 

Selected Paper

# Palladium-Catalyzed Oxidative Carbonylation of 1-Alkynes into 2-Alkynoates with Molecular Oxygen as Oxidant

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A new preparative method to produce alkyl 2-alkynoates from 1-alkynes in alcohol under atmospheric pressure of CO at room temperature was developed with palladium–phosphine catalysts, using molecular oxygen as an oxidant. On the basis of the behavior of model complexes such as methoxycarbonylpalladium and alkynylpalladium complexes, we propose a mechanism accounting for the catalytic carbonylation of alkynes through an intermediate having the both methoxycarbonyl and alkynyl ligands that liberates methyl 2-alkynoates and a Pd(0) species on reductive elimination. The oxidation of Pd(0) to Pd(II) species in the presence of a halide ion was confirmed to proceed cleanly with molecular oxygen as the oxidant. On the basis of the findings on homogeneous catalysts, a heterogeneous catalytic system using Pd/C has also been developed.

2-Alkynoates[1] constitute an important class of compounds as biologically active substances and as versatile intermediates in organic synthesis of biologically important compounds such as butenolides,[2] macrolides,[3] and carbapenem intermediates.[4] Lithiation of 1-alkynes, followed by quenching with chloroformate, is the generally employed method for preparation of alkynecarboxylates. However, the method is stoichiometric and entails the use of a strong base; this excludes the method's application to base-sensitive compounds. Thus, finding a convenient method for catalytically synthesizing these alkynoates will provide an important tool in organic synthesis. In view of the versatile activity of palladium complexes to promote various catalytic processes[5–7] we have been examining applicability of palladium-catalyzed carbonylation processes.[8]

In the palladium-catalyzed alkoxycarbonylation of 1-alkynes, two principal routes to unsaturated carboxylic esters are known. One is hydroesterification of alkynes to give $\alpha,\beta$-unsaturated esters[9] and the other is oxidative carbonylation of alkynes in alcohol to give alkyl 2-alkynoates with retention of the triple bond. In the oxidative carbonylation of alkynes, addition of an oxidant is necessary. The use of a Cu(II) salt as an oxidant in combination with NaOAc to carbonylate 1-alkynes in the presence of a palladium catalyst was first reported by Tsuji (Eq. 1).[10]

$$\mathrm{Ph{-}C{\equiv}C{-}H} + \underset{(1\ \mathrm{atm})}{\mathrm{CO}} + \mathrm{MeOH} \xrightarrow[\mathrm{rt,\ 2\ h}]{\mathrm{cat.\ PdCl_2,\ CuCl_2,\ AcONa}} \underset{74\ \%}{\mathrm{Ph{-}C{\equiv}C{-}CO_2Me}} \quad (1)$$

Other oxidizing agents such as quinones in combination with transition metal complexes have been used to perform the carbonylation of phenylacetylene.[11,12] Use of these additives, however, causes complication in separation processes and addition of these extra oxidizing reagents is not desirable. We have been interested in synthesizing alkynecarboxylates from alkynes and CO by a clean method without using extra oxidizing agents.

Here we report a new palladium-catalyzed oxidative carbonylation of 1-alkynes to 2-alkynoates performed under atmospheric pressure of CO and oxygen at room temperature in DMF–alcohol (Eq. 2).[13] The method provides a simple, inexpensive, and clean catalytic carbonylation process of alkynes with atmospheric oxygen, the cheapest oxidant, without using any other added oxidizing agent such as copper salts, as described below in the first part of the paper.

$$\mathrm{Ph{-}C{\equiv}C{-}H} + \underset{(1\ \mathrm{atm})}{\mathrm{CO/O_2}} + \underset{(50\ \mathrm{mol.\ amounts})}{\mathrm{MeOH}} \xrightarrow[\mathrm{Pd(OAc)_2\ (0.1\ mol.\ amounts)}]{\mathrm{PPh_3\ (0.2\ mol.\ amounts)}} \underset{83\ \%}{\mathrm{Ph{-}C{\equiv}C{-}CO_2Me}} \quad (2)$$

The second part of the paper is concerned with the results of mechanistic studies. Despite the usefulness of alkynecarboxylates, very few mechanistic studies have been made to allow us to get some clues for improving the yields and the selectivity of the process. We report here the results of fundamental studies on the behavior of organopalladium complexes assumed as models of intermediates involved in the catalytic processes.

## Results

**1. Catalytic Oxidative Carbonylation of Alkynes with CO and Molecular Oxygen. 1.1 Examination of Experimental Conditions:** Following our finding that oxygen inadvertently admitted into the catalyst system improved the yield of methyl 2-alkynoates, we examined the experimental conditions to improve the oxidative carbonylation process. Table 1

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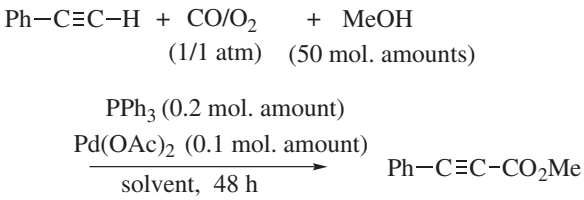
Table 1. Catalytic Oxidative Carbonylation of Phenylacetylene with Molecular Oxygen in Various Solvents




| Run | Temp/°C | Solvent | Yield[a]/% |
|---|---|---|---|
| | | | Ph–C≡C–$CO_2$Me |
| 1 | rt | $(CH_3)_2CO$ | 48 |
| 2 | rt | $CH_3CN$ | 53 |
| 3 | rt | $CH_2Cl_2$ | 20 |
| 4 | rt | DMF | 83 |
| 5 | 50 | DMF | 45 |
| 6 | 80 | DMF | 31 |
| 7 | rt | DMSO | 68 |
| 8 | rt | 1,4-Dioxane | 43 |
| 9 | rt | MeOH | 27 |
| 10 | rt | THF | 79 |
| 11 | rt | $C_6H_5CH_3$ | 32 |

a) Determined by GC.

shows the influences of solvents and temperatures.

Among the solvents examined, DMF gave the highest yield at room temperature, followed by THF and DMSO. Raising the temperature in DMF caused decreases in the yield of the 2-alkynoate (runs 4, 5, and 6).

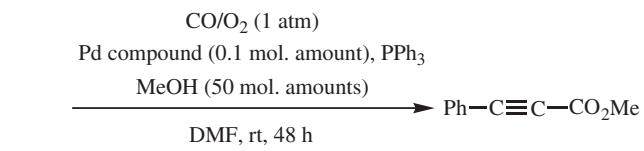
Examination of the effect of the CO pressure increase, while keeping the $O_2$ pressure at 1 atm showed that higher CO pressure caused a decrease in the yield from 83% at 1 atm to 58% (10 atm), 51% (30 atm), and 46% (50 atm). Increase of the oxygen pressure from 1 to 10 atm at 30 atm of CO showed little effect on the yields.

Employment of other transition metal catalysts such as $Ni(cod)_2$ with 2 mol. amounts of $PPh_3$, as well as use of other transition metal complexes such as $IrCl(CO)(PPh_3)_2$, $RhCl(CO)(PPh_3)_2$, proved ineffective in causing the carbonylation of phenylacetylene.

The effects of palladium catalysts and of ligands used in combination with the palladium compound are summarized in Table 2.

Palladium compounds such as $PdCl_2$, $Pd(OAc)_2$, and $Pd(dba)_2$ (dba=dibenzylideneacetone), proved inactive (runs 1, 2, and 11) in catalyzing the carbonylation process when they were used without ligand such as $PPh_3$. Such results suggest the necessity of a proper ligand to generate and maintain the activity of a palladium catalyst. However, addition of more than two molar amounts of triphenylphosphine per mole of palladium had some detrimental effect in giving the carbonylation product (runs 3, 4, 5, and 6). Ligands such as bidentate diphosphines that tend to coordinate strongly to palladium proved less suitable for the carbonylation process (runs 7 and 8). Basic trialkylphosphine ligands and sterically demanding ligands such as $P^nBu_3$, $P^tBu_3$, and P(*o*-tolyl)$_3$ inhibited the reaction, and phosphite and triphenylphosphine oxide suppressed the reaction.

Table 2. Effect of Ligands on Oxidative Carbonylation of Phenylacetylene Using Various Palladium Catalysts under Various Conditions




| Run | Catalyst (0.1 mol. amount) | Yield[a]/% |
|---|---|---|
| | | Ph–C≡C–$CO_2$Me |
| 1 | $Pd(OAc)_2$ | trace |
| 2 | $Pd(dba)_2$ | 0 |
| 3 | $Pd(OAc)_2$ + 2 $PPh_3$ | 83 |
| 4 | $Pd(OAc)_2$ + 3 $PPh_3$ | 69 |
| 5 | $Pd(OAc)_2$ + 4 $PPh_3$ | 47 |
| 6 | $Pd(PPh_3)_4$ | 39 |
| 7 | $Pd(OAc)_2$ + dppb | 40 |
| 8 | $Pd(OAc)_2$ + dppf | 23 |
| 9 | $Pd(OAc)_2$ + 2 P(2-furyl)$_3$ | 20 |
| 10 | $Pd(OAc)_2$ + 2 P(*p*-methoxyphenyl)$_3$ | 46 |
| 11 | $PdCl_2$ | 0 |
| 12[b] | $PdCl_2$ + $2PPh_3$ | 82[c] |

a) Carbonylation was carried out under the balloon pressure of CO and $O_2$ (1:1 ratio). The yield of the product was determined by GC. b) [Cat]=0.05 mol. amount. c) NaOAc was added. d) Addition of $P^tBu_3$, $P^nBu_3$, P(*o*-tolyl)$_3$, $P(PyPh_2)_3$, $P(OPh)_3$, $P(O)Ph_3$, and 1,10-phenanthroline inhibitied the reaction.

