Mechanistic Investigation of Stoichiometric Alkyne Insertion into Pt−B Bonds and Related Chemistry Bearing on the Catalytic Diborylation of Alkynes Mediated by Platinum(II) Diboryl Complexes†

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The insertion reactivity of alkynes with the diboryl complex $(Ph_3P)_2Pt(BCat)_2$ (**1**, Cat ≡ $\{C_6H_4O_2\}^{2-}$) has been investigated. Under stoichiometric conditions **1** mediates cis-diborylation of alkynes and the $(PPh_3)_2Pt$ fragment is trapped by alkyne to give the corresponding Pt−alkyne complexes. Kinetic studies under pseudo first-order conditions of alkyne indicate that the reaction is first order in **1**. In the absence of added phosphine, no alkyne dependence is observed. The stoichiometric reaction is inhibited by phosphine addition, and under these conditions, a first-order dependence on alkyne concentration is observed for the disappearance of **1**. The stoichiometric results exclude simple, bimolecular insertion of an alkyne into Pt−B bonds of **1**, and the observed dependence on phosphine and alkyne strongly favors a mechanism where phosphine dissociation generates a three-coordinate intermediate that mediates alkyne insertion. Activation parameters for the stoichiometric alkyne insertion were derived from the temperature dependence of k_{obs} (70−110 °C). An Eyring plot yielded the following: $\Delta H^{\ddagger} = 25.9(7)$ kcal/mol and $\Delta S^{\ddagger} = 4(2)$ eu. The rates of alkyne diborylation are also sensitive to the nature of the alkyne as 4-octyne reacts much more readily than diphenylacetylene. For *para*-substituted diarylacetylenes, the rate for the bis(*p*-trifluoromethyl) derivative is accelerated and the rate for the bis(*p*-methoxy) derivative is retarded relative to diphenylacetylene. The reactivity of the related diboryl complex, $(PPh_3)_2Pt(BPin)_2$ (**9**, Pin ≡ $\{(CH_3)_2CO-CO(CH_3)_2\}^{2-}$), is much more complex as reductive elimination of PinB−BPin is observed before the onset of the diborylation reaction. This appears to be a general feature for this compound as elimination is promoted by various reagents (*e.g.*, CO, PPh_3, $Me_3Sn-SnMe_3$, and CatB−BCat). The catalytic diborylation of alkynes mediated by **1** (in the presence of added triphenylphosphine) was investigated. Kinetics experiments revealed many similarities to the stoichiometric reaction as an inverse dependence on $[PPh_3]$ and first-order dependence on [alkyne] and [**1**] were observed. Expressions that directly relate the catalytic and stoichiometric observed rate constants were derived, and the measured values for these two systems were identical within experimental error. Thus, the data are consistent with a catalytic manifold that is identical to that observed in the stoichiometric reaction. Under catalytic conditions, the rate of alkyne diborylation exhibited no dependence on [CatB−BCat].

Introduction

Transition metal complexes have shown considerable promise in promoting borylation reactions of unsaturated substrates. Hydroboration is one of the few reductive transformations where chemical functionality is retained, as the B−C bonds that result from borylation can be converted to a wide variety of C−E functional groups with retention of regio- and stereochemistry at carbon.[1] Due in large part to the general utility of the hydroboration reaction, transition-metal-catalyzed borylation chemistry has emerged in the past decade.[2] Catalysis by late transition metals is most prevalent;[3−10] however, lanthanide[11] and early transition metal systems[12−16] offer some interesting possibilities with regard to controlling chemo-, stereo-, and regioselectiv-

† A portion of this work was presented at the 210th National Meeting of the American Chemical Society, Chicago, IL, Aug 1995; Abstract INOR 690.

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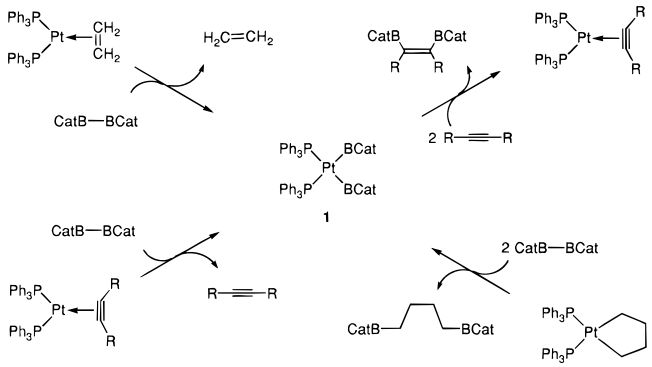
ity. While the modes of interaction in early metal systems are diverse, metal boryl complexes are the principal actors in late metal systems.

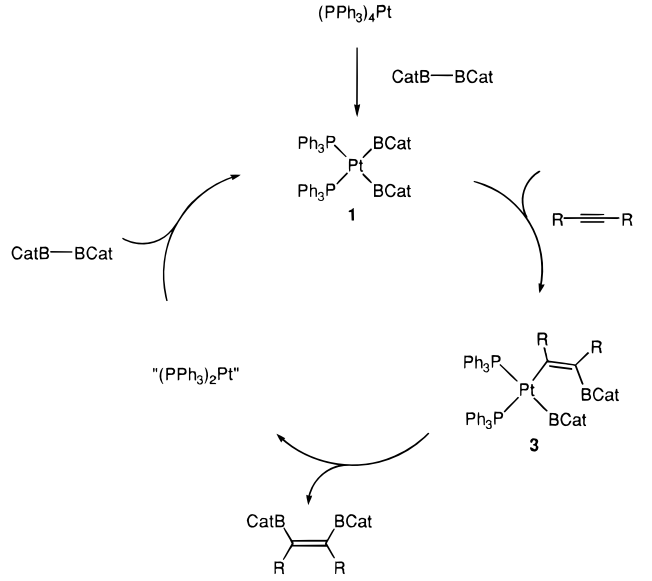
Although diboron tetrahalides react with various unsaturated organic substrates,[17] their difficult preparation dramatically limits their synthetic utility. When the boron−boron bond is supported by amide or alkoxide linkages, the stability of the B−B species is dramatically enhanced at the expense of reactivity. Simple molecular orbital arguments suggest topological similarities between diboron tetrahalides, and their derivatives, with carbon based fragments, as well as dihydrogen. While comparisons to olefinic fragments are experimentally supported by the observation that the B−B bond distance decreases when Ar_2B-BAr_2 derivatives are reduced by two electrons,[18,19] the comparison to H_2 is more tenuous. Nonetheless, preliminary reports indicate that B−B bonds oxidatively add to metal centers with B−B bond cleavage.[20,21] Thus, catalyzed transfer of B−B bonds to unsaturated organic substrates might be expected to parallel metal-mediated reactivity of H_2 and other E−X transfer reactions. Recent reports are consistent with this notion as metal mediated addition of B−B bonds to C≡C,[22,23] C═C,[24,25] and M−C bonds have appeared.[21,26]

Detailed mechanistic information regarding reactivity of M−B bonds is sparse with the most significant work involving B−H activation related to metal-mediated hydroboration.[27,28] Most of these investigations have focused on reactivity of Wilkinson's catalyst where the manifold of accessible intermediates is complex.[6,8] Labeling studies have provided useful information particularly with regard to the reaction pathways favored in this system.[6] Examples where insertions into metal boron bonds proceed cleanly are rare, and factors which determine product selectivities are not well understood.[29−31]

Scheme 1



Scheme 2



We recently reported oxidative and metathetic reactivity of simple B−B bonds with olefin, alkyne, and organometallacyclic bis(triphenylphosphine)platinum complexes.[21] In each case CatB−BCat reacted smoothly to generate a common diboryl complex, $(Ph_3P)_2Pt(BCat)_2$ (**1**, Cat ≡ $\{C_6H_4O_2\}^{2-}$), that has been implicated as the active catalyst in the catalytic diborylation of alkynes mediated by $Pt(PPh_3)_4$. Preliminary experiments showed that the pure diboryl complex catalyzed addition of CatB−BCat to alkynes, consistent with the earlier supposition by Miyaura and Suzuki.[22] Under catalytic conditions, **1** was the sole platinum containing species observed in solution. Since the reactions in Scheme 1 proceeded cleanly and quantitatively as judged by NMR spectroscopy, this system seemed ideally suited for addressing fundamental issues of B−C bond formation in this system. This paper addresses the mechanism for alkyne insertion into Pt−B bonds in bis(phosphine)-platinum systems.

Results and Discussion

Stoichiometric Alkyne Diborylation. A mechanism has been proposed for the diborylation of alkynes

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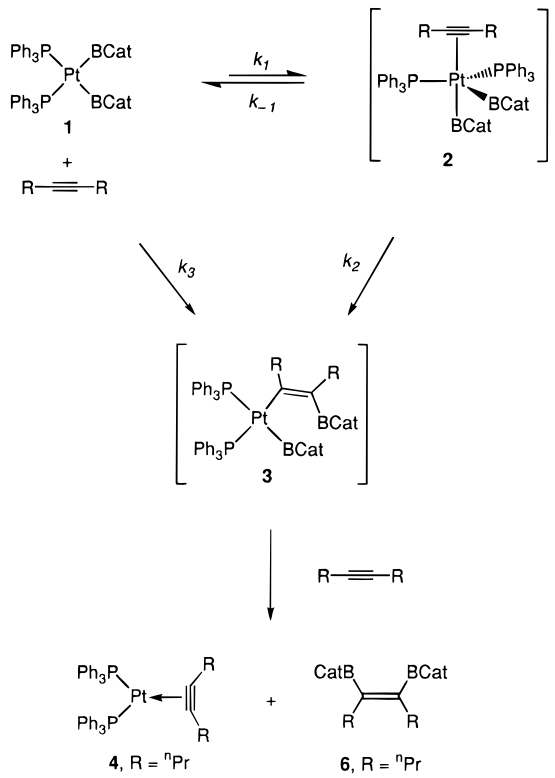
Scheme 3



in the presence of $(PPh_3)_4Pt$.[22,23] In this mechanism, shown in Scheme 2, a species related to **1** is proposed to be the active catalyst, and the initial B−C forming reaction is insertion of the alkyne into the Pt−B bond of *cis*-$(PPh_3)_2Pt(BPin)_2$ (Pin ≡ $\{(CH_3)_2CO-CO-(CH_3)_2\}^{2-}$).[32,33] Reductive elimination from an alkenylboryl species generates "$(PPh_3)_2Pt$" and the diborylated alkene product, and oxidative addition of PinB−BPin to "$(PPh_3)_2Pt$" completes the catalytic cycle.

