs. The reactions are more facile than those of **1** and **2** and occur at 100 °C, giving both the decomposition products and the cycloaddition compounds 1,2-diphenylacenapthylene and 4,5-diphenylbenzo[*e*]pyrene along with Pd black and L_3Pd (eqs 5 and 6). Note that, in contrast to the alkyne cycloaddition reactions of platinacycles **1** and **2**, an alkyne complex is not formed.



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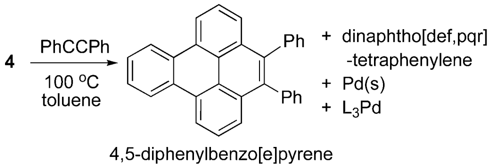

(6)

The relative yields of the organic cycloaddition products to the organic decomposition products depend on the alkyne concentration. The cycloaddition product yield increases with alkyne concentration with a corresponding decrease in the yield of the coupling product. In the case of **3** (12 mM) with an alkyne concentration of 30 mM, the acenaphthylene yield is 35% and that of perylene 61%. Increasing the alkyne concentration to 144 mM increases the acenaphthylene yield to 46% and the yield of perylene decreases to 50%. For **4** (12 mM) and an

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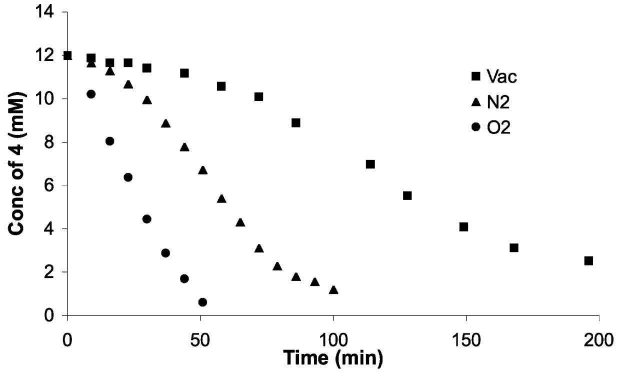

Figure 1. Plots of the disappearance of palladacycle **4** in toluene at 100 °C in a vacuum-sealed tube (■), under dinitrogen (▲), and under dinitrogen with added dioxygen (120 μL, ●).

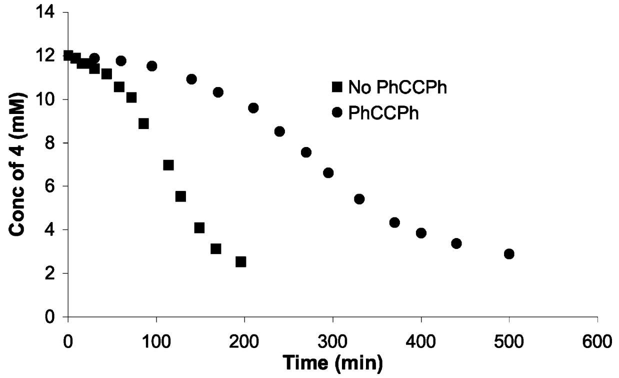

Figure 2. Plots of the disappearance of **4** in the presence (●) and absence (■) of PhCCPh in a vacuum-sealed tube.

alkyne concentration of 30 mM the pyrene yield is 25% and the tetraphenylene yield is 72%. At the higher alkyne concentration of 144 mM the pyrene yield increases to 54% and the tetraphenylene yield drops to 51%.

Kinetic plots (disappearance of the palladacycles **3** and **4** as a function of time) for the cycloaddition reactions show dioxygen-sensitive autocatalytic behavior similar to that shown for the decompositions. A plot for **4** in a vacuum-sealed tube is given in Figure 2. Other plots for **4** and **3** are available in the Supporting Information. Also included in Figure 2 for comparison is a plot of the disappearance of **4** in the absence of alkyne in a vacuum-sealed tube (same data as in Figure 1). The disappearance of **4** is slowed by the presence of the alkyne. A similar retardation is observed under an N_2 atmosphere, but with added O_2 the disappearance is essentially the same as in the absence of alkyne (see the Supporting Information).

Catalyst Identification. The kinetic plots for the decomposition and cycloaddition reactions for **3** and **4** indicate autocatalytic behavior and the formation of a catalyst during the reactions. The presence of colloidal Pd in the decomposition reactions and our previously reported evidence for colloidal Pt catalysis of the cycloaddition reactions of platinacycles **1** and **2** strongly suggest that colloidal Pd is the catalyst for the decomposition and cycloaddition reactions of **3** and **4**. However, the formation of PdL_3 in both the decomposition and cycloaddition reactions of **3** and **4** raises the possibility that this species could be the catalyst. To test this possibility, a PhCCPh cycloaddition reaction of **3** (12 mM) was conducted with independently prepared PdL_3 added at the beginning of the reaction at a 12 mM concentration. A plot comparing the reaction rates with and without added PdL_3 is given in Figure 3. There is only a slight change in the reaction plot, indicating that PdL_3 is not a catalyst for the cycloaddition reaction.