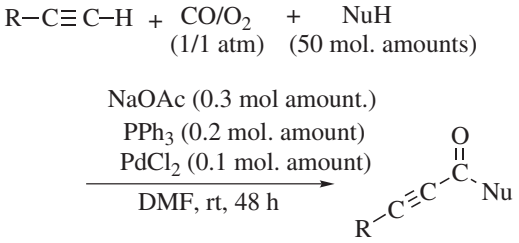
When $Pd(OAc)_2$ was used in combination with $PPh_3$, the catalytic carbonylation reaction proceeded without addition of any extra base (see below), whereas $PdCl_2$ combined with two molar amounts of $PPh_3$ afforded the carbonylation products only in the presence of a base such as NaOAc (run 12).

The oxidative carbonylation of 1-alkynes can be catalyzed not only by homogeneous catalysts but also by heterogeneous systems such as palladium on carbon. The reaction of phenylacetylene with Pd/C (0.05 mol. amount) used in combination with $PPh_3$ (0.1 mol. amounts), $NEt_3$, and $NEt_4Cl$ in DMF at room temperature under the pressure of CO (50 atm) and $O_2$ (7.5 atm) in 50 molar amounts of methanol gave methyl 3-phenyl-2-propynoate in 75% yield in 48 h. The yield of the carbonylation product with the heterogeneous catalyst was quite low when the reaction was carried out at atmospheric pressure of CO and of $O_2$.

**1.2 Scope of the Reaction:** The oxidative carbonylation with molecular oxygen is applicable to various alkynes with aryl and alkyl substituents, as shown in Table 3. The results with other alcohols than methanol and the result with diethylamine as a nucleophile are also included in the table.

Substitution of the phenyl group in phenylacetylene at the para position with methyl group as well as with bromide group gave the carbonylation product in good yields. Simple aliphatic alkynes such as 1-heptyne were carbonylated similarly. A hydroxy group attached to the alkyne somewhat hindered the reaction, but protection with *tert*-butyldimethylsilyl group gave the carbonylation product in a good yield. In the reaction

Table 3. Catalytic Oxidative Carbonylation of Various Terminal Alkynes with Methanol and Other Nucleophiles with Molecular Oxygen




| Run | R | NuH | Yield[a)]/% |
|---|---|---|---|
| 1 | Ph | MeOH | 82[b)] |
| 2 | 4-$MeC_6H_4$ | MeOH | 74 |
| 3[c)] | 4-$BrC_6H_4$ | MeOH | 79 |
| 4 | $n$-$C_5H_{11}$ | MeOH | 75 |
| 5 | $HO(CH_2)_4$ | MeOH | 42 |
| 6 | $TBSO(CH_2)_4$ | MeOH | 83 |
| 7 | Ph | $n$-BuOH | 86 |
| 8 | Ph | $HNEt_2$ | 60 |

a) Isolated yield. b) Determined by GC. c) $Pd(OAc)_2$ (0.1 mol. amount)/$PPh_3$ (0.2 mol. amount) as a catalyst.

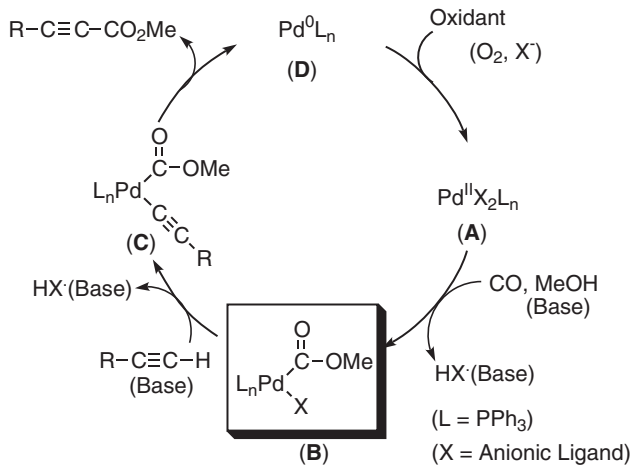
with phenylacetylene, butanol could be used to give butyl 3-phenyl-2-propynoate; *tert*-butyl alcohol was not effective, while diethylamine gave the amide in a moderate yield.

**2. Mechanistic Studies. 2.1 Examination of the Feasibilities of Possible Catalytic Cycles:** Three mechanisms (**a** to **c**) are conceivable for elucidating the catalytic formation of methyl alkynoate from alkyne, CO and MeOH, and an oxidant in the presence of a Pd(II) species and a base, as depicted in Schemes 1–3.

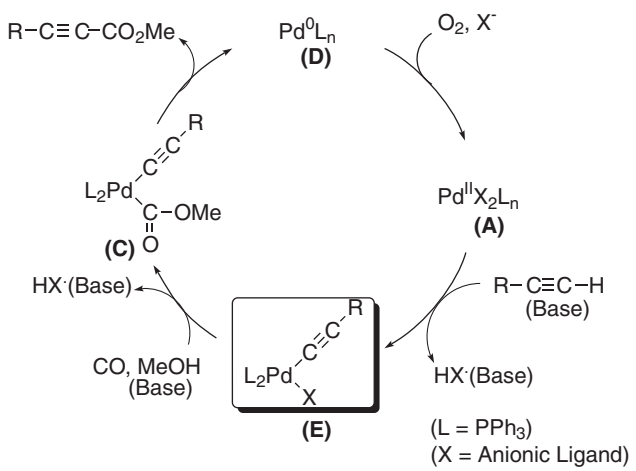
**Mechanism a;** In the mechanism **a** shown in Scheme 1, formation of a methoxycarbonylpalladium species **B** from a Pd(II) species **A** having one or more supporting ligand(s) such as $PPh_3$ and anionic ligands X (X=halide or acetate) is considered as the first step in the catalytic cycle. The methoxycarbonylpalladium species **B**, produced from the Pd(II) complex **A** with CO and methanol, reacts further with an alkyne to form a Pd(II) intermediate that has both methoxycarbonyl and alkynyl groups bound with the palladium center **C** with removal of HX. When $PdCl_2$ was used in combination with $PPh_3$, use of an added base was necessary. On the other hand, with the catalyst system using $Pd(OAc)_2$ and $PPh_3$, addition of the external base was not required. We will later address this problem in Discussion.

Reductive elimination from **C** liberates methyl alkynoate as the product, generating a Pd(0) species **D** that is oxidized with the aid of an oxidant to regenerate the Pd(II) species **A** to drive the catalytic process.

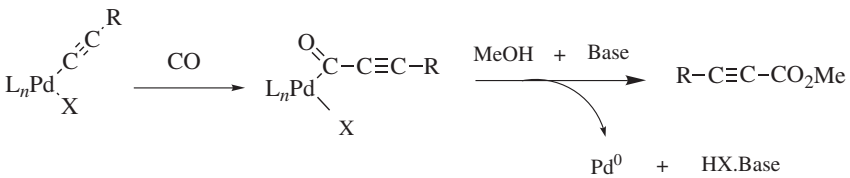
**Mechanism b;** The second mechanism involves the initial formation of an alkynylpalladium complex (**E** in Scheme 2) by the reaction of the alkyne with the Pd(II) species **A** in the presence of a base. The alkynylpalladium species **E** further reacts with CO, methanol, and a base to produce the Pd(II) species **C** that has both the methoxycarbonyl and the alkynyl ligands. The ensuing reductive elimination produces the methyl alkynoate, similarly to Scheme 1.




Scheme 1. A proposed mechanism for catalytic carbonylation of a terminal alkyne using a palladium catalyst.




Scheme 2. A proposed mechanism for catalytic carbonylation of a terminal alkyne via alkynylpalladium complex.

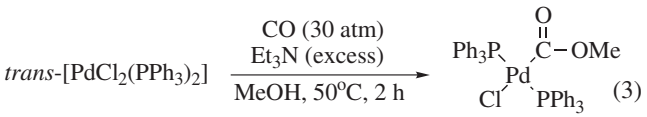



Scheme 3. A conceivable mechanism involving CO insertion into Pd–alkynyl bond in catalytic carbonylation of an alkyne.

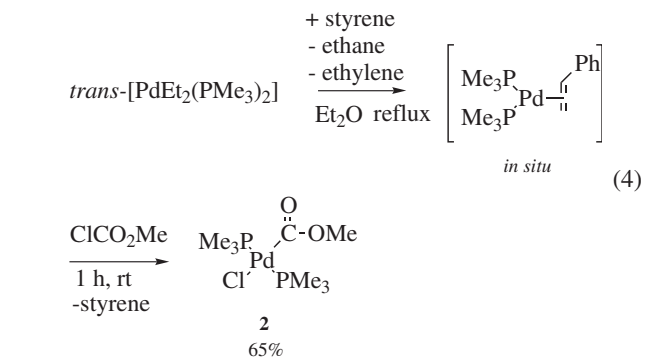
**Mechanism c;** The third mechanism postulates the CO insertion into an alkynylpalladium species, giving an alkynoylpalladium intermediate. Reaction of the alkynoylpalladium species thus formed with methanol and a base liberates the product methyl alkynoate, producing the Pd(0) intermediate that carries the catalytic cycle upon oxidation.

In the following section we probe the feasibility of the three possible mechanisms (**a** to **c**) by examining properties of model organopalladium complexes assumed in the catalytic cycles.