While NMR data indicate that *cis*-$(PPh_3)_2Pt(BPin)_2$ is present under reaction conditions, no experimental evidence has been offered to support or exclude steps in the postulated mechanism. Certainly, a deeper understanding of the steps preceding B−C bond formation could prove useful in designing systems that diborylate other unsaturated substrates. Since direct study of the catalytic reaction is potentially more complex, we attempted to unravel the mechanism by applying stoichiometric constraints to diborylation mediated by **1** (eq 1).

$$(PPh_3)_2Pt(BCat)_2 + 2RC{\equiv}CR \longrightarrow (PPh_3)_2Pt(\eta^2\text{-}RC{\equiv}CR) + (R)(BCat)C{=}C(R)(BCat) \quad (1)$$

In the absence of added diboron reagent, a clean reaction is observed when excess alkyne is present to trap "$(PPh_3)_2Pt$" as $(PPh_3)_2Pt(\eta^2$-alkyne).[34] Two distinct pathways that involve bimolecular reactions between **1** and alkyne are shown in Scheme 3. In both cases, alkyne insertion is presumed to be rate limiting. Both rate laws require a first-order dependence in [**1**] and [RC≡CR], and although these two pathways are mechanistically distinct, they are indistinguishable if intermediate **2** cannot be detected.

When the reaction in eq 1 was monitored under pseudo-first-order conditions with regard to alkyne concentration, plots of ln [**1**] vs time were linear over 3 half-lives. This suggested that the reaction in eq 1 is first order in [**1**]. Although the limited solubility of [**1**] prevented determination over a broad concentration range, k_{obs} appears to be invariant with respect to [**1**]. Significantly, k_{obs} exhibited no alkyne dependence over a wide range of alkyne concentration. Thus, mechanisms corresponding to the rate laws in eqs 2 and 3 can be excluded as the observed kinetics are consistent with the rate law in eq 4.

$$\frac{-d[\mathbf{1}]}{dt} = \frac{k_1k_2}{(k_{-1} + k_2)}[\mathbf{1}][RC{\equiv}CR] \quad (2)$$

$$\frac{-d[\mathbf{1}]}{dt} = k_3[\mathbf{1}][RC{\equiv}CR] \quad (3)$$

$$\frac{-d[\mathbf{1}]}{dt} = k_{obs}[\mathbf{1}] \quad (4)$$

The reactivity of square-planar, d^8 systems has received a great deal of attention in the chemical literature, and mechanistic studies have revealed that alkylbis(phosphine)M(II) systems (M = Pd, Pt) often react by dissociation of phosphine to give three-coordinate reactive intermediates.[35−39] Although boryl ligands are topologically distinct from alkyl or aryl counterparts,[40] the exclusion of the mechanisms in Scheme 3 suggested dissociative pathways involving three-coordinate intermediates as possible alternatives. To test these possibilities the reaction in eq 1 was monitored at various phosphine concentrations. In the stoichiometric reaction, phosphine addition clearly suppressed the reaction rate, and plots of $1/k_{obs}$ vs $[PPh_3]$ were linear (Figure 1). Two mechanisms that involve dissociative first steps are shown in Schemes 4 and 5. In Scheme 4 phosphine dissociation is presumed to be rate-limiting, while the subsequent coordination and insertion steps are rapid. In Scheme 5, alkyne insertion is presumed to be the rate-limiting step, whereas **1**, **4**, and **5** are in rapid equilibrium. Alkenylborane elimination is assumed to be irreversible in both instances.[41] Although we have not been able to probe reversibility of alkyne coordination or insertion, crossover experiments do show that

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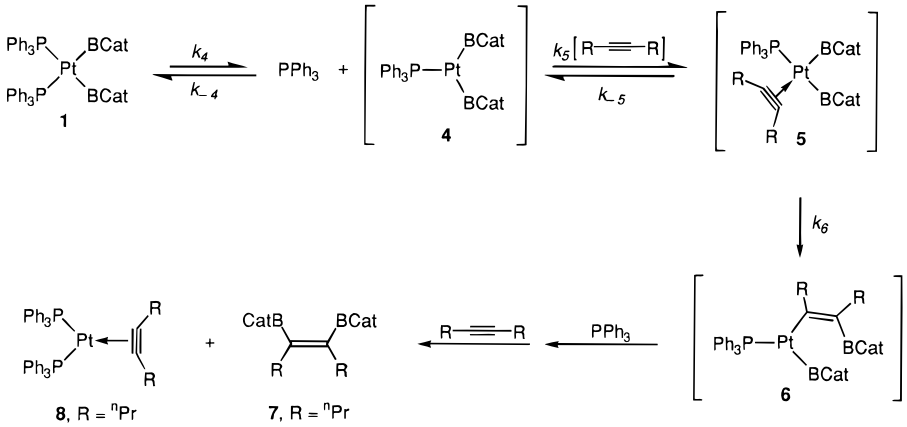
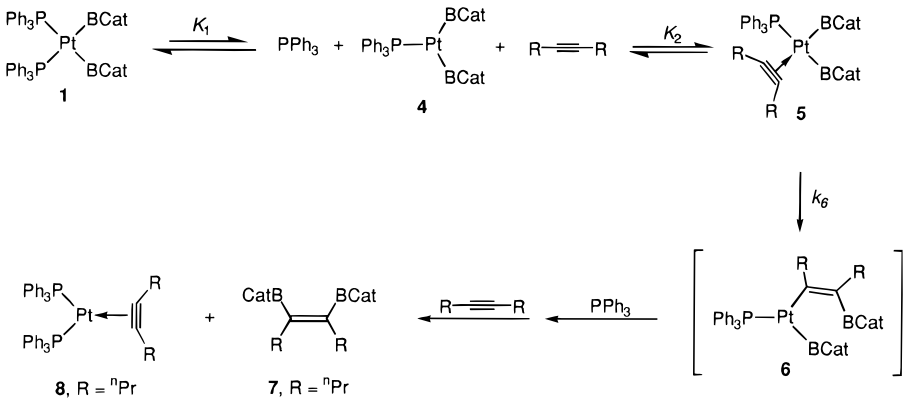
Scheme 4



Scheme 5



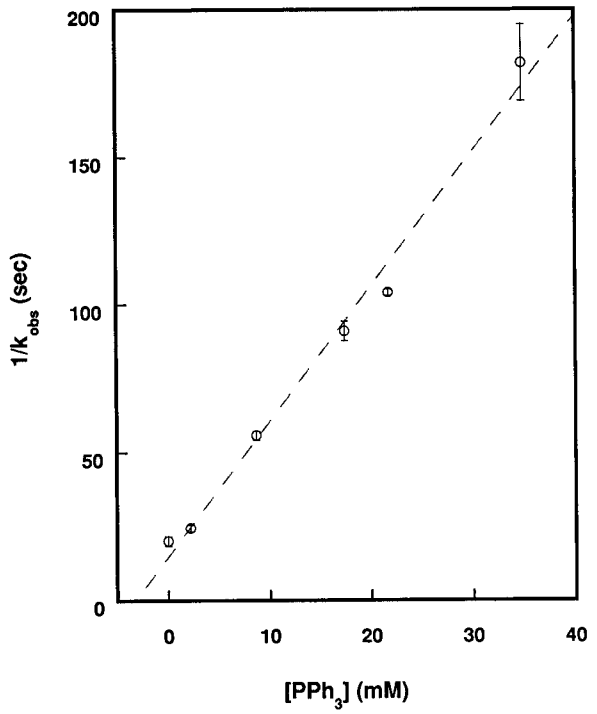


Figure 1. Plot of $1/k_{obs}$ vs PPh_3 concentration for the reaction of **1** with 4-octyne at 90 °C in C_6D_6 ($[\mathbf{1}]_0 = 8.7$ mM, [4-octyne]$_0$ = 52 mM).

elimination of the diborylated alkene is irreversible.[42] Obviously, the failure to observe intermediates has no bearing on the choice of mechanism, since **1** can be thermodynamically favored to the extent that **4** and **5** are not detectable.

Simplified rate expressions can be derived by applying steady-state or equilibrium approximations[43] to Schemes 4 and 5, respectively.[44] Application of the steady-state approximation to Scheme 4 gives the rate law and k_{obs} expression shown in eqs 5 and 6, while the equilibrium treatment for Scheme 5 gives the expressions in eqs 7 and 8.

$$-\frac{d[\mathbf{1}]}{dt} = k_{obs}[\mathbf{1}] \tag{5}$$

$$k_{obs} = \frac{k_4 k_5 k_6 [RC{\equiv}CR]}{k_{-4}(k_{-5} + k_6)[PPh_3] + k_5 k_6 [RC{\equiv}CR]} \tag{6}$$

$$\frac{d[\mathbf{1} + \mathbf{4} + \mathbf{5}]}{dt} = k_{obs}[\mathbf{1} + \mathbf{4} + \mathbf{5}] \tag{7}$$

$$k_{obs} = \frac{-k_6 K_1 K_2 [RC{\equiv}CR]}{K_1 + [PPh_3] + K_1 K_2 [RC{\equiv}CR]} \tag{8}$$

An inverse dependence on phosphine concentration is consistent with either mechanism, as eqs 6 and 8 reduce to eqs 9 and 10 when phosphine terms dominate the denominator. When $[PPh_3] \approx 0$, eq 6 reduces to $k_{obs} = k_4$, while eq 8 yields eq 11. In principle, the two mechanisms are distinguishable in the absence of phos-

(42) 4-Octyne was diborylated under catalytic conditions. Once the reaction was complete, 3-hexyne was added to the reaction mixture and the solution was heated for 5 h at 80 °C. Diborylation of hexyne was not observed.

