

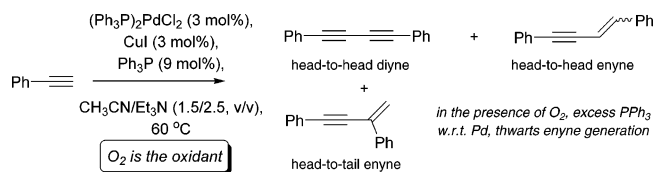
## Requirement for an Oxidant in Pd/Cu Co-Catalyzed Terminal Alkyne Homocoupling To Give Symmetrical 1,4-Disubstituted 1,3-Diynes

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Palladium-catalyzed terminal alkyne dimerization, through oxidative homocoupling, is a useful approach to the synthesis of symmetrical 1,4-diynes. Recent investigations have suggested that this reaction might be accomplished in the absence of intentionally added stoichiometric oxidants (to reoxidize Pd(0) to Pd(II)). In this paper, we have fully addressed the question of whether oxygen (or added oxidant) is required to facilitate this process. The presence of a stoichiometric quantity of air (or added oxidant such as I<sub>2</sub>) is essential for alkyne dimerization. Excess PPh<sub>3</sub> inhibits alkyne dimerization to enyne, which only occurs to a significant extent when the reaction is starved of oxidant. Theoretical studies shed more light on the requirement for an oxidant in the homocoupling reaction in order for the process to be thermodynamically favorable. The employment of I<sub>2</sub> as the stoichiometric oxidant appears to be the method of choice. The dual role of Cu both in transmetalation of alkynyl units to Pd(II) and in assisting reoxidation of Pd(0) to Pd(II) is suggested.

Palladium-catalyzed cross-coupling reactions are widely applied to the formation of C–C bonds.<sup>1</sup> Alkyne dimerization, through oxidative homocoupling, to give 1,3-diynes is important for a number of applications, particularly in the construction of linearly  $\pi$ -conjugated acetylenic oligomers and polymers,<sup>2</sup> natural products,<sup>3</sup>

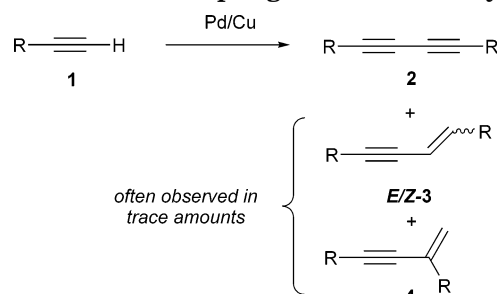
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## SCHEME 1. Homocoupling of Terminal Alkynes



and molecular recognition processes.<sup>4</sup> Here, palladium catalysis has played a key role.<sup>5</sup> Traditional methods for oxidative homocoupling of terminal alkynes **1** to give symmetrical 1,4-disubstituted diynes **2** (Scheme 1) include Cadiot–Chodkiewicz,<sup>6</sup> Eglington,<sup>7</sup> Glaser,<sup>8</sup> Hay,<sup>9</sup> and Sonogashira couplings.<sup>10</sup> Catalytic systems mediated by palladium, Pd(0) or Pd(II), are arguably the most mild, efficient, and selective for the oxidative homocoupling reactions of **1** → **2**.<sup>11</sup> Common side products in these reactions are enynes *E,Z*-**3** and **4**, the former produced through head-to-head coupling and the latter through head-to-tail coupling.<sup>12</sup>

Reported protocols for the oxidative homocoupling include (1) use of (Ph<sub>3</sub>P)<sub>4</sub>Pd(0), CuI, Et<sub>3</sub>N, and chloroacetone (as the reoxidant) in benzene;<sup>13</sup> (2) (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>, CuI, Et<sub>3</sub>N, or DABCO and bromoacetate (as the reoxidant) in THF;<sup>14</sup> (3) (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub>, CuI, and molecular iodine (as the reoxidant) in *i*-Pr<sub>3</sub>N;<sup>15</sup> (4) Pd(0)(dba)<sub>2</sub> (dba