**2.2 Examination of the Behavior of Methoxycarbonylpalladium Complexes in Relation to the Mechanism Represented by Scheme 1:** Methoxycarbonylpalladium complexes have been prepared and their properties have been examined by various workers.[14–16] However, the reactivities of the methoxycarbonyl complexes in relation to catalytic carbonylation have received less attention.[17] We have prepared two types of methoxycarbonylpalladium complexes, **1** and **2**, having $PPh_3$ and $PMe_3$ ligands, respectively, by two different routes for examination of their reactivities toward phenylacetylene. Complexes **1** and **2** have been characterized by spectroscopic methods with $^1H$, $^{13}C$, and $^{31}P$ NMR and IR. In the reaction shown in Eq. 3, methoxycarbonylpalladium(II) chloride having two $PPh_3$ ligands (**1**) was prepared by the reaction of CO and methanol with $PdCl_2(PPh_3)_2$ in the presence of a base such as triethylamine. The reaction is considered to proceed through CO coordination to the cationic Pd(II) species, followed by attack of methanol on the coordinated CO aided by a base to provide the methoxycarbonyl complex **1**. For comparison, a methoxycarbonylpalladium complex **2** having two trimethylphosphine ligands was prepared by oxidative addition of methyl chloroformate to a Pd(0) complex coordinated with trimethylphosphine ligands and styrene with cleavage of the Cl–C bond in the chloroformate (Eq. 4).

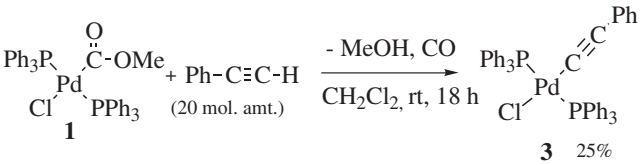



(3)




(4)

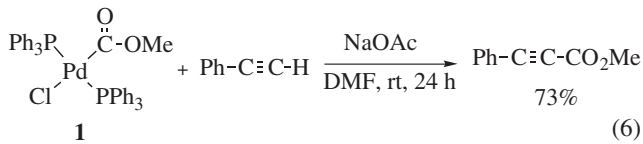
No reaction took place on treatment of the $PPh_3$-coordinated methoxycarbonylpalladium complex **1** with an equimolar amount of phenylacetylene in the absence of a base in $CDCl_3$ at room temperature. Treatment of **1** with an excess of phenylacetylene gave a phenylethynylpalladium complex **3** in a low yield as an exchange product of the methoxycarbonyl entity in **1** with the alkyne, with 60% of **1** remaining unreacted (Eq. 5).




(5)

A similar transformation of a methoxycarbonylpalladium complex having $Ph_2Ppy$ ligand ($Ph_2Ppy$=diphenyl(2-pyridyl)-phosphine) into [Pd($Ph_2Ppy$)(C≡CPh)Cl] quantitatively on treatment with phenylacetylene was recently reported.[18] The transformation of the methoxycarbonylpalladium complex **1** into the alkynylpalladium complex suggests that phenylacetylene, being an acidic alkyne, reacts with the methoxycarbonyl ligand to liberate methanol and CO to form the alkynylpalladium complex **3**.

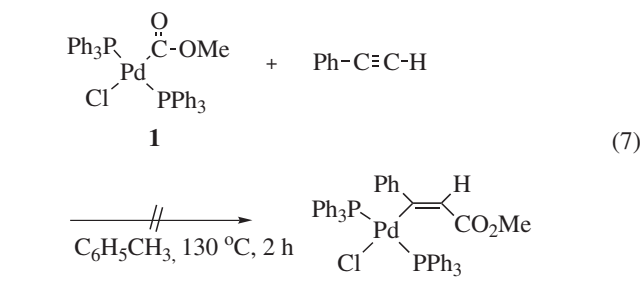
When the reaction of **1** with phenylacetylene was carried out *in the presence of a base* such as NaOAc, methyl phenyl-2-propynoate was produced in 73% yield at room temperature (Eq. 6).




(6)

The reactions of **1** with phenylacetylene using $NEt_3$ in 1 to 4 molar amounts per mole of the methoxycarbonylpalladium complex **1** gave 30 to 40% of the alkynoate. The atmosphere employed for the reaction, either under argon or under CO, had little effect. The effectiveness of the alkaline salt in comparison to the organic nitrogen base is in accord with the experimental results for the catalytic conversion of alkynes into alkynoates with CO.

Another possible reaction course involving the methoxycarbonylpalladium species is the insertion of an alkyne into the MeOCO–Pd bond. No insertion reaction took place, however, when **1** was treated with phenylacetylene in toluene at 130 °C for 2 h (Eq. 7).

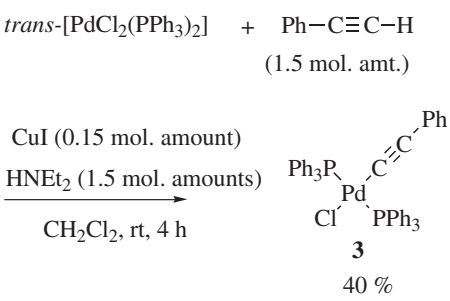



(7)

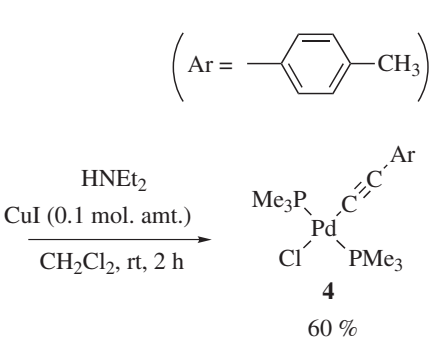
This result disfavors the mechanism involving insertion of an alkyne into the methoxycarbonyl–Pd bond, followed by elimination of the $\beta$-hydrogen in the alkenylpalladium intermediate to liberate the alkynoate. Furthermore, the $\beta$-hydrogen in the alkenylpalladium species is in an inappropriate position for allowing the syn H abstraction without isomerization, making the alkyne insertion mechanism even more unlikely.[19]

**2.3 Examination of the Behavior of Alkynylpalladium**

**Complexes:** Next we examined the properties of the alkynylpalladium species in relation to the mechanism shown in Scheme 2. There are precedents of preparation of alkynylpalladium complexes.[20] The formation of alkynylpalladium complexes from palladium dihalide and an alkyne usually requires addition of a catalytic amount of a copper salt, which produces an intermediate alkynylcopper compound whose alkynyl group is transmetallated to palladium(II) on interaction with the palladium halide.[21,22] Two types of alkynylpalladium complexes **3** and **4**, having $PPh_3$ and $PMe_3$ ligands respectively, have been prepared in the present study from palladium dichloride and alkynes using copper iodide as a promoter in the presence of diethylamine (Eqs. 8, 9).



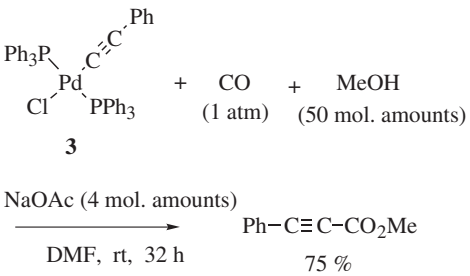

(8)




(9)

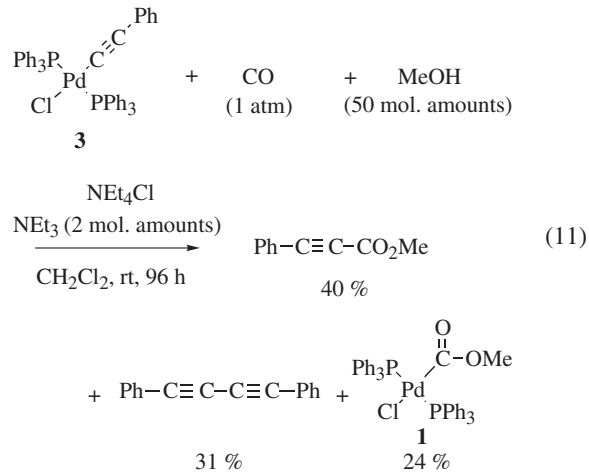
For the preparation of an arylalkynylpalladium complex, we employed *p*-tolylacetylene for facilitating the NMR characterization. The reason we used the *cis*-isomer for the preparation of the $PMe_3$-coordinated complex **4** as the starting product is that treatment of *trans*-$[PdCl_2(PMe_3)_2]$ with an alkyne under similar conditions gives a dialkynylpalladium complex through a disproportionation process.[23]

Treatment of the phenylethynylpalladium chloride having two $PPh_3$ ligands (complex **3**) with methanol and NaOAc in the atmosphere of CO liberated methyl 3-phenyl-2-propynoate in 75% isolated yield (Eq. 10).




(10)

The result suggests that the alkynylpalladium chloride complex **3** reacts with CO and methanol in the presence of NaOAc in DMF to give the assumed intermediate having both the methoxycarbonyl and the alkynyl ligands, corresponding to complex **C** in Scheme 2. The subsequent reductive elimination from **C** liberates methyl 3-phenyl-2-propynoate. The effectiveness of NaOAc over triethylamine, see below (Eq. 11), is in agreement with the effectiveness of an alkaline salt in the catalytic carbonylation processes.




(11)

When $NEt_3$ was used as a base in the presence of $NEt_4Cl$ in the atmosphere of 1 atm of CO in MeOH in the reaction with the phenylethynylpalladium complex **3**, the reaction took a different course, as shown in Eq. 11.

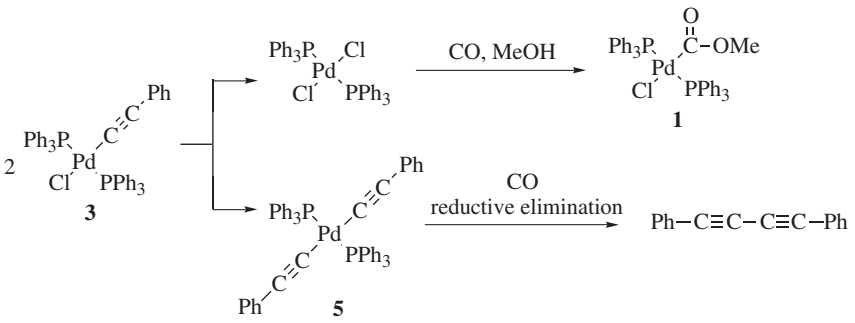
The yield of methyl 3-phenyl-2-propynoate was low (40%) and the reaction was accompanied by formation of 1,4-diphenyl-1,3-butadiyne (31%) and of the methoxycarbonylpalladium complex **1** in 24% yield.