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(44) See the Experimental Section for details regarding rate law derivation.

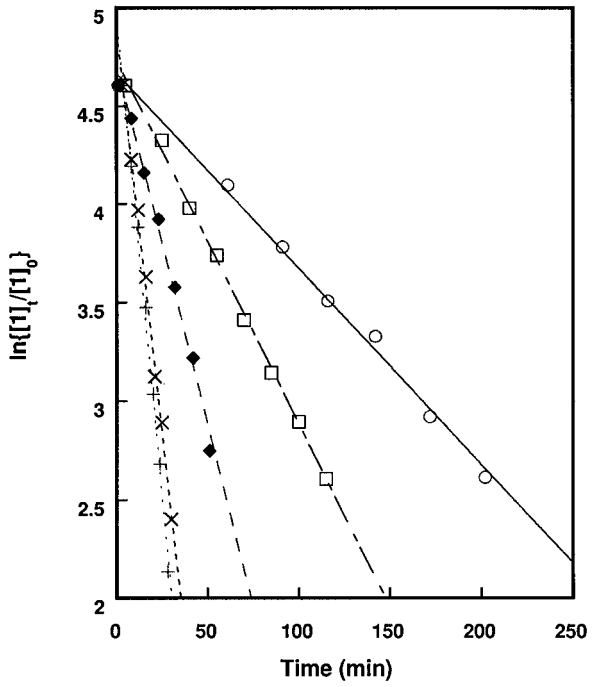

Figure 2. Plot of $\ln\{[\mathbf{1}]_t/[\mathbf{1}]_0\}$ vs time for the reaction of **1** with 4-octyne in the presence of PPh_3-d_{15} ($[\mathbf{1}]_0 = 8.7$ mM, $[PPh_3\text{-}d_{15}] = 70$ mM) at 105 °C in C_6D_6 (○, $[\text{4-octyne}]_0 = 27$ mM], $k_{obs} = 9.8(2) \times 10^{-3}$ s^{-1}: ◆, $[\text{4-octyne}]_0 = 52$ mM, $k_{obs} = 18.9(3) \times 10^{-3}$ s^{-1}; +, $[\text{4-octyne}]_0 = 105$ mM, $k_{obs} = 40(2) \times 10^{-3}$ s^{-1}; ×, $[\text{4-octyne}]_0 = 208$ mM, $k_{obs} = 82(2) \times 10^{-3}$ s^{-1}); +, $[\text{4-octyne}]_0 = 260$ mM, $k_{obs} = 98(4) \times 10^{-3}$ s^{-1}).

phine if $K_1 \gg K_1K_2[RC{\equiv}CR]$. In this regime the

$$k_{obs} = \frac{k_4k_5k_6[RC{\equiv}CR]}{k_{-4}(k_{-5} + k_6)[PPh_3]} \tag{9}$$

$$k_{obs} = \frac{-k_6K_1K_2[RC{\equiv}CR]}{[PPh_3]} \tag{10}$$

$$k_{obs} = \frac{-k_6K_1K_2[RC{\equiv}CR]}{K_1 + K_1K_2[RC{\equiv}CR]} \tag{11}$$

mechanism in Scheme 5 requires an alkyne dependence. We do not see an alkyne dependence at any concentration of alkyne. Thus if the mechanism in Scheme 5 operates, $K_1 \ll K_1K_2[RC{\equiv}CR]$ and $k_{obs} \approx k_6$. Both eqs 9 and 10 predict that an alkyne dependence should be detectable for either mechanism at sufficiently high phosphine concentrations ($k_{-4}[PPh_3] \gg (k_5k_6/k_5 + k_6)$-$[RC{\equiv}CR]$ or $[PPh_3] \gg K_1 + K_1K_2[RC{\equiv}CR]$). This is indeed the case, as k_{obs} exhibits a first-order dependence on $[RC{\equiv}CR]$ at modest phosphine concentrations (Figure 2). Thus, the kinetic data are consistent with either proposal.

In the absence of phosphine, reaction rates were too rapid for deriving reliable activation parameters from the temperature dependence of k_{obs}. This problem was circumvented by suppressing the reaction rate by addition of phosphine, and k_{obs} was measured from 70 to 110 °C. The Eyring plot in Figure 3 yielded the following activation parameters: $\Delta H^{\ddagger} = 25.9(7)$ kcal/mol and $\Delta S^{\ddagger} = 4(2)$ eu. The magnitude of $\Delta S^{\ddagger}$ seems to disfavor a mechanism involving phosphine dissociation

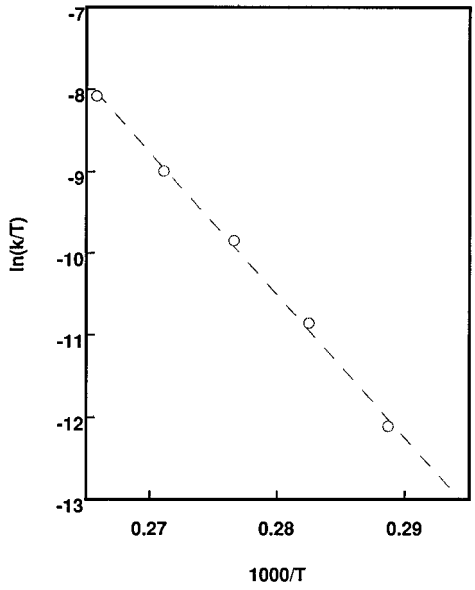

Figure 3. Eyring plot for diborylation of 4-octyne by **1** in the presence of PPh_3-d_{15} (C_6D_6, $T = 343{-}383$ K, $\Delta H^{\ddagger} = 25.9(7)$ kcal/mol, $\Delta S^{\ddagger} = 4(2)$ eu, $[\mathbf{1}]_0 = 8.7$ mM, $[\text{4-octyne}]_0 = 52$ mM, $[PPh_3\text{-}d_{15}] = 8.7$ mM).

as the rate-limiting step;[45] nonetheless, rate-limiting dissociation is not categorically excluded by a small $\Delta S^{\ddagger}$ value.[46] At first glance, a negative value for $\Delta S^{\ddagger}$ might be expected in a pathway involving rate-limiting alkyne insertion into the Pt−B bond; however, investigations of C≡C and C═C insertions into M−X bonds indicate that the magnitude of $\Delta S^{\ddagger}$ can be small, and its sign can be either negative or positive.[35,47]

In the absence of phosphine, k_{obs} reduces to the rate constant for the rate-determining step in the proposed mechanisms. If phosphine dissociation is *truly* rate limiting, borylation rates for different alkynes should be invariant. Conversely, if alkyne insertion is rate limiting, then it might be expected that variations in the steric or electronic requirements of the alkyne could effect k_{obs}. We attempted to compare rates for the stoichiometric reactions between **1** and 1-hexyne, phenylacetylene, and diphenylacetylene. For 1-hexyne and phenylacetylene, ^{31}P-NMR indicated that several metal-containing products form which unfortunately prevents comparisons between internal and external alkynes. Since the acetylene proton seemed the likely culprit, the reaction between **1** and diphenylacetylene was examined. In this case borylation proceeded smoothly, though at a severely retarded rate as compared to dialkyl-substituted alkynes. Thus, k_{obs} is effected by the nature of the alkyne, which would not be expected if the phosphine dissociation were slower than coordination and insertion steps.[48]

The sensitivity of borylation to the electronic properties of the alkyne substrate was probed by comparing the rates of borylation for 4,4′-substituted diarylacety-

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(46) Wilkins, R. G. *Kinetics and Mechanisms of Transition Metal Complexes*; Wilkins, R. G., Ed.; VCH: Weiheim, Germany, 1991, p 109.
(47) Burger, B. J.; Santarsiero, B. D.; Trimmer, M. S.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 3134−3146.
(48) It could be argued that disparities in the equilibrium constants for trapping of **4** with alkyne could account for the discrepancy in rates. We believe that this is unlikely since we observe preferential binding of diphenylacetylene vs 4-octyne to the "$(PPh_3)_2Pt$" fragment.

Table 1. Relative Rates for Stoichiometric Borylations of Alkynes by 1

alkyne	k_{obs}(s^{-1})
octyne	0.0137(1)
diphenylacetylene	0.0064(2)
bis(*p*-anisyl)acetylene	0.0047(1)
bis[*p*-(trifluoromethyl)phenyl]acetylene	fast

lenes. Borylation of 1,2-di-*p*-anisylacetylene proceeded at a slower rate as compared to diphenylacetylene (70 °C). Unfortunately, borylation of 1,2-bis[*p*-(trifluoromethyl)phenyl]acetylene was too rapid for rigorous kinetic analysis,[49] and other substituted diarylacetylenes did not yield tractable data. The rapid reaction rate for 1,2-bis[*p*-(trifluoromethyl)phenyl]acetylene is puzzling as an approximate doubling of the reaction rate was expected from linear free-energy relationships and tabulated σ_{para} values.[50] In this case, rates for substituted diphenylacetylenes appear to offer little information regarding the borylation mechanism; however, the qualitative observations for substituted diarylacetylenes show that gross borylation rates are sensitive to electronic perturbations in the alkyne substrate. The rate data for borylation of alkyne substrates in this work are included in Table 1.