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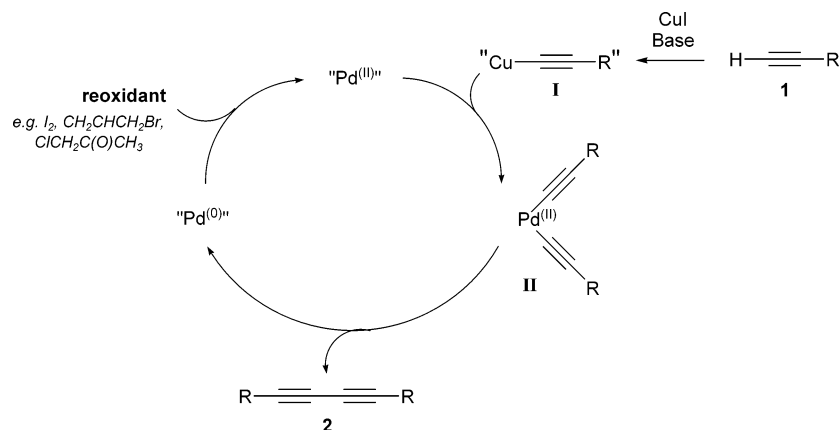
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## SCHEME 2. General Mechanism for the Pd(II) Homocoupling of Alkynes

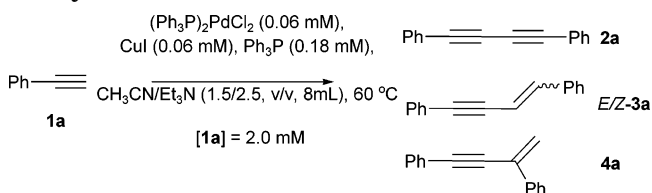


= *E,E*-dibenzylidene acetone), *n*-Bu<sub>4</sub>NBr, NaOH, and allyl bromide (as the oxidant) in CH<sub>2</sub>Cl<sub>2</sub>.<sup>16</sup> Furthermore, the reaction may be conducted in the presence of air to give certain types of diynes.<sup>17</sup>

In all of the above cases, a stoichiometric amount of a reoxidant is required for successful homocoupling. The proposed mechanism for the Pd(II)-catalyzed homocoupling reaction is shown in Scheme 2. The formation of the alkynylcuprate **I**, by base-assisted deprotonation of **1** in the presence of CuI, and subsequent transmetalation with Pd(II), gives a dialkynylpalladium(II) species **II**. Final reductive elimination generates Pd(0) and diyne **2**. The Pd(0) species is reoxidized to Pd(II) with various oxidants to complete the catalytic cycle.

In a recent paper, a member of our group (I.J.S.F.) has reported the homocoupling of **1** to give **2** using a combination of (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> (3 mol %) and CuI (3 mol %) in a CH<sub>3</sub>CN/Et<sub>3</sub>N (1.5/2.5, v/v) solvent mixture, with additional Ph<sub>3</sub>P (9 mol %) at room temperature.<sup>18</sup> The presence of phosphine was essential in eliminating the production of enyne byproducts *E/Z*-**3** and **4**. However, although an added oxidant was not required such as I<sub>2</sub> or chloroacetone, the question of whether air was promoting the homocoupling was unresolved. In this paper, we show conclusive evidence that stoichiometric quantities of air are required under the previously reported conditions. This is consistent with our (T.B.M.) previous findings.<sup>17a</sup> Importantly, theoretical calculations support the requirement for an oxidant in this reaction system. In its absence, H<sub>2</sub> would formally be produced, which we demonstrate is thermodynamically unfavorable. After screening several procedures for the oxidative homocoupling, *vide supra*, we have determined that the use of the I<sub>2</sub> system, developed by Burton and co-workers,<sup>15</sup> is the most versatile at the present time for the homocoupling of electron-deficient arylacetylenes, facilitating access to novel 1,4-diaryl-1,3-diyne.

To establish whether trace quantities of air were promoting the conversion of **1** → **2**, reactions were carried

SCHEME 3. Homocoupling of Phenylacetylene **1a** to Diyne **2a**

out under identical conditions to those reported, but in a nitrogen-filled glovebox (levels of O<sub>2</sub> were < 5 ppm) (Scheme 3).

Specifically, phenylacetylene **1a** (2.0 mM) was added to a reaction vial containing (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> (0.06 mM, 3 mol %) and Ph<sub>3</sub>P (0.18 mM, 9 mol %) in a CH<sub>3</sub>CN/Et<sub>3</sub>N mixture (1.5/2.5, v/v, total volume = 8 mL). The cocatalyst, CuI (0.06 mM, 3 mol %), was added last to initiate the reaction (there is not a Pd-catalyzed background reaction in the absence of CuI). Two reactions were carried out at temperatures of 25 and 60 °C.