These results show that the carbonylation mechanism as shown in Scheme 2 is possible, once the alkynylpalladium intermediate corresponding to **E** is produced. However, in the absence of a copper salt as in the present catalytic system, the alkynylpalladium complex is not readily formed.

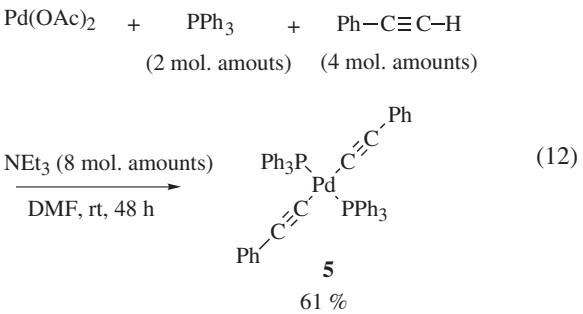
The formation of the dialkyne suggests occurrence of disproportionation of the starting alkynylpalladium chloride complex **3** into palladium dichloride complex and dialkynylpalladium complex **5**, as shown in Scheme 4.

The dialkynylpalladium complex **5** produced would release the dialkyne on reductive elimination in the atmosphere of CO, whereas the dichloropalladium complex further undergoes the reaction with CO and methanol in the presence of a base to give the methoxycarbonylpalladium chloride complex **1** according to Eq. 3. Such a result accounts for the reaction course to produce the diyne as a by-product in catalytic carbonylation of alkynes, particularly when a copper salt is used in combination with alkynes.

For establishing further the reaction course to produce diynes through dialkynylpalladium species, we have prepared the dialkynylpalladium complex **5** from $Pd(OAc)_2$, triphenylphosphine, and phenylacetylene as shown in Eq. 12. The dialkynylpalladium complex **5** is stable *in the absence of CO* and only a trace of the diyne was produced in the reaction to produce **5** from $Pd(OAc)_2$, $PPh_3$, and phenylacetylene.

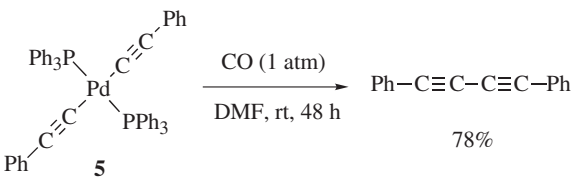


Scheme 4. Reactions of alkynylpalladium complex **3**.



(12)

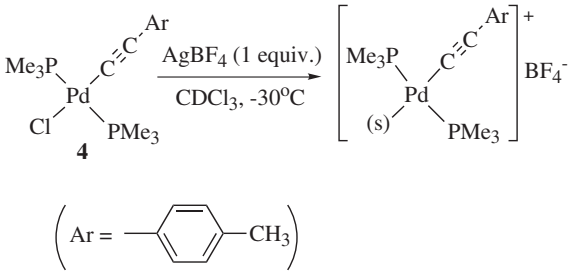
Treatment of the *trans*-dialkynylpalladium complex **5** in DMF at room temperature with CO at atmospheric pressure caused reductive elimination of the two alkynyl ligands, liberating the diyne at room temperature without addition of an extra base (Eq. 13).

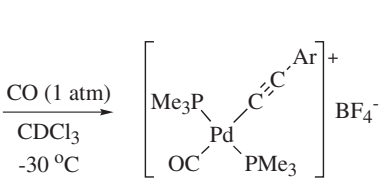


(13)

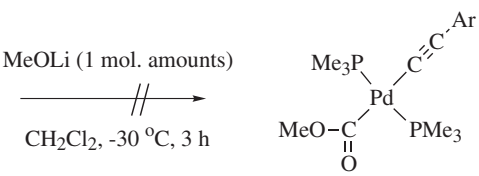
The ready formation of the diyne by reductive elimination from the dialkynylpalladium complex **5** on interaction with CO indicates that the function of CO is to act as a $\pi$ acid to induce the reductive elimination.

Next we attempted the preparation of an alkynyl(methoxycarbonyl)palladium complex corresponding to **C** in Schemes 1 and 2. The reactivity of organopalladium complexes is often enhanced when a cationic organopalladium complex is generated in the reaction system from a neutral species.[24] For examining the properties of the cationic alkynylpalladium complex, possibly involved in the carbonylation reactions of alkynes, we removed the chloride ligand in the alkynylpalladium complex **4** with $AgBF_4$ to generate a cationic alkynylpalladium complex having two $PMe_3$ ligands. Treatment of the solvent-coordinated cationic *para*-tolylethynylpalladium complex with CO afforded the CO-coordinated alkynylpalladium complex (Eq. 14). However, treatment of the CO-coordinated cationic alkynylpalladium complex with LiOMe at $-30$ °C with expectation of getting the postulated *trans*-alkynyl(methoxycarbonyl)palladium complex **C** having two $PMe_3$ ligands resulted in failure, with deposition of palladium black.

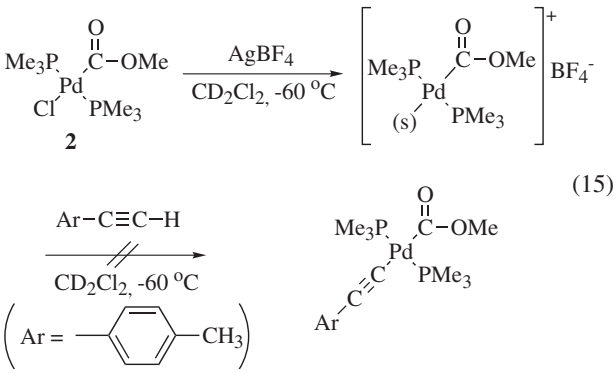




(14)



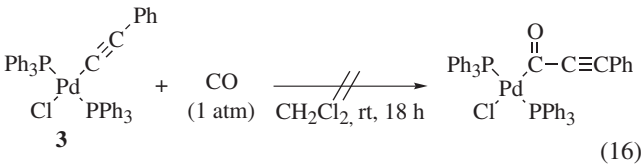
Another approach preparing the presumed alkynyl(methoxycarbonyl)palladium complex starting from the methoxycarbonylpalladium chloride **2**, also gave palladium black on its treatment with $AgBF_4$ and tolylacetylene at $-60$ °C and did not produce the expected complex corresponding to **C** in Schemes 1 and 2 (Eq. 15).



(15)

**2.4 Examination of the Possibility of CO Insertion into the Alkynyl–Palladium Bond:** For examining the feasibility of the third mechanism shown in Scheme 3, the reactivity of the alkynylpalladium complex toward CO insertion was examined. The reaction of complex **3**, the phenylethynylpalladium

complex having two $PPh_3$ ligands, with CO did not give any CO insertion product under the atmospheric pressure of CO nor under 10 atm of CO at room temperature (Eq. 16).




(16)

**2.5 Mechanisms of Oxidation of Pd(0) to Pd(II): Oxidation of Pd(0) to Pd(II) Complex with Molecular Oxygen without a Cu(II) Promoter;** The result, that a palladium complex in combination with molecular oxygen served as the catalyst for oxidative carbonylation of alkynes without use of a copper salt, was unexpected since a copper(II) salt is generally believed to be required for oxidizing a Pd(0) complex. Thus we investigated the course of oxidation of Pd(0) into Pd(II) complex with $O_2$.[25]

We found that treatment of $[Pd(PPh_3)_4]$ with $O_2$ at atmospheric pressure in the presence of LiCl readily gave *trans*-$[PdCl_2(PPh_3)_2]$ (Eq. 17). Formation of two molar amounts of triphenylphosphine oxide was confirmed in the process of oxidation.

$$[Pd(PPh_3)_4] \xrightarrow[\text{THF, rt, 6 h}]{\text{O}_2\text{ (1 atm)},\ \text{LiCl (2.2 mol. amounts)}} \underset{92\ \%}{\textit{trans}\text{-}[PdCl_2(PPh_3)_2]} \quad (17)$$

It was further confirmed that $[Pd(dba)_2]$ was converted into *trans*-$[PdCl_2(PPh_3)_2]$ on treatment with $O_2$ in the presence of two molar amounts each of $PPh_3$ and LiCl in THF at room temperature for 3 h (Eq. 18).

$$[Pd(dba)_2] \xrightarrow[\text{THF, rt, 3 h}]{\text{PPh}_3\text{ (2 mol. amounts)},\ \text{O}_2\text{ (1 atm)},\ \text{LiCl (2 mol. amounts)}} \underset{77\ \%}{\textit{trans}\text{-}[PdCl_2(PPh_3)_2]} \quad (18)$$

The result indicates that the oxidation of a tertiary phosphine ligand to tertiary phosphine oxide is not a prerequisite for driving the oxidation of a Pd(0) complex. We have further found that a mixture of atmospheric pressure of oxygen and CO converted $[Pd(PPh_3)_4]$ into the methoxycarbonylpalladium complex **1** in THF containing methanol, triethylamine, and LiCl at room temperature in 5 h (Eq. 19).

$$[Pd(PPh_3)_4] + CO/O_2\ (1/1\ \text{atm}) + \text{MeOH} \quad (50\ \text{mol. amounts})$$

$$\xrightarrow[\text{THF, rt, 5 h}]{\text{Et}_3\text{N (2 mol. amounts)},\ \text{LiCl (1.1 mol. amounts)}} \underset{78\ \%}{\underset{\mathbf{1}}{Ph_3P(Cl)Pd(C(=O)OMe)PPh_3}} \quad (19)$$

## Discussion

**Mechanism of the Palladium-Catalyzed Oxidative Carbonylation of Alkynes into Alkynoates.** Of the three conceivable mechanisms to account for the palladium-catalyzed oxidative carbonylation (Schemes 1 to 3), the mechanism involving CO insertion into the alkynylpalladium bond (Scheme 3) is not supported by the mechanistic studies based on the behavior of model organopalladium complexes. Although such an insertion mechanism related to the carbonylation of aryl halides developed by Heck[19] is sometimes proposed for explaining the carbonylation of alkynes, there is no solid experimental support.[26]

The possibility of operation of Scheme 2 can not be excluded when a Cu(II) salt is used, since the copper salt facilitates the formation of alkynylpalladium species from alkynes. In the absence of a copper salt as in the present case, however, involvement of an alkynylpalladium species in the first step of the catalytic process is not likely. In cases where diynes are produced as the by-product, the involvement of the alkynylpalladium may be involved, since the dialkynylpalladium can be produced by a disproportionation process as shown by Scheme 4.