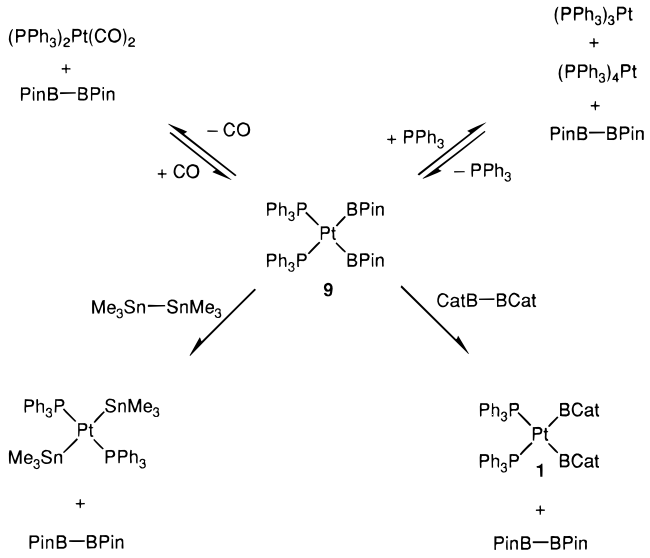
From this stoichiometric investigation emerges an obvious feature concerning reactivity in this system. Specifically, if **1** serves as the active catalyst under catalytic conditions, catalysis by **1** should be more efficient than catalysis mediated by the precatalyst, $(PPh_3)_4Pt$, since conversion to **1** liberates PPh_3. This is indeed the case, as alkynes which were not effectively diborylated by catalysis originating from $(PPh_3)_4Pt$ undergo smooth diborylation when pure **1** is used as the catalyst.

While the mechanism for alkyne diborylation proposed in this work differs from that suggested by Miyaura and Suzuki,[22] our results argue that the original assertion for the diboryl complex, *cis*-$(PPh_3)_2Pt(BPin)_2$ (**9**), being the active catalyst was correct.[22] Since *cis*-$(PPh_3)_2Pt(BPin)_2$ can be readily prepared by the route analogous to that for **1**, comparison of the stoichiometric borylation reaction should be straightforward. However, in contrast to the catecholate boryl chemistry, spectra recorded under ambient conditions prior to initiation of the diborylation reaction indicated chemical equilibrium between **9**, $(PPh_3)_2Pt(\eta^2$-4-octyne) (**8**), 4-octyne, and PinB−BPin (eq 12). To test for

$$\underset{\mathbf{9}}{(PPh_3)_2Pt(BPin)_2} + RC{\equiv}CR \rightleftharpoons \underset{\mathbf{8}}{(PPh_3)_2Pt(\eta^2\text{-}RC{\equiv}CR)} + PinB{-}BPin \quad (12)$$

reversibility of this reaction, the analogous experiment was performed using the volatile alkyne 2-butyne. As was the case for 4-octyne, the alkyne complex formed readily with concurrent elimination of PinB−BPin. Removal of 2-butyne, in *vacuo*, regenerated **9** and

Scheme 6



confirmed the reversibility of the elimination. Reductive elimination of PinB−BPin is observed when **9** is reacted with PPh_3, $Me_3Sn{-}SnMe_3$, CO, and CatB−BCat (Scheme 6).[51] In contrast, elimination of CatB−BCat from **1** is observed only for CO addition. Other qualitative observations suggest that **9** is intrinsically less stable than **1**. For example, when **9** is dissolved in chloroform-d_1 under ambient conditions, *cis*-$(PPh_3)_2PtCl_2$ forms readily while **1** exhibits moderate stability under these conditions. Qualitative disparities between rates for oxidative addition of CatB−BCat and PinB−BPin to Wilkinson's catalyst have been reported;[20] however, the conversion of **9** to **1** obviously has thermodynamic origins. Although we are not yet certain that Pt−B bond cleavage occurs in the reaction between **9** and CatB−BCat, this observation clearly indicates that formation of **1** + PinB−BPin is thermodynamically favored over **9** + CatB−BCat. It is tempting to argue that the equilibrium is driven by formation of stronger Pt−B bonds in **1**; however, a stronger B−B bond in PinB−BPin relative to CatB−BCat would also be consistent with the experimental observations.[52] The ease with which the elimination reactions proceed is in marked contrast to reductive eliminations of alkanes from *cis*-dialkylplatinum bis(phosphine) complexes.[37−39]

The observed equilibria between **9**, PPh_3, and PinB−BPin certainly complicates comparisons between the relative rates of borylation for catecholate and pinacolate $(RO)_2B{-}B(OR)_2$ species under "stoichiometric" conditions. Since the diborylation reaction precludes evaluation of the equilibrium between **9** and alkynes under reaction conditions, the equilibrium constant at elevated temperature was determined by extrapolating data from a van't Hoff plot for the equilibrium in eq 12 (Figure 4). From these data the equilibrium constant at 50 °C was calculated to be 12.9. Thus, under typical conditions for catalytic borylation of 4-octyne (in the absence of added phosphine), **9** is the principal Pt-containing species. Not surprisingly, the equilibrium is sensitive

(49) In all kinetic runs, the NMR tubes were heated briefly at 50 °C to dissolve the substrate. The integrity of the sample was confirmed by NMR prior to kinetic runs at 70 °C. In the case of 1,2-bis[*p*-(trifluoromethyl)phenyl]acetylene, approximately 50% of the alkyne was diborylated during dissolution at 50 °C.

(50) Lowry, T. H.; Richardson, K. S. *Mechanism and Theory in Organic Chemistry*, 2nd ed.; Lowry, T. H., Richardson, K. S., Eds.; Harper and Row: New York, 1981; p 131.

(51) The compounds in Scheme 6 were identified by their $^{31}P\{^1H\}$ NMR spectra, which corresponded to the reported literature values.

(52) The B−B bond in PinB−BPin measures 1.711(6) Å and is significantly *longer* than the B−B bond in related catecholate derivatives where the B−B distances are 1.68 Å: Nöth, H. *Z. Naturforsch.* **1984**, *39b*, 1463−1466.

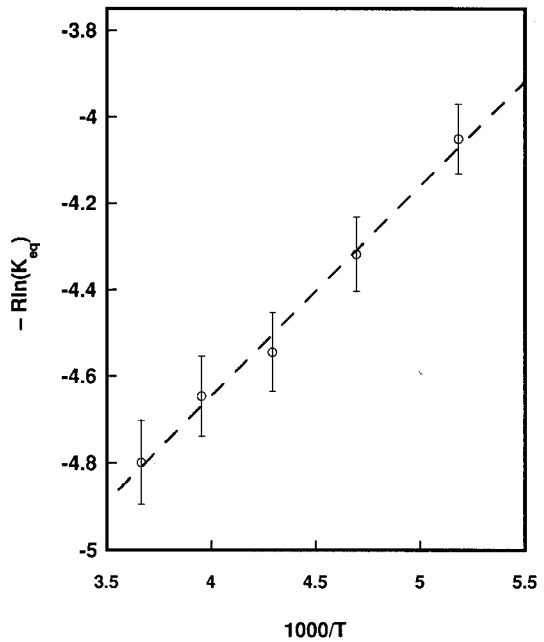


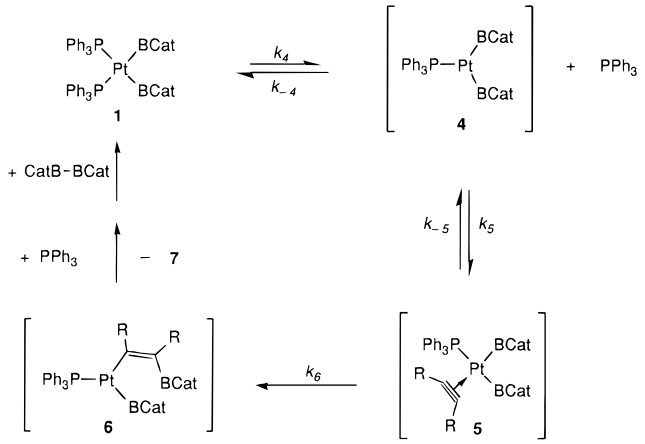
Figure 4. van't Hoff plot for the equilibrium in eq 12 ([**9**]$_0$ = 8.7 mM, [4-octyne]$_0$ = 52 mM; ΔH = 0.49 kcal/mol; ΔS = 6.6 eu).

to the alkyne substrate. For example, when equimolar quantities of **9** and diphenylacetylene are dissolved in C_6D_6, the alkyne complex, $(Ph_3P)_2Pt(\eta^2$-PhCCPh), is the only phosphine-containing species detected by $^{31}P\{^1H\}$ NMR.

Although in stoichiometric reactions between **1** and alkynes neither CatB−BCat nor **8** is detected in solution, the equilibria observed in the reactions of **9** with alkynes raise the possibility that alkyne diborylation in the catecholate system could stem from a bimolecular reaction between trace concentrations of **8** (and related alkyne complexes) and CatB−BCat.[53] This seems unlikely as the borylation rates in the stoichiometric reaction between **1** and alkyne exhibit no alkyne dependence. If borylation proceeded via pathways that are first (or higher) order in **8**, an alkyne dependence would be expected since equilibrium concentrations of **8**, albeit small, depend on alkyne concentration.

Catalytic Diborylation Chemistry. Solutions of the diboryl complexes **1** and **9** both exhibit catalytic activity for diborylation of alkynes by their respective B−B reagents. Addition of CatB−BCat or PinB−BPin to 4-octyne proceeds at comparable rates when catalyzed by **1** or **9**, respectively. Quantititative comparisons of rates were not possible due to deviations from pseudo-first-order consumption of alkyne in the absence of added phosphine. The cause of these deviations in the catecholate system is not clear; however, borylation by other boryl species generated in the presence of excess CatB−BCat could account for the observations. When phosphine is present during catalytic borylation mediated by **1**, well-behaved, pseudo-first-order consumption of 4-octyne was observed. Since **1** was the only Pt-containing complex detected (^1H and ^{31}P NMR) when catalytic diborylations were run in the presence of added phosphine, and comparisons to the stoichiometric reactivity of **1** could be made, the kinetics of the diborylation of 4-octyne, catalyzed by **1**, were investigated.