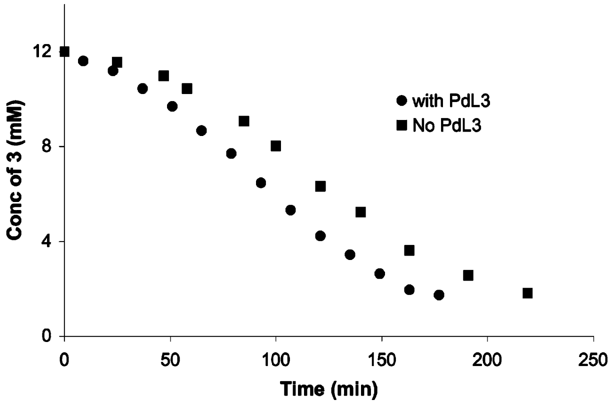

Figure 3. Plots of the disappearance of **3** in the reaction with PhCCPh in the presence (●) and absence (■) of 12 mM PdL_3 under a dinitrogen atmosphere.

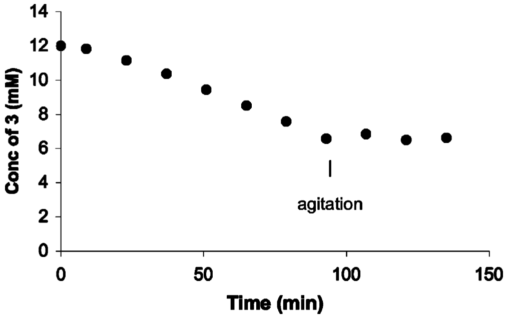

Figure 4. Plot of the disappearance of **3** in the reaction with PhCCPh under a dinitrogen atmosphere, showing the effect of added Hg(l).

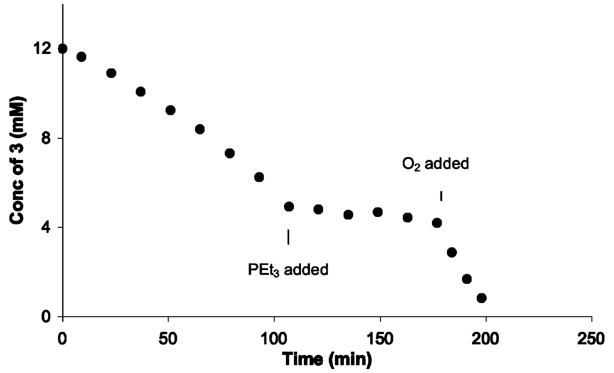

Figure 5. Plot of the disappearance of **3** in the reaction with PhCCPh under a dinitrogen atmosphere, showing the effect of added PEt_3 (0.04%) and the subsequent addition of O_2 (0.6 μL, 0.04%).

Further indications that, like the Pt reactions, the Pd reactions are catalyzed by colloidal metal is the effect of added Hg(l) and PEt_3. Figures 4 and 5 show the consequence of adding Hg(l) or PEt_3 (0.04 mol %) on alkyne cycloaddition reactions of **3** under a dinitrogen atmosphere. For the Hg(l) addition, a drop of Hg was added at the beginning of the reaction without agitation. The reaction begins slightly more slowly than without the drop and is halted completely with agitation of the mixture. For the PEt_3 addition, the PEt_3 was added to an in-progress reaction. The reaction is completely suppressed by the addition but restarts when a small amount of dioxygen is injected. The suppression of the reaction by these additives is consistent with poisoning of the colloidal metal surface.[16,31,32]

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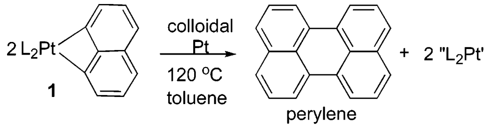
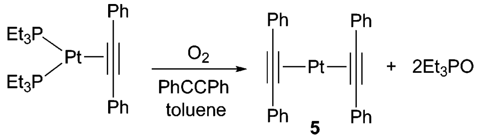
Catalytic Decomposition of the Platinacycle 1. In contrast to the case for the palladacycles, the platinacycles **1** and **2** are thermally stable and do not decompose to yield coupling products up to at least 150 °C.[12] It was therefore puzzling to us why the coupling product perylene was formed in significant yields in the alkyne cycloaddition reactions of **1** (Scheme 1). With our observation of colloidal palladium catalysis of the decomposition of the palladacycles reported here, it occurred to us that decomposition of the platinacycle **1** might also be susceptible to colloidal metal catalysis. The colloidal platinum formed during the cycloaddition reaction of **1** would then not only catalyze the cycloaddition reaction but also the decomposition reaction with formation of perylene. Colloidal catalysis of the decomposition of **1** was confirmed (see the Supporting Information) by heating a solution of **1** in the presence of colloidal platinum (from the reaction of Pt(η^2-PhCCPh)(PEt$_3$)$_2$ with O$_2$[12]). Platinacycle **1** decomposed readily with the formation of perylene (eq 7).