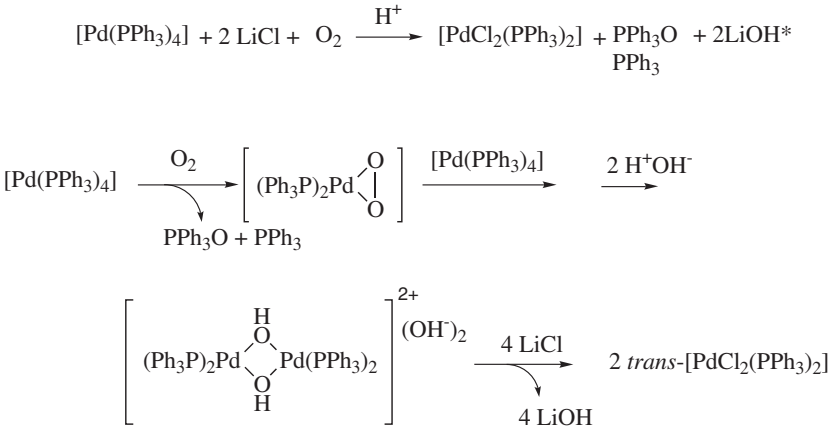
Thus on the basis of examination of various possibilities to account for the mechanism, we propose the mechanism expressed by Scheme 1 as the most reasonable catalytic cycle, the one compatible with experimental results. We have established each elementary step in Scheme 1 (**A** to **B**, **B** to **D** with formation of methyl 2-propynoate, and air oxidation of **D** to **A**) and provided experimental support for the validity of the Scheme.

The initial formation of methoxycarbonylpalladium species, into which alkyne would undergo the insertion, is the remaining conceivable course, but the difficulty of insertion of phenylacetylene into the methoxy–Pd bond in **1** (Eq. 7) does not support the alkyne insertion mechanism.

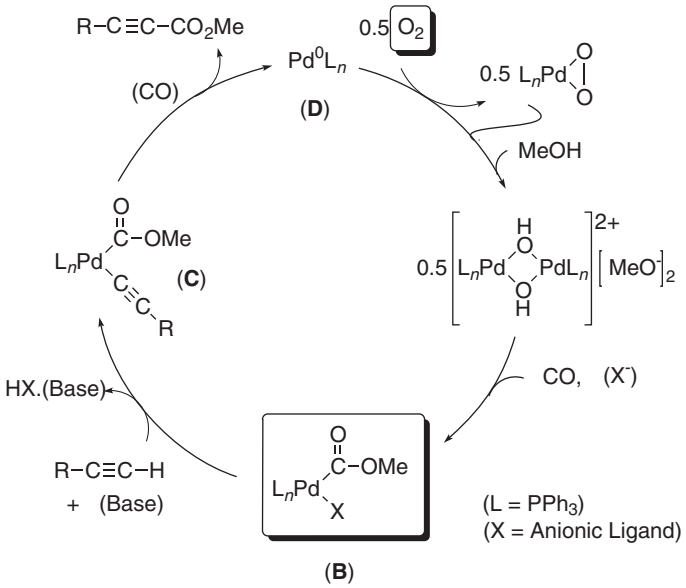
We have also considered the possibility of operation of a mechanism involving the initial formation of an alkynylpalladium hydride by oxidative addition of an alkyne to a Pd(0) species, since such an alkynyl hydride complex was reported previously.[27] However, the experimental results that CO insertion into the alkynylpalladium bond was not observed and that evolution of hydrogen, which is expected to arise from the palladium hydride, was not detected in the catalytic carbonylation of alkynes, disfavor the operation of such a mechanism. We attempted to isolate an alkynylpalladium hydride complex from $PPh_3$- and tricyclohexylphosphine-coordinated hydridopalladium chlorides,[28] but no evidence to suggest the formation of such a complex was obtained. Since the catalytic carbonylation is a slow process at room temperature, the operation of the mechanism involving the alkynylpalladium hydride seems less probable.

We examined the process to convert $[Pd(PPh_3)_4]$ into $[PdCl_2(PPh_3)_2]$ under oxygen in the presence of LiCl (Eq. 17); we found that the reaction proceeded readily in the presence of water and confirmed that the solution became alkaline after completion of the reaction. The result is in agreement with formation of LiOH in the oxidation process. Examination of the $^7Li$ NMR did not provide conclusive evidence regarding the identity of the lithium species formed, because of the proximity of the $^7Li$ signals of $Li_2O$, LiOH, and the hydrate of LiOH.

On the basis of these results, the mechanism of oxidation of




Scheme 5. A proposed mechanism for oxidation of $Pd(PPh_3)_4$ with $O_2$.




Scheme 6. A proposed mechanism for catalytic carbonylation of a terminal alkyne with a palladium catalyst and $O_2$ in methanol.

Pd(0) species by molecular oxygen into Pd(II) species in the catalytic process may be accounted for by Scheme 5.

Formation of a dioxygen adduct with the formula of $[(PPh_3)_2Pd(\eta^2\text{-}O_2)]$ is probably the first step in the oxidation of a Pd(0) complex with molecular oxygen. In the case of the reaction of Pd(0) complexes with molecular oxygen, formation of such an oxygen adduct was previously reported[29] and the catalytic conversion of $PPh_3$ into $OPPh_3$ with the $PPh_3$-coordinated palladium complexes has been established.[30] The dioxygen complex may further react with another Pd(0) species to form an oxygen-bridged dinuclear complex. It is possible that the $\mu$-oxo bridged complex reacts with a trace of water to produce a dimeric species with OH bridges and $OH^-$ anions. The $OH^-$ ligands are replaced with LiCl and the system collapses into a palladium chloride complex, $[PdCl_2(PPh_3)_2]$. A related dimeric OH-bridged complex has been characterized from structural studies as well as by chemical methods by Grushin and Alper.[31] The reaction sequence shown in Scheme 5 is in agreement with experimental results on the properties of palladium complexes. The proposed mechanism presented here to account for the oxidation course of Pd(0) to Pd(II) fills the remaining gap connecting **D** and **A** in Scheme 1 to complete the catalytic cycle. Taking the body of experimental results into consideration, we propose a catalytic cycle to account for the whole sequence of catalytic transformation of an alkyne into methyl 2-alkynoate by oxygen in methanol, as represented by Scheme 6.

The left part in the catalytic cycle in Scheme 6 is the same as in Scheme 1, which was supported by the reaction of the methoxycarbonylpalladium species **B** with an alkyne in the presence of a base to liberate methyl 2-alkynoate and Pd(0) species **D** through **C**. The right part in Scheme 6 is slightly modified from Scheme 5, where only the effect of water was considered. In the actual catalytic process where methanol is used, it is likely that methanol is involved in the oxidation process of Pd(0) species. Thus transformation of a Pd(0) species with $O_2$ is assumed to give first an $(\eta^2\text{-}O_2)$Pd complex, which further reacts with another Pd(0) species and methanol to give the OH-bridged dimer. In Scheme 6, the intermediate dimeric complex is tentatively presented as the OH-bridged

complex with the methoxide anions, but the possibility of formation of a methoxy-bridged complex having OH anions can not be excluded. Through either species, the Pd(II) species formed by oxidation with $O_2$ is then transformed into the methoxycarbonylpalladium species **B** on interaction with CO and methanol.

As we described in the Results section in the present paper, addition of a base such as NaOAc was required for making the catalytic carbonylation process operative when $PdCl_2$ was used, whereas no base was required when $Pd(OAc)_2$ was employed in combination with two molar amounts of $PPh_3$. The reason behind this is not clear at the moment. The acetate anion may be playing a special role to abstract a proton because of its greater affinity with protons than the $Cl^-$ anion. Another possibility is generation of a base in the course of oxidation of a Pd(0) species with $O_2$ into a Pd(II) species, as we discussed regarding Scheme 5. As we assumed the interaction of water to make the system alkaline in Scheme 5, water might participate in transformation of the $[(PPh_3)_2Pd(\eta^2\text{-}O_2)]$ into Pd(II) species with liberation of an $OH^-$ anion. Since the catalytic conversion of alkynes into methyl 1-alkynoates proceeded smoothly with the $Pd(OAc)_2/2PPh_3$ catalyst system with oxygen as the oxidant, we did not address the problem further.

The overall catalytic cycle represented in Scheme 6 is in agreement with the experimental results obtained in the present study. A similar mechanism involving the hydroxy-bridged palladium intermediate has been proposed recently by Sheldon to account for the aerobic oxidation of alcohols by atmospheric oxygen.[32]

## Conclusion

A new process of converting alkynes into 2-alkynecarboxylates using molecular oxygen as the sole oxidant in the absence of any other oxidizing agent has been discovered and the mechanisms that reasonably account for the catalytic cycles have been presented. On the basis of studies on the properties of model organopalladium complexes, a methoxycarbonylpalladium intermediate is proposed to play the most critical role. The $O_2$-promoted oxidation course of a Pd(0) into Pd(II) species in the presence of LiCl without assistance of any external oxidant was examined and a mechanism to account for the reaction course is presented.