Scheme 7



A potential mechanism for this catalysis is illustrated in Scheme 7. Similarities to the mechanism proposed for the stoichiometric reactivity of **1** with alkyne (Schemes 4 and 5) are readily apparent; however, in contrast to the stoichiometric reaction, [**1**] remains constant throughout the course of the catalysis. Scheme 7 represents the case where rates for equilibration are rapid compared to the rate for alkyne insertion. Again, application of either steady-state or equilibrium approximations gives rate laws for the consumption of alkyne.

$$\frac{-\mathrm{d[RC{\equiv}CR]}}{\mathrm{d}t} = \left(\frac{k_4k_5k_6[\mathbf{1}]}{k_{-4}(k_5+k_6)[\mathrm{PPh_3}]+k_5k_6[\mathrm{RC{\equiv}CR}]}\right)[\mathrm{RC{\equiv}CR}] \quad (13)$$

$$\frac{-\mathrm{d[RC{\equiv}CR+5]}}{\mathrm{d}t} = \frac{-k_6K_1K_2[\mathbf{1}]}{[\mathrm{PPh_3}]+K_1K_2[\mathbf{1}]}[\mathrm{RC{\equiv}CR+5}] \quad (14)$$

The rate laws in eqs 13 and 14 simplify under limiting conditions where $k_{-4}(k_5 + k_6)[PPh_3] \gg k_5k_6[RC{\equiv}CR]$ (eq 15) or $[PPh_3] \gg K_1K_2[\mathbf{1}]$ (eq 16). Under these conditions

$$\frac{-\mathrm{d[RC{\equiv}CR]}}{\mathrm{d}t} = k_{\mathrm{obs}}[\mathrm{RC{\equiv}CR}] \quad (15)$$

$$k_{\mathrm{obs}} = \frac{(k_4k_5k_6)[\mathbf{1}]}{k_{-4}(k_5+k_6)[\mathrm{PPh_3}]}$$

$$\frac{\mathrm{d[RC{\equiv}CR+5]}}{\mathrm{d}t} = -k_{\mathrm{obs}}[\mathrm{RC{\equiv}CR+5}] \quad (16)$$

$$k_{\mathrm{obs}} = \frac{-k_6K_1K_2[\mathbf{1}]}{[\mathrm{PPh_3}]}$$

both mechanisms require that the reaction is first order in [**1**] and [RC≡CR] and exhibits an inverse dependence on phosphine concentration. Even at modest phosphine concentrations, plots of ln [RC≡CR] vs time in Figure 5 are linear through 3 half-lives confirming a first-order dependence on alkyne and [**1**], and plots of $1/k_{obs}$ vs $[PPh_3]$ are linear as required by eqs 15 and 16 (Figure

(53) Alkyne complexes in these systems are known to react *via* associative and dissociative pathways: Birk, J. P.; Halpern, J.; Pickard, A. L. *Inorg. Chem.* **1968**, *7*, 2672−2673.

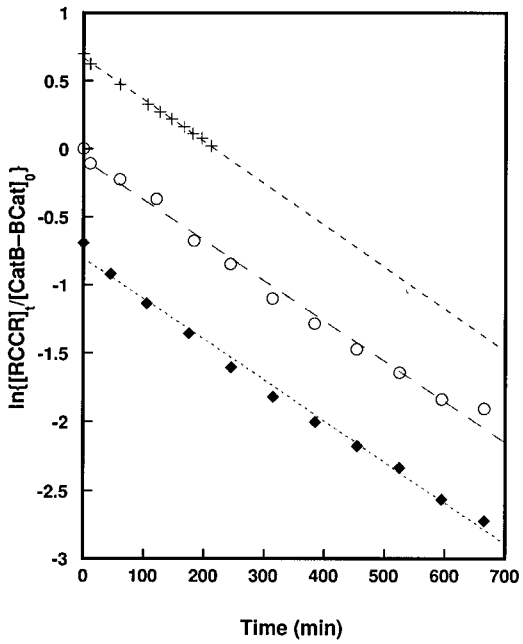


Figure 5. Plot of $\ln\{[\text{4-octyne}]_t/[\text{CatB}-\text{BCat}]_0\}$ vs time for the catalytic diborylation of 4-octyne by CatB−BCat in the presence of **1** and PPh_3 at 105 °C in C_7D_8 (◆, $[\text{4-octyne}]_0$ = 42 mM, [CatB−BCat] = 84 mM; ○, $[\text{4-octyne}]_0$ = 42 mM, [CatB−BCat] = 42 mM; +, $[\text{4-octyne}]_0$ = 84 mM, [CatB−BCat] = 42 mM, $[\mathbf{1}]_0$ = 7.0 mM, $[PPh_3]$ = 55 mM).

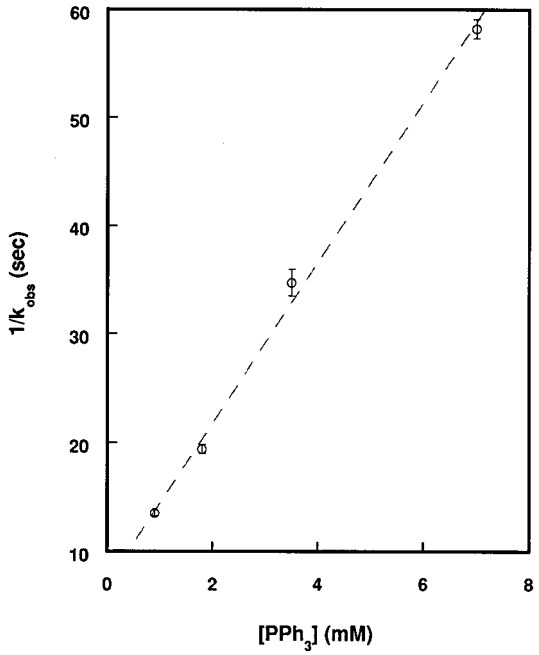


Figure 6. Plot of $1/k_{obs}$ vs PPh_3 concentration for the catalytic diborylation of 4-octyne by CatB−BCat in the presence of **1** and PPh_3 at 100 °C in C_6D_6 ($[\text{4-octyne}]_0$ = [CatB−BCat] = 42 mM, [**1**] = 7.0 mM).

6). The rate for alkyne consumption was unaffected by the concentration of CatB−BCat. Again, this finding, in conjunction with the facility with which CatB−BCat oxidative addition to Pt(0) complexes occurs, is consistent with the assumption that regeneration of [**1**] is rapid and follows the rate-determining step. The data from catalytic runs in the presence of phosphine are reliably reproducible and exhibit dependencies that are required by the mechanism in Scheme 7.

The dependence of k_{obs} on concentrations of alkyne, phosphine, and **1** suggests that the mechanisms for diborylation under stoichiometric and catalytic conditions are essentially identical. Clearly, a direct comparison of rate constants between the stoichiometric and catalytic systems could corroborate this supposition. Inspection of eqs 10 and 16 immediately reveals that a direct comparison can be made, as $k_6K_1K_2$ can be expressed in terms of k_{obs} and concentrations of **1**, PPh_3, and alkyne. The calculated values for $k_6K_1K_2$ from the stoichiometric and catalytic measurements are 0.019(3) and 0.024(3) s^{-1}, respectively. Thus, the data support the notion that the mechanisms for diborylation in both systems are identical as the values derived from eqs 17 and 18 are identical within experimental error.

$$k_6K_1K_2 = \frac{k_{obs}[PPh_3]}{[RC{\equiv}CR]} \tag{17}$$

$$k_6K_1K_2 = \frac{k_{obs}[PPh_3]}{[\mathbf{1}]} \tag{18}$$

Conclusions

The results from this detailed investigation of the diborylation of alkynes by **1** under stoichiometric and catalytic conditions are most consistent with a mechanism whereby phosphine dissociation from **1** generates a three-coordinate species which mediates alkyne insertion. Clearly, catalytic activity of **1** is enhanced when the pure complexes are isolated, instead of generated from $(PPh_3)_4Pt$ and the corresponding boron reagents. The identity of the heteroatom substituents has pronounced effects on the metal-containing species in stoichiometric and catalytic systems, and the borylation rate is sensitive to the nature of the alkyne. This is not surprising if alkyne insertion into the Pt−B bond is the rate-limiting step in the diborylation reaction. The requirement for phosphine dissociation has clear implications for design of other catalysts that effect diborylation of other unsaturated substrates. This may account for the empirical observations that $Pt(NBE)_3$,[21] and related base-free Pt complexes,[54] will effect catalytic diborylation of olefins, while these same substrates are not borylated by **1** or **9**.

Experimental Section

General Considerations. All manipulations were performed using glovebox, Schlenk, or vacuum-line techniques. B_2Cat_2 was prepared by the literature method.[55] B_2Pin_2 was prepared in analogous fashion, except that trace HCl impurities were removed by washing the solid with triethylamine prior to pentane extraction and crystallization of the product. Diethyl ether, pentane, and toluene were predried over sodium and distilled from sodium/benzophenone ketyl. Methylene chloride was predried and then distilled from CaH_2. Benzene-d_6 and toluene-d_8 were dried over 3 Å sieves, and the distilled solvents were stored over sodium. Methylene chloride-d_2 and chloroform-d_1 were dried over 3 Å sieves and distilled prior to use. Dinitrogen was purified by passage through a column of MnO on silica. ^1H NMR spectra were recorded on Varian

(54) Iverson, C. N.; Smith, M. R., III. Manuscript in preparation.
(55) Welch, C. N.; Shore, S. G. *Inorg. Chem.* **1968**, *7*, 225−230.