(7)

Formation of Pt(η^2-PhCCPh)$_2$. We noted previously an inhibition of the cycloaddition reactions of **1** and **2** with high alkyne concentrations.[12] This was attributed to alkyne saturation of the catalytic sites, but we came to suspect another possibility. In the cycloaddition reactions of **1** and **2**, the O$_2$ oxidation of the phosphine ligands of Pt(η^2-PhCCPh)(PEt$_3$)$_2$ is thought to produce unsaturated fragments that agglomerate to give colloidal Pt (Scheme 1). Is it possible that the unsaturated fragments are competitively trapped by alkyne to give known Pt(η^2-PhCCPh)$_2$ (**5**),[23] thereby reducing the amount of colloidal Pt catalyst? To test this possibility, we heated a mixture of Pt(η^2-PhCCPh)(PEt$_3$)$_2$, excess O$_2$, and excess PhCCPh. The resulting yellow solution was examined by NMR spectroscopy and showed the presence of Et$_3$PO and **5** as the only major products. Complex **5** was isolated in 67% yield from the mixture. Remarkably, this procedure (eq 8) appears to be among the best preparative methods for this complex.[24]



(8)

The catalytic efficacy of **5** in the cycloaddition reaction of **2** with PhCCPh was examined. Little to no effect on the reaction is detected when **5** is added at stoichiometric levels, ruling out **5** as a catalyst or catalyst precursor (see the Supporting Information).

Water-Promoted Reactions. The cycloaddition reaction of platinacycle **1** and PhCCPh in a vacuum-sealed tube is accelerated with added water (Figure 6). The kinetic plot is qualitatively similar to that for the dioxygen-promoted reaction. The short induction period followed by rate acceleration clearly suggests that the reaction involves in situ transformation of a small quantity of either **1** or Pt(η^2-PhCCPh)(PEt$_3$)$_2$ to the active colloidal Pt catalyst. Examination of the final reaction mixture by TEM confirms the presence of colloidal platinum (see the Supporting Information). The Pt−alkyne complex Pt(η^2-PhCCPh)(PEt$_3$)$_2$ is very stable in water-saturated toluene and does not decompose, but platinacycle **1** slowly decomposes with an accelerating rate (see Supporting Information) to platinum black, naphthalene, perylene, and other products (eq 9), indicating that the reaction of platinacycle **1** with water is a source of colloidal platinum catalyst in the water-promoted cycloaddition reaction.

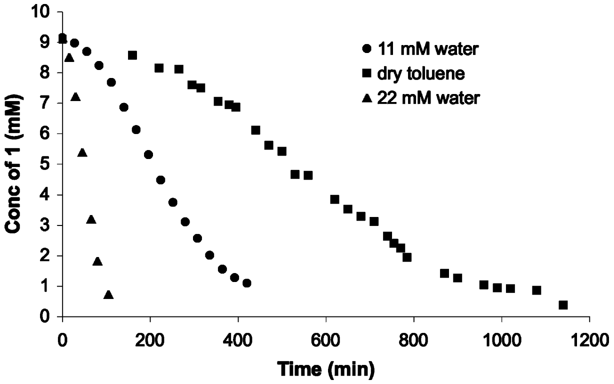
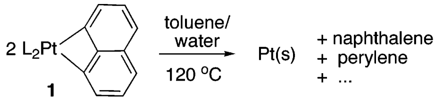


Figure 6. Plots of the disappearance of **1** in the reaction with PhCCPh in the presence (11 mM, ●; 22 mM, ▲) and absence (■) of water in a vacuum-sealed tube.



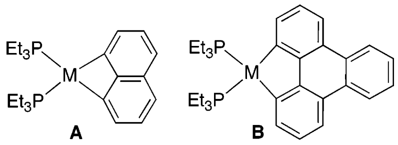
(9)

Cross-Metal Catalysis. The ability of colloidal palladium to catalyze the reactions of platinacycle **1** and of colloidal platinum to catalyze the reactions of palladacycle **3** was examined. A toluene palladium colloid was prepared by decomposing palladacycle **3** in toluene as described above. The colloidal palladium sample was then used to prepare NMR samples of platinacycle **1** with and without added PhCCPh. The mixtures were heated at 120 °C but showed no significant effect of the colloidal palladium on the reaction rates.

Colloidal platinum samples were prepared by heating a toluene solution of Pt(η^2-PhCCPh)(PEt$_3$)$_2$ with added dioxygen.[12] The colloidal platinum sample was then used to prepare NMR samples of palladacycle **3** with and without added PhCCPh. The mixtures were heated at 100 °C and showed rapid initial reaction rates (see Supporting Information), indicating catalysis of the decomposition and cycloaddition reactions of palladacycle **3** by colloidal platinum. In addition, the ratio of the PhCCPh cycloaddition product, 1,2-diphenylacenaphthylene, to the coupling product, perylene, increases from 1:0.75 for the colloidal palladium catalyzed reaction to 1:0.3, approaching that observed in the cycloaddition reaction of platinacycle **1** (1:0.01) under similar conditions.

Discussion

We have now studied the decomposition and alkyne cycloaddition chemistry of the Ni,[18,19] Pd, and Pt[12] metallacycles of structures **A** and **B**. In keeping with the known properties of



A **B**

M = Pt (**1**), Pd(**3**) M = Pt (**2**), Pd(**4**)

these elements, the Pd and Pt complex chemistries are closely related, while that for the Ni complexes is substantially different. The stability order to decomposition is Ni < Pd < Pt, with the five-membered-ring complexes **B** markedly more stable than the four-membered complexes **A**. Along with the stability differences, there are dramatic differences in the decomposition and alkyne reaction pathways. The Pd and Pt complexes (except **2**) decompose autocatalytically, apparently on the surface of colloidal metal particles generated during the decomposition, whereas the Ni complexes decompose by binuclear coupling pathways.[18,20] The end result is the same for all the metals with perylene or dinaphtho[*def*,*pqr*]tetraphenylene, free metal, and metal phosphine complexes being produced.