## Experimental

**General Procedures.** All manipulations except for palladium-catalyzed carbonylation of terminal alkynes were performed under argon atmosphere using Schlenk tube techniques. Solvents were purified by the usual methods under argon. NMR spectra were recorded on a JEOL Lamda 500 or a JEOL AL-400 spectrometer for $^1H$ (referenced to $SiMe_4$ via residual solvent protons), $^{13}C\{^1H\}$ (referenced to $SiMe_4$ via the solvent resonance) and $^{31}P\{^1H\}$ (referenced to 85% $H_3PO_4$ as an external standard). NMR Coupling constants ($J$ values) are given in hertz (Hz), and spin multiplicities are indicated as follows: s (singlet), d (doublet), t (triplet), m (multiplet), vt (virtual triplet), and br (broad). Gas chromatographic analyses (GC) were carried out on a GC-353 equipped with TC1 column (0.25 mm I.D. × 30 m), using $N_2$ as carrier gas. Low-resolution mass spectra were obtained with a JEOL JMS-Automass 150 that is coupled with a gas chromatograph. Elemental analyses were performed by the Materials Characterization Central Laboratory of Waseda University. The pH values were measured on a D21 pH meter (Horiba).

**Reagents.** All alkyne compounds except for 6-*t*-butyldimethylsiloxy-1-hexyne were commercial products (Aldrich: 4-bromoethynylbenzene, Tokyo Kasei Kogyo Co. for the other alkynes) and they were used without further purification. The 6-*t*-butyldimethylsiloxy-1-hexyne was synthesized by the reaction of 5-hexyn-1-ol with TBS–Cl in the presence of imidazole. Methanol (Kanto Kagaku), 1-butanol (Kanto Kagaku), diethylamine (Tokyo Kasei Kogyo Co.), sodium acetate (Kokusan Chemical Co.), triethylamine (Kanto Kagaku), lithium chloride (Kanto Kagaku), tetraethylammonium chloride (Tokyo Kasei Kogyo Co.), and CuI (Kanto Kagaku) were commercial products, and were used directly. $[Pd(PPh_3)_4]$[33] was prepared by the reported procedure. $[Pd(dba)_2]$[34] and *trans*-$[PdCl_2(PPh_3)_2]$[35] were prepared according to the references and were used without recrystallization of the crude precipitate obtained at the end of the synthesis. $[Pd(OAc)_2]$ (Aldrich), 10% Pd/C (Kojima Chemicals Co.), and $[PdCl_2]$ (Tanaka Kikinzoku) were used as received from commercial suppliers. All tertiary phosphines were commercial products and were used without further purification.

**Synthesis of Model Organopalladium Complexes and Their Reactions. Synthesis of *trans*-[PdCl(COOMe)($PPh_3$)$_2$] (1):**[15,16] A mixture of *trans*-$[PdCl_2(PPh_3)_2]$ and triethylamine in 20 $cm^3$ of methanol was placed in an autoclave. The autoclave was purged with carbon monoxide and pressurized with 30 atm of CO at room temperature. After heating at 50 °C for 2 h, the autoclave was cooled to room temperature and depressurized. The orange suspension obtained was transferred to a 50 $cm^3$ Schlenk tube and was filtered to obtain a solid, which was washed with methanol (five times) and was dissolved in 15 $cm^3$ of $CH_2Cl_2$. Addition of diethyl ether (25 $cm^3$) at −30 °C yielded yellow crystals. The crystals were collected by filtration, washed with ether (5 $cm^3$, twice), and were dried at room temperature under vacuum to give 1.04 g (72%) of an off-white solid. It was identified by comparison with the NMR and IR spectra of the known sample: $^1H$ NMR ($CDCl_3$, r. t., 400 MHz) $\delta$ 7.2–7.8 (m, 30H, Ph), 2.38 (s, 3H, COOC$H_3$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, r. t., 125 MHz) $\delta$ 184.6 (s, *C*=O) 51.3 (s, COO$CH_3$); $^{31}P\{^1H\}$ NMR ($CDCl_3$, r. t., 161 MHz) $\delta$ 19.0 (s); IR (KBr disc), $\nu_{C=O}$ 1673 $cm^{-1}$.

**Synthesis of *trans*-[PdCl(COOMe)($PMe_3$)$_2$] (2):** In a 50 $cm^3$ Schlenk tube filled with argon and cooled to −30 °C were placed 515 mg (1.63 mmol) of *trans*-$[PdEt_2(PMe_3)_2]$[36] and 15 $cm^3$ of diethyl ether. Styrene (0.279 $cm^3$, 2.44 mmol) was added to the system and the mixture was heated at 50 °C for 3 h to give a yellow homogeneous solution. To the solution was added methyl chloroformate (0.125 $cm^3$, 1.63 mmol) and the mixture was stirred at the room temperature for 45 min. To the dark orange homogeneous solution was added hexane (25 $cm^3$) at −30 °C to allow white needles to precipitate. After separation of the liquid phase by filtration, the solid was washed with hexane (5 $cm^3$ × 3), and dried under vacuum to give 374 mg (65%) of **2**. $^1H$ NMR (400 MHz, $CDCl_3$, r. t.) $\delta$ 3.62 (3H, s, COOC$H_3$), 1.44 (18H, vt, $J_{PH}$ = 3.66 Hz, P(C$H_3$)$_3$); $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$, r. t.) $\delta$ 186.1 (s, *C*=O), 51.4 (s, COO$CH_3$), 14.4 (m, P($CH_3$)$_3$); $^{31}P\{^1H\}$ NMR (161 MHz, $CDCl_3$, r. t.) $\delta$ −14.71 (s); IR (KBr disc) 1650 $cm^{-1}$ ($\nu_{C=O}$).

**Synthesis of *trans*-[PdCl(C≡CPh)($PPh_3$)$_2$] (3):** A mixture of *trans*-$[PdCl_2(PPh_3)_2]$ (705 mg, 1.00 mmol) and phenylacetylene (0.165 $cm^3$, 1.50 mmol) in dichloromethane (50 $cm^3$) was allowed to react in the presence of diethylamine (0.156 $cm^3$, 1.50 mmol) and CuI (28.2 mg, 0.150 mmol) at room temperature for 4 h to

give a turbid red-brown suspension. A saturated aqueous NaCl solution was added to the resultant mixture and the aqueous layer was extracted with dichloromethane. The combined dichloromethane solution was dried over $MgSO_4$. After filtration to remove insoluble impurities, the solution was cooled to $-30$ °C to cause deposition of yellow crystals. The solid was subsequently washed twice with pentane and dried under vacuum to give 305 mg (40%) of **3**. It was identified as *trans*-[PdCl(C≡CPh)($PPh_3$)$_2$], (**3**) by comparison of spectroscopic data. $^1$H NMR ($CDCl_3$, r. t., 400 MHz) $\delta$ 7.3–7.8 (m, 30H, P*Ph*$_3$), 6.8–6.9 (m, 3H, *m*,*p*-C$_6$*H*$_5$), 6.10 (d, 2H, $^3J_{HH} = 7.1$ Hz, *o*-C$_6$*H*$_5$); $^{13}$C{$^1$H} NMR ($CDCl_3$, r. t., 125 MHz) $\delta$ 111.7 (t, $^3J_{PC} = 7.2$ Hz, C≡*C*–Ph), 96.4 (t, $^2J_{PC} = 15.0$ Hz, *C*≡C–Ph); $^{31}$P{$^1$H} NMR ($CDCl_3$, r. t., 161 MHz) $\delta$ 25.0 (s); IR (KBr disc) $\nu_{C\equiv C}$ 2121 cm$^{-1}$.

**Synthesis of *trans*-[PdCl(C≡C–*p*-tol)($PMe_3$)$_2$] (4):** *cis*-[$PdCl_2$($PMe_3$)$_2$] (506 mg, 1.53 mmol) was dissolved in dichloromethane (100 cm$^3$) in an Erlenmeyer flask at room temperature. To the solution were added diethylamine (0.160 cm$^3$), CuI (29.5 mg, 0.153 mmol), and *p*-tolylethyne; then the mixture was stirred at room temperature for 2 h. Water was added to the dichloromethane solution; the organic layer was first extracted, then washed with aqueous solutions of ammonium chloride and NaCl. After the organic layer was dried with magnesium sulfate, the organic layer was separated by filtration and concentrated to dryness. After the residue was dissolved in dichloromethane (3 cm$^3$), hexane (25 cm$^3$) was added at $-30$ °C to give yellow-needles, which were separated and washed with hexane (8 cm$^3$ × 4). Drying the crystals at room temperature gave a yellowish white solid (378 mg, 60%). $^1$H NMR ($CDCl_3$, r. t., 400 MHz) $\delta$ 7.0–7.3 (4H, aromatic protons), 2.31 (3H, s, C$_6$H$_4$-*p*-C*H*$_3$), 1.58 (18H, vt, $J_{PH} = 3.66$ Hz, P(C*H*$_3$)$_3$); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$, r. t.) $\delta$ 124–136 (aromatic carbons), 106.4 (t, $^3J_{PC} = 5.2$ Hz, C≡*C*–*p*-tol), 94.2 (t, $^2J_{PC} = 16.1$ Hz, *C*≡C–*p*-tol); $^{31}$P{$^1$H} NMR (161 MHz, $CDCl_3$, r. t.) $\delta$ $-12.64$ (s); IR (KBr disc) 2117 cm$^{-1}$ ($\nu_{C\equiv C}$).