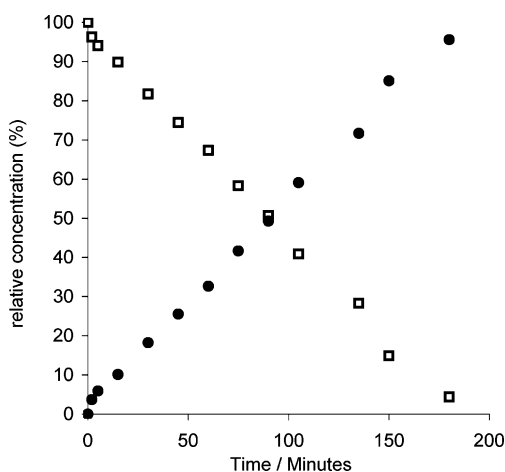
GC/MS analysis of the reaction conducted at 25 °C after 0.25 h indicated the disappearance of a small amount of **1a** and the formation of **2a** (0.058 mM), but critically, no further change was seen after 24 h (concentration of **2a** = 0.058 mM ± 0.005 mM; samples withdrawn at 4, 8, 18, and 24 h). The total formation of **2a** can be accounted for by reduction of Pd(II) to Pd(0) in the first step of the catalytic cycle shown in Scheme 2 (theoretical amount of **2a** produced through the first turnover = 0.06 mM, overall theoretical conversion of **1a** → **2a** = 1 mM). A similar result was observed at 60 °C. Conducting the reaction in the presence of freshly prepared (Ph<sub>3</sub>P)<sub>4</sub>Pd (0.06 mM, 3 mol %), instead of (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> and additional Ph<sub>3</sub>P, resulted in no turnover at all under the glovebox conditions.

The effect of air on the reaction of **1a** → **2a** was assessed using identical reactant/catalyst/cocatalyst concentrations as for the above glovebox reactions. Careful kinetic experiments were performed to monitor the disappearance of **1a** and appearance of **2a** with time, using the (Ph<sub>3</sub>P)<sub>2</sub>PdCl<sub>2</sub> precatalyst, in the presence and absence of additional Ph<sub>3</sub>P ligand at 60 °C (Figures 1 and 2, respectively). A small quantity of air was introduced by opening the reaction vessel for 2 min, once all the components of the reaction mixture had been added (the reaction mixture was prepared under a stream of dried

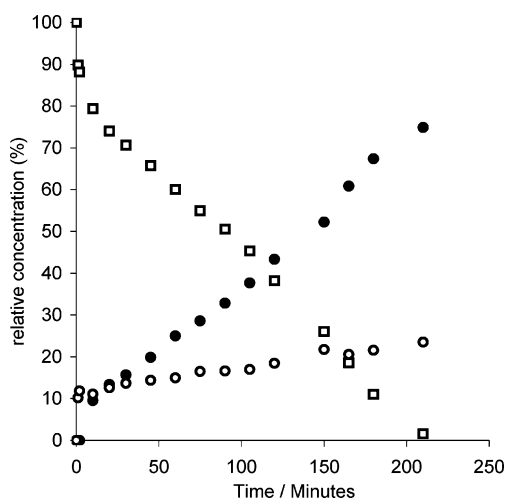
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**FIGURE 1.** Concentration versus time plot for the conversion of **1a** ( $\square$ , 2.0 mM) to **2a** ( $\blacklozenge$ ) in the presence of additional  $\text{Ph}_3\text{P}$ : reaction vessel opened to air for 2 min at  $t_0$ , where the relative concentrations of **1a** and **2a** refer to  $[\mathbf{1a}]_t/[\mathbf{1a}]_0$  and  $[\mathbf{2a}]_t/[\mathbf{1a}]_0$ , respectively.



**FIGURE 2.** Concentration versus time plot for the conversion of **1a** ( $\square$ , 2.0 mM) to **2a** ( $\blacklozenge$ ) and  $E/Z$ -**3a**+**4a** ( $\circ$ ) in the absence of additional  $\text{Ph}_3\text{P}$ : reaction vessel opened to air for 2 min at  $t_0$ , where the relative concentrations of **1a**, **2a**, and  $E/Z$ -**3a**+**4a** refer to  $[\mathbf{1a}]_t/[\mathbf{1a}]_0$ ,  $[\mathbf{2a}]_t/[\mathbf{1a}]_0$ , and  $[E/Z\text{-}\mathbf{3a}+\mathbf{4a}]_t/[\mathbf{1a}]_0$ , respectively.