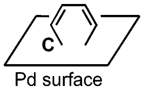
The difference between the Pd and Pt complexes is the greater stability of the Pt complexes, especially in the presence of dioxygen. The Pt complexes are thermally robust in the presence of dioxygen to more than 150 °C in the absence of colloidal Pt. Even in the presence of colloidal Pt only four-membered **1** decomposes at a significant rate at 120 °C. Complex **2** appears stable, even in the presence of colloidal Pt. In contrast, the Pd complexes both decompose readily at 100 °C without added colloidal Pd and show faster rates in the presence of dioxygen. While the facile decomposition of **3** and **4** probably indicates a lower stability of the palladacycles in both the presence and the absence of dioxygen, it could also indicate greater reactivity with the colloidal metal.

Similar mechanistic differences hold for the cycloaddition reactions with PhCCPh. The Pt and Pd reactions again appear to involve catalytic reactions on colloidal metal surfaces, while the Ni complexes show mononuclear or dinuclear pathways. For Pd complexes **3** and **4** and four-membered-ring Pt complex **1** colloidal metal catalyzed decomposition occurs in competition with the cycloaddition reaction. This is indicated by the formation of both the cycloaddition products and the decomposition products perylene and dinaphtho[*def*,*pqr*]tetraphenylene. Interestingly, the disappearance of the Pd and Pt metallacycles in the presence of alkyne is slower than the decomposition reactions, indicating that decomposition is retarded by the alkyne. This is likely due to coordination of the alkyne on the colloidal surface (cf. PEt_3 poisoning), resulting in fewer active sites and in dilution of surface-bound metallacycles. Dilution is expected to inhibit the formation of coupled organic products, which requires the combination of two metallacycle fragments. Another possible process for retarding colloidal metal catalyzed decomposition for Pt is alkyne trapping of the Pt(0) produced by the oxidative deligation of $Pt(PEt_3)_2(\eta^2\text{-PhCCPh})$ by dioxygen. We have shown that this is a possible reaction and gives good yields of $Pt(\eta^2\text{-PhCCPh})_2$ when a large excess of alkyne is present. Trapping of Pt(0) by alkyne would limit the amount of colloidal Pt being formed and thereby slow the reaction. This is not an issue in the Pd chemistry, as no alkyne complexes are formed.

The Pd complexes are unique in the cycloaddition reactions in not forming an alkyne complex. The end metal-containing products for both Pt and Ni are the alkyne complexes $M(PEt_3)_2(\eta^2\text{-PhCCPh})$ (M = Ni, Pt). In contrast, the products for Pd are Pd black and $Pd(PEt_3)_3$. While the analogous Pd alkyne complex $Pd(PEt_3)_2(\eta^2\text{-PhCCPh})$ is unknown, many analogues have been reported,[33−39] indicating that $Pd(PEt_3)_2(\eta^2\text{-PhCCPh})$ should exist but must be less stable than the Pt analogue and probably decomposes under the cycloaddition reaction conditions.

A question that arises in any autocatalytic reaction is what initiates the reaction. The uncatalyzed reaction may occur slowly, giving the product that then catalyzes the reaction. This could be the case for the decomposition of the Pd complexes, where a slow uncatalyzed decomposition gives small amounts of colloidal Pd that then catalyze further decomposition. This would also be the initial colloidal Pd source in the cycloaddition reaction. This cannot be the case for the Pt reactions, since both **1** and **2** are stable in the absence of colloidal platinum. Reaction of the metallacycles with traces of dioxygen and/or water is another possible source of the initial colloidal metal. We established previously that platinacycles **1** and **2** are stable in the presence of dioxygen. Here we find that **1** is unstable in the presence of water, although the millimolar concentrations needed to observe decomposition are much higher than trace amounts. (An example of colloidal palladium formation and catalysis by reaction of a Pd complex with water is given in ref 40.) A final possibility is that compounds that decompose to colloidal metal or colloidal metal itself may be present as impurities in samples of the metallacycles. The metallacycles are prepared under reductive conditions (organolithium reagents), suggesting the possibility of reduced species impurities.

Finally, we come to the topic of how the colloidal particles might mediate the reactions. Pt and Pd surfaces catalyze a number of reactions. Of particular interest here is the trimerization of acetylene to benzene on the Pd(111) surface. This reaction has been well-studied, and mechanistic details have been elucidated.[41] A key intermediate is metallacycle **C**, formed by coupling two surface-bound acetylene molecules. Subsequent cycloaddition of a third surface-bound acetylene yields benzene π-bonded to the Pd surface:



Formation of analogous metallacycles on the colloid surface is proposed for our colloidal metal catalyzed reactions and is depicted for the triphenylene system in Scheme 2. Interaction of the molecular metallacycle (**2** or **4**) with the colloid surface occurs first through π-bonding of the aromatic moiety, similar to the bonding of aromatic hydrocarbons to Pd and Pt surfaces.[41−45] Subsequent transmetalation transfers the metallacycle from the metal atom to the metal surface, yielding the triphenylene analogue **D** of surface metallacycle **C**. Once on the surface, the metallacycle can follow two pathways, giving either a cycloaddition product (path a) or a dimerization product (path b). Which pathway dominates depends on the amount of acetylene on the metal surface and on the identity of the metal.