**Reaction of *trans*-[PdCl(COOMe)($PPh_3$)$_2$] (1) with Phenylacetylene in the Presence of a Base:** Phenylacetylene (0.017 cm$^3$, 0.156 mmol) was added to a dimethylformamide solution (5 cm$^3$) containing *trans*-[PdCl(COOMe)($PPh_3$)$_2$] (113 mg, 0.156 mmol) and sodium acetate (51.2 mg, 0.624 mmol) at room temperature. The mixture was stirred for 24 h under balloon pressure of carbon monoxide at room temperature. The GC analysis of the reaction mixture with *n*-$C_{12}H_{26}$ as an internal standard revealed the formation of methyl 3-phenyl-2-propynoate (73%), which was identified by $^1$H NMR on comparison with an authentic sample (Tokyo Kasei Kogyo Co.).

**Reaction of *trans*-[PdCl(COOMe)($PPh_3$)$_2$] (1) with Phenylacetylene in the Absence of a Base:** When the reaction of **1** (6.20 mg, 0.00900 mmol) dissolved in $CDCl_3$ (0.4 cm$^3$) with phenylacetylene ($0.930 \times 10^{-3}$ cm$^3$, 0.00900 mmol) was carried out in an NMR tube for 16 h at room temperature, no change of the NMR spectrum was observed. When a similar reaction of **1** (112 mg, 0.154 mmol) dissolved in dichloromethane (5 cm$^3$) with 20 mol. amounts of phenylacetylene (0.339 cm$^3$, 3.08 mmol) was carried out at room temperature, an orange suspension was obtained. After concentration of the solution in vacuo and addition of hexane (20 cm$^3$), an orange precipitate was produced. This was collected and washed with pentane (5 cm$^3$ × 3). Formation of *trans*-[PdCl(C≡CPh)($PPh_3$)$_2$] (**3**) in 25% yield was confirmed.

**Reaction of *trans*-[PdCl(C≡CPh)($PPh_3$)$_2$] (3) with Methanol under CO:** Methanol (0.208 cm$^3$, 5.13 mmol) was added at room temperature to a dimethylformamide solution (5 cm$^3$) of *trans*-[PdCl(C≡CPh)($PPh_3$)$_2$] (**3**) (113 mg, 0.156 mmol) containing sodium acetate (51.2 mg, 0.624 mmol). The mixture was stirred for 32 h under a balloon pressure of carbon monoxide at room temperature. The GC and GC–MS analyses of the products were performed with *n*-$C_{12}H_{26}$ as an internal standard. Formation of methyl 3-phenyl-2-propynoate (75%) was confirmed by comparison with a sample prepared by carbonylation of phenylacetylene (NMR and GC–MS). *m*/*z* (rel. intensity) 162 (9), 129 (73), 102 (94), 75 (100).

When a similar reaction of the alkynylpalladium complex **3** (77 mg, 0.10 mmol) dissolved in dichloromethane (9 cm$^3$) with CO (1 atm) and methanol (0.200 cm$^3$, 4.9 mmol) was carried out at room temperature for 4 d in the presence of triethylamine (0.0289 cm$^3$, 0.207 mmol) and tetraethylammonium chloride (17 mg, 0.10 mmol), GC analysis of the reaction mixture revealed the formation of methyl 3-phenyl-2-propynoate (40%) and 1,4-diphenyl-1,3-butadiyne (31%). Formation of *trans*-[PdCl(COOMe)($PPh_3$)$_2$] (**1**) in 24% yield was also confirmed.

**Synthesis of *trans*-[Pd(C≡CPh)$_2$($PPh_3$)$_2$] (5):** Palladium acetate (56 mg, 0.250 mmol) was dissolved at room temperature in dimethylformamide (20 cm$^3$) together with triphenylphosphine (131 mg, 0.500 mmol). Phenylacetylene (0.110 cm$^3$, 1.00 mmol) and triethylamine (0.270 cm$^3$, 1.94 mmol) were added to the solution; this mixture was stirred at room temperature for 2 d to cause formation of a white precipitate. The solvent was removed by filtration and the residue was washed with hexane (5 cm$^3$ × 3) and dried to give a white powder (127 mg corresponding to 61% of **5**). $^1$H NMR (400 MHz, $CDCl_3$, r. t.) $\delta$ 7.3–7.9 (30H, phenyl protons), 6.85–6.95 (6H, m, *m*,*p*-C$_6$H$_5$), 6.25–6.35 (4H, m, *o*-C$_6$H$_5$); $^{13}$C{$^1$H} NMR (125 MHz, $CDCl_3$, r. t.) $\delta$ 124–136 (phenyl carbons), 114.8 (t, $^3J_{PC} = 4.15$ Hz, C≡*C*Ph), 113.6 (t, $^2J_{PC} = 16.6$ Hz, *C*≡CPh); $^{31}$P{$^1$H} NMR (161 MHz, $CDCl_3$, r. t.) $\delta$ 26.45 (s); IR (KBr disc) 2106 cm$^{-1}$ ($\nu_{C\equiv C}$); Found: C, 74.81; H, 4.65%. Calcd for $C_{52}H_{40}P_2Pd$: C, 74.69; H, 4.84%.

**Reaction of *trans*-[Pd(C≡CPh)$_2$($PPh_3$)$_2$] (5) with CO:** The dialkynylpalladium complex *trans*-[Pd(C≡CPh)$_2$($PPh_3$)$_2$] (**5**) (123 mg, 0.48 mmol) was dissolved in dimethylformamide (7 cm$^3$) in a Schlenk tube; the mixture was stirred at room temperature for 24 h under the atmosphere of carbon monoxide. The GC analysis of the product with *n*-$C_{10}H_{22}$ as an internal standard revealed the formation of 1,4-diphenyl-1,3-butadiyne (78%).

**Reaction of *trans*-[PdCl(C≡CPh)($PPh_3$)$_2$] (3) with CO:** The monoalkynylpalladium chloride *trans*-[PdCl(C≡CPh)($PPh_3$)$_2$] (**3**) (29 mg) was dissolved in dichloromethane (5 cm$^3$) and the mixture was treated with CO (balloon pressure) at room temperature for 18 h. Examination of the reaction product with NMR revealed that the starting complex remained unreacted.

**Attempt at Preparation of an Alkynyl(methoxycarbonyl)-palladium Complex from 4.** The reaction of *trans*-[PdCl(COOMe)($PMe_3$)$_2$] (**2**) (11.7 mg, 0.0331 mmol) in $CD_2Cl_2$ (0.400 cm$^3$) with phenylacetylene (0.0042 cm$^3$, 0.0331 mmol), carried out in an NMR tube at $-60$ °C in the presence of $AgBF_4$ (acetone-$d_6$ solution, 0.0331 cm$^3$, 1 mol dm$^{-3}$, 0.0331 mmol), gave a complex mixture as indicated by observation of a complicated spectrum. Formation of the expected alkynyl(methoxycarbonyl)palladium species could not be confirmed.

Another approach using *trans*-[PdCl(C≡C–*p*-tolyl)($PMe_3$)$_2$] (**4**) by its first treatment with $AgBF_4$ (1 molar amount) at $-30$ °C in $CDCl_3$ followed by reaction with CO and LiOMe in MeOH gave a black reaction product. No indication of formation of the expected alkynyl(methoxycarbonyl)palladium species was obtained.

**Reaction of [Pd($PPh_3$)$_4$] with $O_2$ (1 atm).** A tetrahydrofuran

solution (10 $cm^3$) of [$Pd(PPh_3)_4$] (593 mg, 0.513 mmol) and lithium chloride (47.8 mg, 1.13 mmol), was treated with a balloon pressure of oxygen at room temperature. After the solution was stirred at room temperature for 6 h, the resultant mixture was examined by GC with *n*-$C_{12}H_{26}$ as an internal standard to reveal the formation of triphenylphosphine oxide. The transformation of [$Pd(PPh_3)_4$] into *trans*-[$PdCl_2(PPh_3)_2$] was also confirmed by examination of NMR of the yellow solid (333 mg, 92%) recovered from the system. Water (30 $cm^3$) was added to the reaction mixture and the pH of the filtrate was measured to be 12.2.

Reaction of $Pd(dba)_2$, 2 molar amounts of $PPh_3$, and LiCl with molecular oxygen under similar conditions also gave *trans*-[$PdCl_2(PPh_3)_2$].

**Reaction of [$Pd(PPh_3)_4$] with $O_2$, LiCl, Triethylamine, and CO in MeOH.** Triethylamine (0.141 $cm^3$, 1.01 mmol) dissolved in 1 $cm^3$ of methanol was added to a THF solution (12 $cm^3$) containing [$Pd(PPh_3)_4$] (584 mg, 0.505 mmol) and LiCl (23.4 mg, 0.552 mmol). The reaction mixture was stirred at room temperature under the balloon pressure of molecular oxygen and carbon monoxide for 22 h. The light yellow suspension produced was filtered to give a white solid, which was washed with methanol (5 $cm^3$ × 2) and pentane (5 $cm^3$ × 2). Examination of the NMR spectra of the white solid (287 mg, 78%) confirmed the formation of *trans*-[$PdCl(COOMe)(PPh_3)_2$].

**General Procedure in Catalytic Oxidative Carbonylation of Alkynes (Method A).** A typical procedure is as follows. Palladium acetate (22.4 mg, 0.100 mmol) and triphenylphosphine (52.4 mg, 0.200 mmol) were mixed in dimethylformamide (20 $cm^3$) in a 100 $cm^3$ two-necked round-bottomed flask under argon. A rubber balloon filled with carbon monoxide was attached to the flask. Methanol (2 $cm^3$) and phenylacetylene (0.110 $cm^3$, 1.00 mmol) were added, followed by attachment of a rubber balloon of oxygen to the flask. The reaction mixture was allowed to react with stirring at room temperature for 48 h. The mixture was then treated with diethyl ether and water and the aqueous layer was extracted with diethyl ether. The combined ether solution was dried over $MgSO_4$ and the solvent was evaporated in vacuo. Purification of the residue by column chromatography (hexane/ethyl acetate) gave the corresponding product.