$\text{N}_2$  using standard Schlenk techniques; dried solvents were degassed using three freeze–thaw–pump cycles). The reactions were then sampled using a gastight syringe, and all GC samples were quenched through a small plug of silica (analysis aliquot = 50  $\mu\text{L}$ , 0.69 g of Kieselgel 60 silica; particle size 0.035–0.070 mm, 220–440 mesh), eluted with  $\text{CH}_2\text{Cl}_2$  ( $\sim 3$  mL), and then stored at  $-30$   $^\circ\text{C}$  prior to analysis by GC. The time-dependence of post-quenched samples showed no change after 72 h at this temperature, proving to be a reliable quenching procedure in this case.<sup>19</sup>

The initial rate seen in Figure 1 is somewhat faster than the overall rate, which is presumably associated with rapid reaction of the alkynylcuprate, derived from reaction of **1a** with  $\text{CuI}$  in the presence of  $\text{Et}_3\text{N}$ , with

**TABLE 1.** Isolated Yields of  $p$ -R- $\text{C}_6\text{H}_4\text{-C}\equiv\text{C-C}\equiv\text{C-C}_6\text{H}_4$ - $p$ -R Using  $\text{O}_2$  or Anaerobic  $\text{I}_2$  as Oxidant

entry	R	% yield ( $\text{O}_2$ )	% yield ( $\text{I}_2$ )
1	H, <b>2a</b>	80	81
2	CN, <b>2b</b>	22	31
3	$\text{CO}_2\text{Me}$ , <b>2c</b>		73
4	$\text{CF}_3$ , <b>2d</b>	41	66
5	Me, <b>2e</b>	42	52
6	SMe, <b>2f</b>	85	
7	OMe, <b>2g</b>	69	78
8	NMe <sub>2</sub> , <b>2h</b>	80	59

$(\text{Ph}_3\text{P})_2\text{PdCl}_2$ , to give  $(\text{Ph}_3\text{P})_n\text{Pd}(0)$  (where  $n = 1\text{--}4$ ) and diyne **2a**, through the intermediate species,  $(\text{Ph}_3\text{P})_n\text{Pd}(\sigma\text{-alkynyl})_2$  ( $n = 1$  or 2). Subsequent turnovers will be dependent on the efficiency of reoxidation of  $\text{Pd}(0)$  to  $\text{Pd}(\text{II})$  by  $\text{O}_2$  vide infra. Note that in this reaction we do not observe the formation of enynes  $E/Z$ -**3a** and **4a** and that the formation of  $\text{Ph}_3\text{P}=\text{O}$  is only observed toward the latter stages of the reaction (by GC/MS).

In the absence of  $\text{Ph}_3\text{P}$ , one can see that the rate of enyne formation is faster in the initial stages ( $<2$  min during which air is being introduced) as compared to the remaining course of the reaction (Figure 2). The  $\text{O}_2$  concentration in solution is expected to be lower at this stage, and hence, the  $\text{Pd}(0)$  concentration will be higher, facilitating generation of the enyne byproducts ( $E/Z$ -**3a** and **4a**) probably via alkyne C–H oxidative addition, alkyne insertion into  $\text{Pd-H}$ , and C–C reductive elimination. This suggests that excess phosphine slows down/inhibits enyne generation, probably by tying up needed coordination sites on  $\text{Pd}(0)$  (Figure 1).

Overall, these reactions demonstrate that air ( $\text{O}_2$ ) does promote the homocoupling process and that the role of excess phosphine is to thwart enyne generation. It is important to note, however, that if  $\text{O}_2$  is bubbled through a solution of **1a**  $\rightarrow$  **2a** at room temperature, under the standard conditions given above, we find that only low conversions to **2a** are seen ( $\sim 20\%$ ). Furthermore, a number of other products are observed by GC/MS analysis, not least the formation of  $\text{Ph}_3\text{P}=\text{O}$  in the early stages of the reaction, the production of other tri- and tetrameric acetylenic products, and the rapid production of palladium black. The separation of the minor side products from **2a** has so far proven unsuccessful.

To compare the use of  $\text{O}_2$  and  $\text{I}_2$  as oxidants, a series of symmetric para-R-substituted 1,4-diphenyl-1,3-butadiynes (**2b–h**) was prepared. Details of the synthesis and characterization are provided in the Supporting Information and the results are summarized in Table 1. The reactions with  $\text{O}_2$  as the oxidant were easier to set up and the product was easier to isolate, but these often gave lower yields and incomplete reactions.