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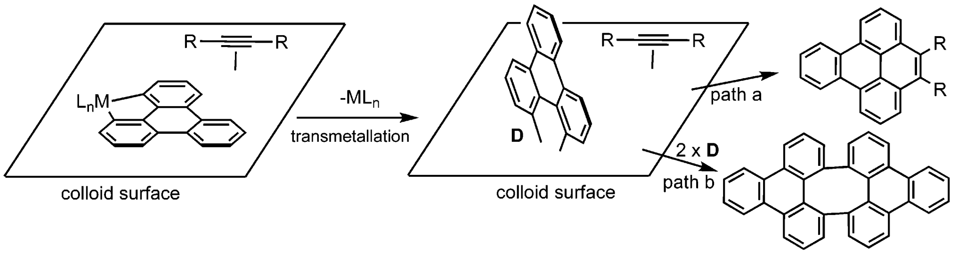
Scheme 2



When the metal is Pd, both pathways are operative and competitive, with partitioning to the cycloaddition pathway increasing with increasing acetylene concentration. With Pt, only the cycloaddition product is observed, indicating that dimerization pathway b is absent on Pt in the triphenylene system.

The colloid surface reactions of the naphthalene-based metallacycles **1** and **3** must be similar, with both pathways again operating on Pd. In contrast to the triphenylene system, where only path a is observed on Pt, both pathways occur on Pt for the naphthalene system. However, the product distribution in the presence of PhCCPh and the sluggishness of the decomposition of platinacycle **1** on the colloid indicate that the cycloaddition pathway a dominates over the dimerization pathway b.

With this model we can address the cross-metal colloid catalysis results. Colloidal Pd does not catalyze platinacycle **1** decomposition or alkyne cycloaddition. We believe this is due to the absence of transmetalation to the Pd surface. Pt−C bonds are stronger than Pd−C bonds, and this would disfavor transfer of the metallacycle from the Pt center of **1** to the Pd surface. On the other hand, transmetalation from the Pd center of **3** to the Pt colloid surface should be facile and we do observe colloidal Pt catalysis of palladacycle **3** decomposition and alkyne cycloaddition.

An interesting point emerges here. Once the metallacycle is transferred from Pd to the Pt surface, the reaction chemistry is then that of Pt and not Pd. As pointed out above, the dimerization pathway b on Pt is much less active than that on Pd and this should be reflected in a change in the product distribution in the alkyne cycloaddition reaction of palladacycle **3**. This is observed in the ratio of cycloaddition product acenaphthylene to dimerization product perylene. In the colloidal Pt catalyzed reaction the ratio (1:0.3) is more than 2 times greater than that in the colloidal Pd catalyzed reaction (1:0.75). This approaches but does not match the ratio for the all-Pt reaction (1:0.01), because colloidal Pd is produced from the Pt-catalyzed reaction and contributes more and more to product formation as the reaction progresses.

Another interesting feature of the colloidal Pt catalyzed reaction of palladacycle **3** is that the surface reactions (path a and b) on Pt occur at 100 °C, 20 °C lower than for platinacycle **1** suggesting that the rate-limiting step in the colloidal Pt catalyzed reactions of platinacycle **1** is transmetallation, i.e., transfer of the metallacycle to the surface. The following surface reactions (path a and path b) are evidently then facile even at 100 °C.

In conclusion, we have shown that the Pt and Pd metallacycles **1**, **3**, and **4** decompose autocatalytically. The product catalyst in the autocatalytic decompositions appears to be colloidal metal, which also catalyzes the alkyne cycloaddition reactions of the metallacycles. Though slowed by the presence of alkyne, decomposition occurs in competition with alkyne cycloaddition. Catalysis of decomposition and cycloaddition reactions by colloidal metal may be peculiar to these polycyclic aromatic metallacycles, but our results and those of other groups[22,40,46−50] indicate that colloidal metal involvement must be thoroughly considered in the mechanism of organic reactions mediated by Pd and Pt.

Experimental Section

General Considerations. *cis*-$PdCl_2(PEt_3)_2$,[51] $Pd(PEt_3)_3$,[30] 1,8-dilithionaphthalenediyl·TMEDA,[52] 1,8-dilithionaphthalenediyl·TMEDA,[53] Pt(1,8-naphthalenediyl)$(PEt_3)_2$ (**1**),[12] Pt(1,12-triphenylenediyl)$(PEt_3)_2$ (**2**),[12] and Pt(η^2-PhCCPh)$(PEt_3)_2$[12] were prepared by reported procedures. PhCCPh was purchased from commercial sources and recrystallized from toluene/hexanes for the kinetic studies. Experiments were performed under a dinitrogen atmosphere in a Vacuum Atmospheres Corp. drybox or on a Schlenk line with dried and degassed solvents stored under dinitrogen over 4 Å molecular sieves or sodium metal. NMR spectra were recorded on Bruker AMX-250, -300, and -500 spectrometers at ambient probe temperatures, except as noted. Shifts are given in ppm with positive values downfield of TMS (^1H and ^{13}C), external H_3PO_4 (^{31}P), or external K_2PtCl_4(aq) (^{195}Pt, −1630 ppm). ^{13}C and ^1H NMR spectra were recorded in proton-decoupled mode. Desert Analytics performed the microanalyses (inert atmosphere).