Gemini-300 (300.1 MHz) and Varian VXR-300 (300.0 MHz) spectrometers and referenced to residual proton solvent signals. ^{11}B and ^{31}P spectra were recorded using a Varian VXR-300 spectrometer operating at 96.234 and 121.994 MHz, respectively. Boron chemical shifts are referenced to a $BF_3 \cdot Et_2O$ (15% v/v in $CDCl_3$) external standard. Phosphorous chemical shifts are referenced to a 85% phosphoric acid external standard. Mass spectroscopic data were obtained on a portable Trio-1 VG Masslab Ltd. mass spectrometer. Elemental analyses were determined by Desert Analytics, Tuscon, AZ.

***cis*-$(PPh_3)_2Pt(BCat)_2$.** $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$[56] (100 mg, 0.134 mmol) and B_2Cat_2 (35 mg, 0.15mmol) were placed in a flask and dissolved in 5 mL of toluene. A white precipitate formed immediately. The solution was stirred for 2 h at room temperature, and the supernatant was removed via cannula. Additional product was obtained by removing the solvent under reduced pressure and washing the residue with toluene (2 mL). The overall yield was 96 mg (75%). ^1H NMR (C_6D_6): δ 6.54 (m, 4 H, $BO_2C_6H_4$), δ 6.77 (m, 4 H, $BO_2C_6H_4$), δ 6.80 (m, 18 H, $P(C_6H_5)_3$), δ 7.55 (m, 12 H, $P(C_6H_5)_3$). ^{31}P NMR (C_6D_6): δ 30.19 ($^1J_{Pt-P} = 1608$ Hz). ^{11}B NMR (C_6D_6, quartz NMR tube): δ 47.2 (broad). Mp: 193−195 °C (dec).

***cis*-$(PPh_3)_2Pt(BPin)_2$ (9).**[23] $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ (100 mg, 0.134 mmol) and B_2Pin_2 (35 mg, 0.15 mmol) were placed in a flask and dissolved in 5 mL of toluene. The golden yellow solution was stirred for 2 h at room temperature, and subsequent solvent evaporation yielded a light orange-yellow powder. The residue was recystallized from CH_2Cl_2/ethanol, washed with hexanes, and dried *in vacuo* to give white crystals (91 mg, 70%). ^1H NMR (C_6D_6): δ 1.02 (s, 24 H, $BO_2C_6H_{12}$), δ 6.88 (m, 18 H, $P(C_6H_5)_3$), δ 7.58 (m, 12 H, $P(C_6H_5)_3$). ^{31}P NMR (C_6D_6): δ 29.77 ($^1J_{Pt-P} = 1506$ Hz). ^{11}B NMR (C_6D_6, quartz NMR tube): δ 46.3 (broad). Mp: 183−187 °C (dec). Anal. Calcd for $C_{48.5}H_{55}B_2O_4P_2ClPt$: C, 57.29; H, 5.45. Found: C, 55.28; H, 5.27. Analyses for crystalline samples of $\mathbf{9}\cdot{}^1/_2CH_2Cl_2$ were consistently low in carbon. Although this compound has been structurally characterized, the combustion analysis was not reported.[23] Our melting points for crystalline materials were consistently 40 °C higher than the reported value.

***trans*-$(PPh_3)_2Pt(SnMe_3)_2$.** This preparation is analogous to that reported in the literature.[57] $(PPh_3)_2Pt(\eta^2\text{-}C_2H_4)$ (100 mg, 0.134 mmol) was placed in a flask and dissolved in 7 mL of toluene. A bright yellow solution formed on addition of Me_6Sn_2 (28 μL, 0.134 mmol), and within 15 min a bright yellow precipitate formed. After the solution was stirred for 2 h, the solvent was removed under reduced pressure to afford a bright yellow powder. ^1H NMR (C_6D_6): δ 0.40 (s, 18 H, $SnMe_3$, $^4J_{Pt-H} = 8$ Hz, $^3J_{Sn-H} = 20$ Hz), δ 6.86 (m, 18 H, $P(C_6H_5)_3$), δ 7.46 (m, 12 H, $P(C_6H_5)_3$). ^{31}P NMR (C_6D_6): δ 35.1 ($^1J_{Pt-P} = 2621$ Hz, $^2J_{Sn-P} = 614$, 642 Hz).

Reaction of $(PPh_3)_2Pt(BCat)_2$ with Me_6Sn_2. *cis*-$(PPh_3)_2Pt(BCat)_2$ (100 mg, 0.104 mmol) and Me_6Sn_2 (21.6 μL, 0.208 mmol) were placed in a Schlenk tube and dissolved in 5 mL of toluene in a glovebox. The solution was stirred at 55 °C for 3 h. The solvent was removed *in vacuo* and the residue washed with 10 and 5 mL of pentane to yield 51 mg (49% yield) of a light tan solid. ^1H, ^{31}P, and ^{11}B NMR spectroscopy indicated formation of *cis*-$(PPh_3)_2Pt(BCat)(SnMe_3)$. ^1H NMR ($CDCl_3$): δ −0.45 (m, 9 H, $Sn(CH_3)_3$ ($^5J_{P-H} = 0.9$ Hz, $^4J_{Pt-H} = 12$ Hz, $^3J_{Sn-H} = 42$ Hz), δ 6.72 (m, 2 H, $BO_2C_6H_4$), δ 6.81 (m, 2 H, $BO_2C_6H_4$), δ 6.92−7.37 (m, 30 H, $P(C_6H_5)_3$). ^{31}P NMR ($CDCl_3$, −50 °C): δ 26.63 (d, trans $SnMe_3$, $^2J_{P-P} = 23$ Hz, $^1J_{Pt-P} = 2371$ Hz, $^2J_{Sn-P} = 1268$ Hz), δ 32.84 (br d, trans BCat, $^2J_{P-P} = 20$ Hz, $^1J_{Pt-P} = 1761$ Hz, $^2J_{Sn-P} = 815$ Hz).

NMR Tube Reactions: *cis*-$(PPh_3)_2Pt(\eta^2\text{-4-octyne})$ with B_2Cat_2. *cis*-$(PPh_3)_2Pt(\eta^2\text{-4-octyne})$ (7.2 mg, 0.0087 mmol) and B_2Cat_2 (4.1 mg, 0.017 mmol) were mixed in C_6D_6 and transferred to a sealable NMR tube. After sealing, the tube was thawed, and traces of a white precipitate indicated *cis*-$(PPh_3)_2Pt(BCat)_2$ deposition. ^1H NMR indicated that *cis*-$(PPh_3)_2Pt(BCat)_2$, 4-octyne, and B_2Cat_2 were the sole soluble species. The tube was heated for 4 h at 80 °C to yield *cis*-$(PPh_3)_2Pt(BCat)_2$ (by ^1H and ^{31}P NMR) as the free alkyne was converted to the *cis*-4,5-diboryl-4-octene. ^1H NMR (C_6D_6): δ 0.90 (tr, 6H, $-CH_2CH_2CH_3$), δ 1.53 (sextet, 4H, $-CH_2CH_2CH_3$), δ 2.49 (tr, 4H, $-CH_2CH_2CH_3$), δ 6.73 (m, 4H, $BO_2C_6H_4$), δ 6.91 (m, 4 H, $BO_2C_6H_4$). ^{11}B NMR (C_6D_6): δ 32.7.

Reaction of *cis*-$(PPh_3)_2Pt(BPin)_2$ with Me_6Sn_2. $(PPh_3)_2Pt(BPin)_2$ (10 mg, 0.010 mmol) was dissolved in 600 μL of C_6D_6. Addition of Me_6Sn_2 (2.0 μL, 0.010 mmol) *via* syringe immediately generated a bright yellow solution. ^1H, ^{31}P, and ^{11}B NMR spectroscopy all indicated complete conversion to *trans*-$(PPh_3)_2Pt(SnMe_3)_2$ and B_2Pin_2.

Reaction of *cis*-$(PPh_3)_2Pt(BPin)_2$ with B_2Cat_2. $(PPh_3)_2Pt(BPin)_2$ (12.0 mg, 0.013 mmol) and B_2Cat_2 (3.0 mg, 0.013 mmol) were placed in a sealable NMR tube, and 600 μL of C_6D_6 was added *via* vacuum transfer. Upon warming of the sample to room temperature, traces of a white precipitate indicated $(PPh_3)_2Pt(BCat)_2$ deposition. ^1H, ^{31}P, and ^{11}B NMR spectroscopy all indicated conversion to $(PPh_3)_2Pt(BCat)_2$ and B_2Pin_2, as *cis*-$(PPh_3)_2Pt(BPin)_2$ was not detected.

Equilibrium of *cis*-$(PPh_3)_2Pt(BCat)_2$ with CO. $(PPh_3)_2Pt(BCat)_2$ (10.0 mg, 0.010 mmol) was dissolved in 600 μL of CD_2Cl_2 in a J. Young NMR tube. After the solution was frozen, the argon atmosphere was evacuated and replaced with CO. Upon warming of the sample to room temperature conversion to $(PPh_3)_2Pt(CO)_2$ had occurred as evidenced by ^1H and ^{31}P NMR spectra, and reductive elimination of B_2Cat_2 was confirmed by ^{11}B NMR. Chemical reversibility was confirmed by the regeneration of $(PPh_3)_2Pt(BCat)_2$ upon evacuation of the CO atmosphere.

Equilibrium of *cis*-$(PPh_3)_2Pt(BPin)_2$ with CO. $(PPh_3)_2Pt(BPin)_2$ (10.0 mg, 0.010 mmol) was dissolved in 600 μL of C_7D_8 in a J. Young NMR tube. After the solution was frozen, the argon atmosphere was evacuated and replaced with CO. Upon warming of the sample to room temperature, ^1H and ^{31}P NMR indicated complete conversion to $(PPh_3)_2Pt(CO)_2$. ^{11}B also confirmed reductive elimination of B_2Pin_2. After evacuation of the CO atmosphere, a trace of $(PPh_3)_2Pt(BPin)_2$ was regenerated.