$\text{I}_2$  oxidation, in the absence of  $\text{O}_2$ , proved to be higher yielding in several cases (entries 1, 2, 4, 5, and 7; compounds **2a**, **2b**, **2d**, **2e**, and **2g**). Here, an extra synthetic step involving a sodium thiosulfate wash to remove any unreacted iodine gave purer products. The R =  $\text{CF}_3$  product (entry 4, **2d**) was further characterized by single-crystal X-ray diffraction (see the Supporting Information), and the bond distances and angles are quite

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**TABLE 2. Reaction Energies and Free Energies (kcal mol<sup>-1</sup>) of Reactions (1) ( $\Delta E_1$  and  $\Delta G_1$ ), (2) ( $\Delta E_2$  and  $\Delta G_2$ ), and (3) ( $\Delta E_3$  and  $\Delta G_3$ ) Calculated with Different Theoretical Methods**

		$\Delta E_1$	$\Delta G_1$	$\Delta E_2$	$\Delta G_2$	$\Delta E_3$	$\Delta G_3$
B3LYP	R = Me	0.9	-0.8	-57.9	-51.3	-58.3	-50.6
	R = Ph	-1.2	-1.3	-60.0	-51.8		
CCSD(T)	R = Me	3.7		-56.4		-60.1	

similar to those we recently found for the R = CO<sub>2</sub>Me derivative.<sup>20</sup>

### Computational Results

To investigate the thermodynamics of the homocoupling process, a series of density functional theory calculations were performed at the B3LYP level to optimize all the species in reactions (1)–(3). Frequency calculations at the same level of theory have also been performed to identify all stationary points as minima (zero imaginary frequencies). The 6-311++G\*\* basis set was used in the calculations. On the basis of the optimized structures, single-point calculations at the CCSD(T) level, using the same basis set, were performed to calculate the reaction energies for R = Me. All calculations were performed using the Gaussian 98 package.<sup>21</sup>

The energetics of the following reactions have been theoretically evaluated for R = Me and Ph at the B3LYP level of density functional theory.

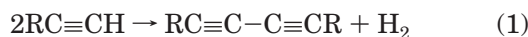


Table 2 gives the results of our energetic calculations. At the B3LYP level, reactions (1) are found to be almost energetically neutral. The high exothermicity of reactions (2) is clearly driven by the formation of H<sub>2</sub>O because eq 2 is the sum of eqs 1 and 3. The CCSD(T) calculations

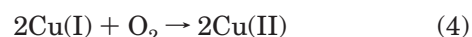
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for R = Me suggest that the B3LYP calculations slightly underestimate the endothermicity of reactions (1) by 2.8 kcal/mol. The experimental formation enthalpy and free energy of H<sub>2</sub>O(g) are -57.8 and -54.6 kcal/mol, respectively.<sup>22</sup> Both the B3LYP and CCSD(T) calculations give comparable values. From these calculations, we conclude that reactions (1) are expected to be slightly endothermic and are thus not particularly favorable thermodynamically. The presence of oxidants, e.g., O<sub>2</sub>, provides the thermodynamic driving force for alkyne homocoupling reactions.

### Comments on the Reoxidation of Pd(0) to Pd(II).

It being clear that an oxidant is required to carry out the homocoupling, it remains to consider the process by which the Pd(0) is reoxidized to Pd(II) under the reaction conditions. While direct reoxidation of Pd is feasible, it may be rather slow. Indeed, Figure 1 indicates a zero-order dependence of the reaction rate on alkyne concentration which would be consistent with the rate-determining step being Pd reoxidation. However, it is important to point out that Cu is widely used to accelerate the reoxidation of Pd(0) to Pd(II) with O<sub>2</sub> as in the industrially important Wacker process for the aerobic oxidation of alkenes to aldehydes.<sup>23</sup> Thus, Cu may well have a dual role in the alkyne homocoupling reaction, first being utilized to mediate alkynyl transfer to Pd(II) via transmetalation from a Cu-alkynyl species, and second in the redox sequence shown in eqs 4 and 5. Further studies of the role of Cu in these and related systems are in progress.



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**Supporting Information Available:** Experimental procedures and characterization data for the diyne compounds, crystallographic data (CIF), and details of the kinetic studies by GC and GC/MS. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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