Syntheses. Pd(1,8-naphthalenediyl)$(PEt_3)_2$ (3). A diethyl ether solution (5 mL) of *cis*-$PdCl_2(PEt_3)_2$ (80.7 mg, 0.195 mmol) was added dropwise to a diethyl ether solution (5 mL) of 1,8-dilithionaphthalenediyl·TMEDA (50.0 mg, 0.195 mmol). The mixture was stirred for about 30 min and then filtered to give a yellow solution. The solution was concentrated and stored at −20 °C to give yellow crystals of **3**, which were isolated by filtration, washed with cold hexane, and dried in vacuo. Yield: 68.8 mg (76%). ^1H NMR (250 MHz, C_6D_6): 7.71 (d, $J = 8.25$ Hz, 1H), 7.56−7.42 (m, 2H), 1.63−1.51 (m, 6H), 0.96−0.83 (m, 9H). ^{31}P NMR (101 MHz, C_6D_6): 16.46 (s). ^{13}C NMR (75.5 MHz, C_6D_6): 8.75 (s, CH-3), 17.92 (m, CH-2), 120.4 (s), 120.7 (t, $J_{PC} = 6.04$ Hz), 125.5 (t, $J_{PC} = 5.3$ Hz), 126.7 (s), 128.9 (s), 129.1 (s). Anal. Calcd (found) for $C_{22}H_{36}P_2Pd$: C, 56.36 (56.27); H, 7.74 (7.60).

Pd(1,12-triphenylenediyl)$(PEt_3)_2$ (4). A solution of *cis*-$PdCl_2(PEt_3)_2$ (44.0 mg, 0.106 mmol in 5 mL of THF) was added dropwise to a solution of 1,12-dilithiotriphenylenediyl·2TMEDA (50.0 mg, 0.105 mmol, in 5 mL of THF). The mixture was stirred for ca. 40 min. The volatiles were then removed in vacuo, and the residue was dissolved in 5 mL of diethyl ether. The filtered clear yellow

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solution was then concentrated to 2 mL and stored at −20 °C to obtain the yellow crystalline product. Yield: 49.2 mg (82%). ^{1}H NMR (250 MHz, C_6D_6): 8.75 (m, 1H), 8.46 (d, $J = 8.7$, 1H), 7.86 (m, 1H), 7.58 (m, 2H), 1.69−1.64 (m, 6H), 1.03−0.93 (m, 9H). ^{31}P NMR (101 MHz, C_6D_6): 6.74 (s). ^{13}C NMR (75.5 MHz, C_6D_6): 8.9 (s, CH-3), 18.5 (m, CH-2), 118.6 (s), 123.7 (s), 123.9 (s), 125.6 (t, $J_{PC} = 6.04$ Hz), 126.1 (s), 127.3 (s), 127.9 (s), 132.1 (s), 134.8 (t, $J_{PC} = 7.55$ Hz). Anal. Calcd (found) for $C_{30}H_{40}P_2Pd$: C, 63.33 (63.09); H, 7.09 (7.02).

Pt(η^2-PhCCPh)$_2$ (5). Pt(η^2-PhCCPh)(PEt$_3$)$_2$ (50 mg, 0.082 mmol) in 2 mL of toluene was mixed with a 2 mL toluene solution of PhCCPh (36 mg, 0.20 mmol). The mixture was divided into two equal parts and placed in two screw-cap NMR tubes. Dioxygen (1.5 mL) was syringed into each tube. The tubes were then heated for 7 h in a constant-temperature oil bath at 120 °C. The reaction was monitored by ^{31}P NMR spectroscopy, where the singlet for Pt(η^2-PhCCPh)(PEt$_3$)$_2$ at 12.5 ppm disappeared and a new peak for phosphine oxide grew in at 45.3 ppm. The two samples were combined and concentrated. Pentane (2 mL) was added, and the mixture was cooled to −78 °C to give yellow crystalline **5**, which was isolated by decantation, washed with cold pentane, and dried in vacuo. Yield: 30.3 mg (67%). Spectroscopic data match those previously reported.[23,24]

Reaction of 3 with PhCCPh. Previously reported procedures for the reaction of **1** with PhCCPh in toluene[12] were followed for the reaction of **3** with PhCCPh. With a molar ratio of **3** to PhCCPh of 1:2.5 (12.0 mM in **3** and 30.0 mM in PhCCPh) the yield of acenaphthylene was 35% and that of perylene was 61%. When the PhCCPh concentration was increased to give a 1:12 ratio (12.0 mM in **3** and 144 mM in PhCCPh), the yield of acenaphthylene increased to 46%, whereas the perylene yield dropped to 50%. Yields were determined by ^{1}H NMR spectroscopy.

Reaction of 4 with PhCCPh. Previously reported procedures for the reaction of **2** with PhCCPh in toluene[12] were followed for the reaction of **4** with PhCCPh. With a molar ratio of **4** to PhCCPh of 1:2.5 (12 mM in **4** and 30 mM in PhCCPh) the yield of 4,5-diphenylbenzo[*e*]pyrene was 25% and that of the tetraphenylene was 72%. When the PhCCPh concentration was increased to give a 1:12 ratio (12 mM in **4** and 144 mM in PhCCPh), the yield of 4,5-diphenylbenzo[*e*]pyrene increased to 54%, whereas the perylene yield dropped to 41%. Yields were determined by ^{1}H NMR spectroscopy.