Equilibrium of *cis*-$(PPh_3)_2Pt(BPin)_2$ with 2-Butyne. $(PPh_3)_2Pt(BPin)_2$ (7.5 mg, 0.0077 mmol) was dissolved in 600 μL of C_6D_6 in a J. Young NMR tube. The atmosphere above the frozen solution was evacuated and replaced with approximately 10 molar equiv of 2-butyne. Upon warming of the sample to room temperature, ^1H and ^{31}P NMR indicated nearly complete conversion to *cis*-$(PPh_3)_2Pt(\eta^2\text{-}CH_3CCCH_3)_2$, and reductive elimination of B_2Pin_2 was confirmed by ^{11}B NMR. Reversibility was demonstrated by regeneration of *cis*-$(PPh_3)_2Pt(BPin)_2$ upon evacuation of the 2-butyne atmosphere. Evacuation to dryness and dissolution of the residue in C_6D_6 showed *cis*-$(PPh_3)_2Pt(BPin)_2$ to be the major product (^{31}P NMR); however, ^1H NMR indicated that some diborylation of 2-butyne had occurred.

Equilibrium of *cis*-$(PPh_3)_2Pt(BPin)_2$ with 4-Octyne. $(PPh_3)_2Pt(BPin)_2$ (5.1 mg, 0.0052 mmol) was placed in a sealable NMR tube, 4.6 μL of 4-octyne was added *via* syringe, and toluene-d_8 was added to 600 mL. After sealing, ^{31}P NMR spectra were recorded at 193, 213, 233, 253, and 273 K. The concentrations of *cis*-$(PPh_3)_2Pt(BPin)_2$, $(PPh_3)_2Pt(\eta^2\text{-4-octyne})$, B_2Pin_2, and 4-octyne were determined by the relative intensities of the Pt-containing species.

Reaction of *cis*-$(PPh_3)_2Pt(BPin)_2$ with PPh_3. *cis*-$(PPh_3)_2Pt(BPin)_2$ (10 mg, 0.010 mmol) and PPh_3 (30 mg, 0.11 mmol) were dissolved in 600 μL of CD_2Cl_2 in an NMR tube. NMR spectra (^1H and ^{31}P at −80 °C) of the yellow solution indicated reductive elimination of B_2Pin_2 and formation of tris(triphenylphosphino)platinum(0) and tetrakis(triphenylphosphino)platinum(0).

(56) Camalli, M.; Caruso, F.; Chaloupka, S.; Leber, E. M.; Rimml, H.; Venanzi, L. M. *Helv. Chim. Acta* **1990**, *73*, 2263−2274.

(57) ^{31}P data were not available in the original report: Akhtar, M.; Clark, H. C. *J. Organomet. Chem.* **1970**, *22*, 233−240.

Reaction of *cis*-$(PPh_3)_2Pt(BCat)_2$ with PPh_3. *cis*-$(PPh_3)_2Pt(BCat)_2$ (10 mg, 0.010 mmol) and PPh_3 (30 mg, 0.11 mmol) were placed in an NMR tube and dissolved in 600 μL of CD_2Cl_2 to form a clear, colorless solution. ^1H, ^{31}P, and ^{11}B NMR (−80 and 20 °C) showed **1** to be the exclusive Pt-containing species.

Crossover Experiment. *cis*-$(PPh_3)_2Pt(BCat)_2$ (4 mg, 0.0042 mmol), B_2Cat_2 (1 mg, 0.0042 mmol), and 4-octyne (4.6 μL, 0.032 mmol) were placed in a sealable NMR tube and 595 μL of C_6D_6 was added while in a glovebox. The tube was flame-sealed, and the mixture was heated at 80 °C in a constant-temperature oil bath until **1** was consumed. The sealed tube was opened in the glovebox. The solution was transferred to a new sealable tube, and 3-hexyne (2 μL, 0.02 mmol) was added. After flame-sealing, the solution was heated at 80 °C for 5 h. ^1H NMR spectra showed no evidence for diborylation of hexyne.

Diborylation of 1,2-Bis(*p*-anisolyl)acetylene. 1,2-bis(*p*-anisolyl)acetylene[58] (50 mg, 0.21 mmol), B_2Cat_2 (50 mg, 0.21 mmol), and 2.5 mol % **1** were dissolved in 4 mL of toluene. The solution was heated at reflux for 4 h, and then the solvent was removed *in vacuo*. A 20 mL volume of Et_2O was added, and the mixture was filtered. Evaporation of the filtrate yielded 74 mg (74%) of the diborylated product. ^1H NMR ($CDCl_3$): δ 3.76 (s, 3 H, OCH_3, δ 6.76 (m, 2 H, $BO_2C_6H_4$), δ 7.05 (m, 4 H, C_6H_4OMe), δ 7.11 (m, 2 H, $BO_2C_6H_4$). ^{11}B NMR ($CDCl_3$): δ 32.3. EI/MS: m/z = 476 (M^+), I = 100 (100); m/z = 477 ($[M + 1]^+$), I = 30 (30); m/z = 475 ($[M - 1]^+$), I = 48 (45). Mp; 146−151 °C.

Diborylation of 1,2-Bis[*p*-(trifluoromethyl)phenyl]acetylene. 1,2-Bis[*p*-(trifluoromethyl)phenyl]acetylene (57 mg, 0.18 mmol), bis[*p*-(trifluoromethyl)phenyl]acetylene, B_2Cat_2 (43 mg, 0.18 mmol), and 2.5% **1** were dissolved in 4 mL of toluene. The solution was heated at reflux for 2 h, and then the solvent was removed *in vacuo*. A 5 mL volume of Et_2O was added, and the mixture was filtered. Evaporation of the filtrate yielded 85 mg (85%) of the diborylated product. ^1H NMR ($CDCl_3$): δ 7.09 (m, 4 H, $C_6H_4CF_3$), δ 7.27 (m, 2 H, $BO_2C_6H_4$), δ 7.49 (d, 2 H, $BO_2C_6H_4$). ^{11}B NMR ($CDCl_3$): δ 31.5. EI/MS: m/z = 552 (M^+), I = 100 (100); m/z = 553 ($[M + 1]^+$), I = 31 (30); m/z = 551 ($[M - 1]^+$), I = 51 (45). Mp; 140−145 °C.

Protonolysis of Diborylated Phenylacetylenes.[59] A 51 mg amount of the alkene derived from diborylation of 1,2-bis(*p*-anisolyl)acetylene (0.11 mmol) was dissolved in 0.5 mL of diglyme. Several drops of glacial acetic acid were added, and the solution was heated at 45 °C for 15 h. The solvent was removed *in vacuo*. Formation of the *cis*-stilbene was confirmed by comparing the ^1H NMR shift of the olefinic protons (δ = 6.43 ppm) to the literature value (δ = 6.44 ppm).[60]

A 50 mg amount of the alkene derived from diborylation of 1,2-bis[*p*-(trifluoromethyl)phenyl]acetylene (0.091 mmol) was dissolved in 0.5 mL of diglyme. Several drops of glacial acetic acid were added, and the solution was heated at reflux for 12 h. The solvent was removed *in vacuo*. Formation of the *cis*-stilbene was confirmed by comparing the ^1H NMR shift of the olefinic protons (δ = 6.70 ppm) to the literature value (δ = 6.72 ppm).[61]

Kinetic Experiments. All kinetic experiments were run in sealed NMR tubes with a total solution volume of 600 μL. PPh_3 was added to the tubes in the form of 0.2 M solutions of PPh_3 in C_6D_6 and C_7D_8. The reactions were heated in constant temperature oil baths (Cole-Parmer Polystat Constant Temperature Circulator or Tekmar RCT) or in the Varian 300 MHz spectrometer when the reaction temperature and completion times were convenient.

A typical experimental run for the stoichiometric diborylation of alkynes by *cis*-$(PPh_3)_2Pt(BCat)_2$ is described as follows: *cis*-$(PPh_3)_2Pt(BCat)_2$ (5.0 mg, 0.0052 mmol) and 4-octyne (4.6 μL, 0.032 mmol) were placed in an NMR tube. In a drybox, 595 μL of C_6D_6 was added via syringe. The solution was frozen in liquid nitrogen, and the tube was flame-sealed. The tube was heated briefly to dissolve the Pt complex. The tube was then placed in a constant-temperature oil bath. At specific intervals the tube was removed from the oil bath and the reaction was quenched by rapid cooling in an ice bath. ^1H NMR spectra were then recorded at room temperature. The progress of the reaction was monitored to 3 half-lives by measuring the disappearance of the catecholate resonance at δ 6.54.

A typical experimental run under catalytic conditions is described as follows: *cis*-$(PPh_3)_2Pt(BCat)_2$ (4 mg, 0.0042 mmol), CatB−Bcat (6 mg, 0.025 mmol), 4-octyne (3.7 μL, 0.025 mmol), and C_6D_6 (595 μL) were added to an NMR tube. The tube was then brought out of the glovebox and flame-sealed. The mixture was heated to 50 °C in the Varian 300 MHz NMR spectrometer, and the reaction was monitored to 3 half-lives completion. A program supplied within the spectrometer's software was used to take scans of the mixture at specified intervals, and the time-dependent alkyne concentration was calculated by integrating the resonance of the methylene group adjacent to the alkyne triple bond.

Derivation of Rate Expressions. In Scheme 4, the time-dependent concentrations for **1**, **4**, **5**, and **8** are governed by the eqs 19-22. Application of the steady state approximation

$$-\frac{d[\mathbf{1}]}{dt} = k_4[\mathbf{1}] - k_{-4}[\mathbf{4}][PPh_3] \tag{19}$$

$$\frac{d[\mathbf{4}]}{dt} = k_4[\mathbf{1}] + k_{-5}[\mathbf{5}] - (k_{-4}[PPh_3] + k_5[RC{\equiv}CR])[\mathbf{4}] \tag{20}$$

$$\frac{d[\mathbf{5}]}{dt} = k_5[RC{\equiv}CR][\mathbf{4}] - (k_{-5} + k_6)[\mathbf{5}] \tag{21}$$

$$\frac{d[\mathbf{8}]}{dt} = k_6[\mathbf{5}] \tag{22}$$

to [**5**] yields 23, and combination of the steady-state expression

$$\frac{d[\mathbf{5}]}{dt} \approx 0 \Rightarrow [\mathbf{5}] = \left(\frac{k_5[RC{\equiv}CR]}{k_{-5} + k_6}\right)[\mathbf{4}] \tag{23}$$

$$\frac{d[\mathbf{4}]}{dt} \approx 0 \Rightarrow [\mathbf{4}] = \left(\frac{k_{-5} + k_6}{k_{-4}(k_{-5} + k_6) + k_5k_6[RC{\equiv}CR]}\right)[\mathbf{1}] \tag{24}$$

$$\therefore -\frac{d[\mathbf{1}]}{dt} = \left(\frac{k_4k_5k_6}{k_{-4}(k_{-5} + k_6)[PPh_3] + k_5k_6[RC{\equiv}CR]}\right)[\mathbf{1}] \tag{25}$$

for [**4**] and eq 23 gives eq 24. The first-order rate law in eq 25 follows from substitution of the expression for [**4**] (eq 24) in eq 19.

In the application of the equilibrium approximation to Scheme 5, the assumption in eq 26 is made. From the

$$-\frac{d[\mathbf{1} + \mathbf{4} + \mathbf{5}]}{dt} \approx \frac{d[\mathbf{8}]}{dt} = k_6[\mathbf{5}] \tag{26}$$

equilibrium constants K_1 and K_2, [**1**] and [**4**] can be expressed in terms of [**5**] (eqs 27 and 28). Equations 27 and 28 provide

$$K_2 = \frac{[\mathbf{5}]}{[\mathbf{4}][RC{\equiv}CR]} \Rightarrow [\mathbf{4}] = \frac{[\mathbf{5}]}{K_2[RC{\equiv}CR]} \tag{27}$$

$$K_1 = \frac{[\mathbf{4}][PPh_3]}{[\mathbf{1}]} \Rightarrow [\mathbf{1}] = \frac{[\mathbf{4}][PPh_3]}{K_1} \Rightarrow [\mathbf{1}] = \frac{[\mathbf{5}][PPh_3]}{K_1K_2[RC{\equiv}CR]} \tag{28}$$

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(60) For olefinic protons: (a) Engman, L. *J. Org. Chem.* **1984**, *49*, 3559−3563. For methoxy protons: (b) Todrez, Z. V.; Ionina, E. A. *J. Organomet. Chem.* **1993**, *453*, 193−195.
(61) Bellucci, G.; Bianchini, R.; Chiappe, C.; Brown, R. S.; Sleboka-Tilk, H. *J. Am. Chem. Soc.* **1991**, *113*, 8012−8016.

an expression of [**5**] in terms of [**1** + **4** + **5**] (eq 30), and

$$[\mathbf{1}+\mathbf{4}+\mathbf{5}] = \left(1 + \frac{1}{K_2[\mathrm{RC{\equiv}CR}]} + \frac{[\mathrm{PPh_3}]}{K_1K_2[\mathrm{RC{\equiv}CR}]}\right) \quad (29)$$

$$\therefore [\mathbf{5}] = \left(\frac{K_1K_2[\mathrm{RC{\equiv}CR}]}{K_1 + [\mathrm{PPh_3}] + K_1K_2[\mathrm{RC{\equiv}CR}]}\right)[\mathbf{1}+\mathbf{4}+\mathbf{5}] \quad (30)$$

$$-\frac{\mathrm{d}[\mathbf{1}+\mathbf{4}+\mathbf{5}]}{\mathrm{d}t} = \left(\frac{k_6K_1K_2[\mathrm{RC{\equiv}CR}]}{K_1 + [\mathrm{PPh_3}] + K_1K_2[\mathrm{RC{\equiv}CR}]}\right)[\mathbf{1}+\mathbf{4}+\mathbf{5}] \quad (31)$$

substitution for [5] in eq 26 gives the final form of the rate law in eq 31. Under catalytic conditions the diboryl complex, **1**, is regenerated. The rate laws that govern the time-dependent concentrations of the species in Scheme 7 are given as follows:

$$-\frac{\mathrm{d}[\mathbf{1}]}{\mathrm{d}t} = k_4[\mathbf{1}] - k_{-4}[\mathbf{4}][\mathrm{PPh_3}] - k_6[\mathbf{5}] \quad (32)$$

$$\frac{\mathrm{d}[\mathbf{4}]}{\mathrm{d}t} = k_4[\mathbf{1}] + k_{-5}[\mathbf{5}] - (k_{-4}[\mathrm{PPh_3}] + k_5[\mathrm{RC{\equiv}CR}])[\mathbf{4}] \quad (33)$$

$$\frac{\mathrm{d}[\mathbf{5}]}{\mathrm{d}t} = k_5[\mathrm{RC{\equiv}CR}][\mathbf{4}] - (k_{-5} + k_6)[\mathbf{5}] \quad (34)$$

$$\frac{\mathrm{d}[\mathrm{RC{\equiv}CR}]}{\mathrm{d}t} = -k_6[\mathbf{5}] + k_{-5}[\mathbf{5}] - k_5[\mathrm{RC{\equiv}CR}][\mathbf{4}] \quad (35)$$

With application of the steady-state approximation to [**4**] and [**5**], eqs 33 and 34 yield the expressions in eqs 36 and 37. Application of the steady-state approximation to [**1**] in eq

$$[\mathbf{4}] = \frac{k_4[\mathbf{1}] + k_{-5}[\mathbf{5}]}{k_{-4}[\mathrm{PPh_3}] + k_5[\mathrm{RC{\equiv}CR}]} \quad (36)$$

$$[\mathbf{4}] = \left(\frac{k_{-5} + k_6}{k_5[\mathrm{RC{\equiv}CR}]}\right)[\mathbf{5}] \quad (37)$$

31, with substitution of the value for [**4**] in eq 36, yields eq 38. Similarly, substitution of the expression for [**4**] in eq

$$[\mathbf{5}] = \left(\frac{k_4k_5[\mathrm{RC{\equiv}CR}]}{k_{-4}(k_{-5} + k_6)[\mathrm{PPh_3}] + k_5k_6[\mathrm{RC{\equiv}CR}]}\right)[\mathbf{1}] \quad (38)$$

$$\frac{\mathrm{d}[\mathrm{RC{\equiv}CR}]}{\mathrm{d}t} = -k_6[\mathbf{5}] \quad (39)$$

37 in eq 35 gives eq 39. Combining eqs 38 and 39 gives the rate law in eq 40. This is identical to that in eq 13. Applying

$$\frac{-\mathrm{d}[\mathrm{RC{\equiv}CR}]}{\mathrm{d}t} = \left(\frac{k_4k_5k_6[\mathrm{RC{\equiv}CR}]}{k_{-4}(k_{-5} + k_6)[\mathrm{PPh_3}] + k_5k_6[\mathrm{RC{\equiv}CR}]}\right)[\mathbf{1}] \quad (40)$$

the equilibrium approximation to the catalytic reaction in Scheme 7 gives eq 41. From the equilibrium constants in eqs

$$-\frac{\mathrm{d}[\mathrm{RC{\equiv}CR} + \mathbf{5}]}{\mathrm{d}t} \approx \frac{\mathrm{d}[\mathbf{8}]}{\mathrm{d}t} = k_6[\mathbf{5}] \quad (41)$$

42 and 43, [**5**] can be expressed in terms of [**5** + RC≡CR] (eq 45). Substituting this expression for [**5**] in eq 41 gives the

$$K_2 = \frac{[\mathbf{5}]}{[\mathbf{4}][\mathrm{RC{\equiv}CR}]} \Rightarrow [\mathrm{RC{\equiv}CR}] = \frac{[\mathbf{5}]}{K_2[\mathbf{4}]} \quad (42)$$

$$K_1 = \frac{[\mathbf{4}][\mathrm{PPh_3}]}{[\mathbf{1}]} \Rightarrow [\mathbf{4}] = \frac{K_1[\mathbf{1}]}{[\mathrm{PPh_3}]} \Rightarrow [\mathrm{RC{\equiv}CR}] = \frac{[\mathrm{PPh_3}][\mathbf{5}]}{K_1K_2[\mathbf{1}]} \quad (43)$$

$$[\mathrm{RC{\equiv}CR} + \mathbf{5}] = \left(1 + \frac{[\mathrm{PPh_3}]}{K_1K_2[\mathbf{1}]}\right)[\mathbf{5}] \quad (44)$$

$$\therefore [\mathbf{5}] = \left(\frac{K_1K_2[\mathbf{1}]}{[\mathrm{PPh_3}] + K_1K_2[\mathbf{1}]}\right)[\mathrm{RC{\equiv}CR} + \mathbf{5}] \quad (45)$$

rate law in eq 46. This is identical to the rate equation in eq 14.

$$-\frac{\mathrm{d}[\mathrm{RC{\equiv}CR} + \mathbf{5}]}{\mathrm{d}t} = \left(\frac{k_6K_1K_2[\mathbf{1}]}{[\mathrm{PPh_3}] + K_1K_2[\mathbf{1}]}\right)[\mathrm{RC{\equiv}CR} + \mathbf{5}] \quad (46)$$

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Supporting Information Available: Text and tables for kinetic studies (3 pages). Ordering information is given on any current masthead page.

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