Kinetic Studies. Decomposition of Pd(1,8-naphthalenediyl)-(PEt$_3$)$_2$ (3) and Pd(1,12-triphenylenediyl)(PEt$_3$)$_2$ (4). Toluene solutions (0.40 mL, 12.0 mM) of **3** or **4** were placed into three different NMR tubes: (a) a tube fitted with a vacuum stopcock, (b) a screw-cap tube under N_2, and (c) a screw-cap tube with added O_2 (120 μL by microsyringe). The tube fitted with the stopcock was flame-sealed on a vacuum line after freezing the sample and evacuating the headspace (no freeze−pump−thaw cycles applied). The three NMR tubes of each complex (**3** and **4**) were heated simultaneously in a constant-temperature oil bath at 100 °C, with periodic monitoring by ^{31}P NMR spectroscopy and integration against an external H_3PO_4 standard.

Cycloaddition Reactions of 3 and 4. Procedures for the cycloaddition reactions of the palladacycles (12.0 mM) with PhCCPh (30.0 mM) in toluene were similar to those previously reported for the platinacycles,[12] except for the lower temperature (100 °C) and the higher quantity of oxygen (120 μL). Concentration data were obtained by palladacycle peak integration against an external H_3PO_4 standard. All cycloaddition reactions were conducted either in the NMR probe (fast reactions) or in an oil bath (slow reactions).

Cycloadditions with 12 Equiv of PhCCPh. The cycloaddition kinetics were carried out with **3** (12.0 mM) and 12 equiv of PhCCPh (144 mM) in toluene under N_2 at 100 °C and compared to the N_2 experiment with 2.5 equiv of PhCCPh (30.0 mM) (see the Supporting Information).

Platinacycle Cycloaddition with Initial [Pt(η^2-PhCCPh)$_2$] (6). A 0.60 mL toluene sample that was 12.1 mM in **6**, 12.1 mM in **2**, and 24.0 mM in PhCCPh was placed in a screw-cap NMR tube under N_2, heated at 150 °C, and monitored as above. The resulting data were plotted and compared to the same cycloaddition reaction in the absence of added **6** under nitrogen environment.

Palladacycle Cycloaddition with Initial Pd(PEt$_3$)$_3$. A 0.60 mL toluene sample that was 12.0 mM in Pd(PEt$_3$)$_3$, 12.0 mM in **3**, and 24.1 mM in PhCCPh was placed in a screw-cap NMR tube under N_2, heated at 100 °C, and monitored as above. The resulting data were plotted and compared to the same cycloaddition reaction in the absence of added Pd(PEt$_3$)$_3$ (see the Supporting Information).

Palladacycle (3) Alkyne Cycloaddition with Initial Colloidal Palladium. A toluene solution of **3** (28.1 mg, 0.06 mmol, 12.0 mM) in 5.0 mL of toluene was placed into a sealable 25 mL tube under N_2. The tube was sealed and heated in a constant-temperature oil bath at 100 °C for 1 h, resulting in complete decomposition of **3**. The resulting yellow solution and palladium black mixture was filtered through diatomaceous earth. The resulting clear yellow filtrate containing colloidal palladium was used to prepare a screw-cap NMR sample that was 12.0 mM in **3** and 24.1 mM in PhCCPh under dinitrogen. The tube was heated at 100 °C and monitored as above.

Colloidal Platinum Catalyzed Decomposition of Platinacycle 1. To a toluene solution of Pt(η^2-PhCCPh)(PEt$_3$)$_2$ (12.5 mg, 0.0205 mmol in 1.00 mL of toluene) in a screw-cap NMR tube was injected 1.5 mL of O_2. The tube was heated in an oil bath at 120 °C for 12 h, completely decomposing the alkyne complex. The resulting yellow solution and platinum black mixture was filtered through diatomaceous earth to give a clear yellow filtrate containing colloidal platinum.[12] A 0.30 mL portion of a 20.0 mM toluene solution of **1** and a 0.30 mL portion of the colloidal platinum solution were placed in a screw-cap NMR tube under N_2. The mixture was then heated at 120 °C and monitored by ^{31}P NMR spectroscopy.

Platinacycle Decomposition and Cycloaddition in the Presence of H_2O. Water-saturated toluene was prepared by stirring a mixture of dry toluene (10 mL) and degassed HPLC grade water (5 mL) overnight. The mixture was then allowed to stand for 12 h to ensure complete separation of the water and toluene layers. The water-saturated toluene was then used to prepare a mixture of **1** (10.0 mM) and PhCCPh (20.0 mM). An aliquot was placed into a NMR tube fitted with a vacuum stopcock. The tube was flame-sealed on a vacuum line after freezing the sample and evacuating the headspace. The NMR tube was heated in a constant-temperature oil bath at 120 °C with periodic monitoring (by integration with respect to external H_3PO_4) by ^{31}P NMR spectroscopy. At the end of the reaction, a small amount of brown precipitate was observed at the bottom of the NMR tube. The cycloaddition experiment was conducted similarly with **1** (9.15 mM) and PhCCPh (18.3 mM) in water-saturated toluene. No precipitation was observed in the cycloaddition reaction. The water concentration (22.2 mM) was calculated by using the solubility data of water in toluene (0.046% w/w).[54] A second cycloaddition reaction with the same concentrations of **1** and PhCCPh was conducted with a sample prepared using a 50:50 mixture of dry toluene and water-saturated toluene, giving a water concentration of 11.1 mM.

Mercury Poisoning. The experiment was started under N_2 as in the PEt$_3$ experiment, above, except with a drop of Hg(l) at the bottom of the NMR tube. The reaction proceeded, until the tube was agitated. With agitation, the reaction was completely halted. See Figure 4 and the Supporting Information.

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PEt_3 Poisoning. The cycloaddition reaction of **3** (15.2 mM) with PhCCPh (2.5 equiv) was started at 120 °C under N_2, as described above, and monitored by ^{31}P NMR spectroscopy. After 110 min (complete reaction takes ~170 min under these conditions) the NMR tube was cooled to room temperature and taken into the glovebox and PEt_3 was added (20 μL of a 1.1 mM solution, 0.40% of initial **3**). The mixture was again heated to 120 °C. The addition of PEt_3 completely halted the reaction, and this was followed for 55 min (i.e., total 165 min time at 120 °C). The NMR tube was again cooled to room temperature, and O_2 (~0.6 μL, 0.40% of initial **3**) was injected. The tube was shaken carefully to ensure that the O_2 had fully mixed with the reaction solution. Finally, the tube was heated to 120 °C and the reaction followed until completion. See Figure 5 and the Supporting Information.

Decomposition of Pt(1,8-naphthalenediyl)$(PEt_3)_2$ (1) in the Presence of Colloidal Palladium. Into a solution of **3** (11.3 mg, 0.024 mmol in 1.0 mL of dry toluene) in a screw-cap NMR tube was injected 1.5 mL of O_2. The tube was heated in an oil bath at 100 °C for 1 h to completely decompose the metallacycle. The resulting yellow solution and palladium black mixture was filtered through diatomaceous earth to give a clear filtrate containing colloidal palladium. The filtrate was then deoxygenated on a vacuum line by several freeze−pump−thaw processes and used as a source of colloidal palladium. A 0.20 mL (18.3 mM) portion of **1** was mixed with a 0.20 mL solution of colloidal palladium solution and placed in an NMR tube fitted with a vacuum stopcock. The tube was flame-sealed on a vacuum line after freezing the sample and evacuating the headspace (no freeze−pump−thaw cycles applied). The mixture was then heated in a constant-temperature NMR probe at 120 °C with periodic monitoring by ^{31}P NMR spectroscopy. No significant decomposition was observed.

Cycloaddition Reaction of Pt(1,8-naphthalenediyl)$(PEt_3)_2$ (1) with PhCCPh in the Presence of Colloidal Palladium. A colloidal palladium solution was prepared by following the above procedure. The colloidal palladium solution was used to prepare an evacuated flame-sealed NMR sample that was 9.15 mM in **1** and 18.3 mM in PhCCPh. The mixture was then heated in a constant-temperature NMR probe at 120 °C with periodic monitoring by ^{31}P NMR spectroscopy. No change in the rate of reaction over that in the absence of colloidal palladium was observed.

Colloidal Platinum Catalyzed Decomposition of Pd(1,8-naphthalenediyl)$(PEt_3)_2$ (3). Into a toluene solution of Pt(η^2-PhCCPh)$(PEt_3)_2$ (12.5 mg, 0.0205 mmol in 1.00 mL of toluene) in a screw-cap NMR tube was injected 1.5 mL of O_2. The tube was heated in an oil bath at 120 °C for 12 h to completely decompose the alkyne complex. The resulting yellow solution and platinum black mixture was filtered through diatomaceous earth, and the clear yellow filtrate containing colloidal palladium[12] was subjected to several freeze−pump−thaw cycles to removed dissolved O_2. A mixture of 0.20 mL of 24.0 mM **3** and 0.20 mL of the colloidal platinum solution was placed in an NMR tube fitted with a vacuum stopcock. The tube was flame-sealed on a vacuum line after freezing the sample and evacuating the headspace (no freeze−pump−thaw cycles). The mixture was then heated in a constant-temperature NMR probe at 100 °C with periodic monitoring by ^{31}P NMR spectroscopy. See the Supporting Information for data.

Colloidal Platinum Catalyzed Cycloaddition of Pd(1,8-naphthalenediyl)$(PEt_3)_2$ (3) with PhCCPh. A colloidal platinum solution, prepared as above, was used to prepare an NMR sample that was 12.0 mM in **3** and 24.0 mM in PhCCPh. The NMR tube was flame-sealed on a vacuum line after freezing the sample and evacuating the headspace (no freeze−pump−thaw cycles) and heated at 100 °C with periodic monitoring by ^{31}P NMR spectroscopy. See the Supporting Information for data.

TEM Analyses. TEM samples were prepared by evaporation of 7 μL of the solutions applied to a copper grid with a carbon support film. The micrographs were obtained on a JEOL 1200 EX transmission electron microscope. Micrograph images are supplied as Supporting Information.

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Supporting Information Available: Tables and figures giving additional kinetic data and plots and TEM images. This material is available free of charge via the Internet at http://pubs.acs.org.

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