**General Procedure (Method B).** A typical procedure is as follows. Palladium dichloride (8.7 mg, 0.050 mmol), triphenylphosphine (26.3 mg, 0.100 mmol), and sodium acetate (26.4 mg, 0.300 mmol) were mixed in *N*,*N*-dimethylformamide (10 $cm^3$) in a 50 $cm^3$ two-necked round-bottomed flask under argon. A rubber balloon filled with carbon monoxide was connected to the flask. Methanol (2 $cm^3$) and phenylacetylene (0.110 $cm^3$, 1.00 mmol) were added to the solution and then a rubber balloon of oxygen was attached to the flask. The reaction mixture was allowed to react with stirring at room temperature for 48 h. The reaction was quenched by adding diethyl ether and water; then the aqueous layer was extracted with diethyl ether. The combined ether solution was dried over $MgSO_4$ and the solvent was evaporated in vacuo. Purification of the residue by column chromatography (hexane/ethyl acetate) gave the corresponding product.

**Catalytic Carbonylation of Alkynes with Pd/C Catalyst.** Into a 100 $cm^3$ stainless steel autoclave filled with argon were added 10% Pd/carbon (53.4 mg, 0.0502 mmol), triphenylphosphine (26.7 mg, 0.102 mmol), tetraethylammonium chloride (163 mg, 0.984 mmol), and *N*,*N*-dimethylformamide (20 $cm^3$) and the mixture was stirred at room temperature. To this system were added methanol (2 $cm^3$, 50 mmol), triethylamine (0.275 $cm^3$, 2.00 mmol), and phenylacetylene (0.110 $cm^3$, 1.0 mmol). The autoclave was pressurized with CO (50 atm) and oxygen (7.5 atm) and the contents were stirred at room temperature for 48 h. The reaction mixture was filtered and separated into water-soluble and ether-soluble fractions. The ether solution was washed with aqueous solutions containing ammonium chloride and NaCl; the resultant ether solution was dried over magnesium sulfate. The product esters were analyzed with NMR using $(CHCl_2)_2$ as an internal standard.

**Characterization of Products. Methyl 3-Phenyl-2-propynoate:**[37] Yield, 82%; $^1$H NMR ($CDCl_3$, r. t., 400 MHz) $\delta$ 7.2–7.6 (5H, aromatic H), 3.84 (3H, s, COOC$H_3$). $^{13}$C{$^1$H} NMR ($CDCl_3$, r. t., 125.6 MHz) $\delta$ 154.3 (s, carbonyl C), 132.9 (s, aromatic C), 130.6 (s, aromatic C), 128.5 (s, aromatic C), 119.5 (s, aromatic C), 86.5 (s, PhC≡C), 80.3 (s, PhC≡C), 52.8 (s, OC$H_3$).

**Butyl 3-Phenyl-2-propynoate:**[38] Yield, 86%; $^1$H NMR ($CDCl_3$, r. t., 500 MHz) $\delta$ (d, 2H, $^3J_{HH}$ = 7.32 Hz, aromatic H), 7.46–7.43 (m, 1H, aromatic H), 7.38–7.35 (m, 2H, aromatic H), 4.24 (t, 2H, $^3J_{HH}$ = 6.96 Hz, OC$H_2$), 1.70 (tt, 2H, $^3J_{HH}$ = 7.51, 6.96 Hz, OCH$_2$C$H_2$), 1.44 (tq, 2H, $^3J_{HH}$ = 7.51, 7.32 Hz, C$H_2$CH$_3$), 0.96 (t, 3H, $^3J_{HH}$ = 7.32 Hz, CH$_2$C$H_3$); $^{13}$C{$^1$H} NMR ($CDCl_3$, r. t., 125.6 MHz) $\delta$ 154.2 (s, carbonyl C), 133.0 (s, aromatic C), 130.5 (s, aromatic C), 128.5 (s, aromatic C), 119.7 (s, aromatic C), 86.0 (s, PhC≡C), 80.7 (s, PhC≡C), 65.9 (s, OCH$_2$), 30.5 (s, OCH$_2$CH$_2$), 19.0 (s, CH$_2$CH$_3$), 13.6 (s, CH$_2$CH$_3$). IR (neat) $\nu$ 2221, 1708 $cm^{-1}$.

***N*,*N*-Diethyl-3-phenyl-2-propynamide:**[39] Yield, 60%; $^1$H NMR ($CDCl_3$, r. t., 500 MHz) $\delta$ 7.52–7.55 (m, 2H, aromatic H), 7.34–7.43 (m, 3H, aromatic H), 3.67 (q, 2H, $^3J_{HH}$ = 7.17 Hz, NC$H_2$), 3.48 (q, 2H, $^3J_{HH}$ = 7.17 Hz, NC$H_2$), 1.28 (t, 3H, $^3J_{HH}$ = 7.17 Hz, NCH$_2$C$H_3$), 1.18 (t, 3H, $^3J_{HH}$ = 7.17 Hz, NCH$_2$C$H_3$); $^{13}$C{$^1$H} NMR ($CDCl_3$, r. t., 125.6 MHz) $\delta$ 153.9 (s, carbonyl C), 132.3 (s, aromatic C), 129.8 (s, aromatic C), 128.4 (s, aromatic C), 120.8 (s, aromatic C), 88.9 (s, PhC≡C), 81.9 (s, PhC≡C), 43.5 (s, NCH$_2$), 39.3 (s, NCH$_2$), 14.4 (s, NCH$_2$CH$_3$), 12.8 (s, NCH$_2$CH$_3$). IR (neat) $\nu$ 2220, 1626 $cm^{-1}$.

**Methyl 3-(4-Methylphenyl)-2-propynoate:**[11] Yield, 74%; $^1$H NMR ($CDCl_3$, r. t., 500 MHz) $\delta$ 7.48 (d, 2H, $^3J_{HH}$ = 8.06 Hz, aromatic H), 7.18 (d, 2H, $^3J_{HH}$ = 8.06 Hz, aromatic H), 3.83 (s, 3H, OC$H_3$), 2.38 (s, 3H, PhC$H_3$); $^{13}$C{$^1$H} NMR ($CDCl_3$, r. t., 125.6 MHz) $\delta$ 154.6 (s, carbonyl C), 141.3 (s, aromatic C), 133.0 (s, aromatic C), 129.4 (s, aromatic C), 116.4 (s, aromatic C), 87.1 (s, PhC≡C), 80.0 (s, PhC≡C), 52.7 (s, OC$H_3$), 21.7 (s, –C$_6$H$_4$–C$H_3$). IR (KBr disc) $\nu$ 2221, 1713 $cm^{-1}$.

**Methyl 3-(4-Bromophenyl)-2-propynoate:**[40] Yield, 79%; $^1$H NMR ($CDCl_3$, r. t., 500 MHz) $\delta$ (d, 2H, $^3J_{HH}$ = 7.32 Hz, aromatic H), 7.59 (d, 2H, $^3J_{HH}$ = 7.32 Hz, aromatic H), 3.84 (s, 3H, OC$H_3$), $^{13}$C{$^1$H} NMR ($CDCl_3$, r. t., 125.6 MHz) $\delta$ 154.2 (s, carbonyl C), 134.3 (s, aromatic C), 132.0 (s, aromatic C), 125.5 (s, aromatic C), 118.5 (s, aromatic C), 85.2 (s, PhC≡C), 81.3 (s, PhC≡C), 52.9 (s, OC$H_3$). IR (KBr disc) $\nu$ 2226, 1714 $cm^{-1}$. Found: C, 50.04, H, 2.87%. Calcd for $C_{10}H_7O_2Br$: C, 50.24; H, 2.95%.

**Methyl 2-Octynoate:**[38] Yield, 75%; $^1$H NMR ($CDCl_3$, r. t., 500 MHz) $\delta$ 69 (s, 3H, OC$H_3$), 2.26 (t, 2H, $^3J_{HH}$ = 7.14 Hz, C$H_2$C≡C), 1.52 (tt, 2H, $^3J_{HH}$ = 7.51, 7.14 Hz, C$H_2$CH$_2$C≡C), 1.18–1.35 (m, 4H, CH$_3$(C$H_2$)$_2$), 0.83 (t, 3H, $^3J_{HH}$ = 7.14 Hz, C$H_3$CH$_2$); $^{13}$C{$^1$H} NMR ($CDCl_3$, r. t., 125.6 MHz) $\delta$ 154.3 (s, carbonyl C), 89.9 (s, CH$_2$C≡C), 72.8 (s, CH$_2$C≡C), 52.5 (s, OCH$_3$), 30.9 (s, CH$_3$CH$_2$CH$_2$), 27.2 (s, CH$_2$CH$_2$C≡C), 22.1 (s, CH$_3$CH$_2$), 18.6 (s, CH$_2$C≡C), 13.8 (s, CH$_3$CH$_2$). IR (neat) $\nu$ 2238, 1716 $cm^{-1}$.

**Methyl 7-Hydroxy-2-heptynoate:**[41] Yield, 42%; $^1$H NMR

($CDCl_3$, r. t., 500 MHz) $\delta$ 3.76 (s, 3H, $OCH_3$), 3.67 (m, 2H, $OCH_2$), 2.40 (m, 2H, $CH_2C{\equiv}C$), 1.69 (m, 4H, $OCH_2(CH_2)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, r. t., 125.6 MHz) $\delta$ 154.2 (s, carbonyl C), 89.4 (s, $CH_2C{\equiv}C$), 73.0 (s, $CH_2C{\equiv}C$), 62.0 (s, $OCH_2$), 52.5 (s, $OCH_3$), 31.5 (s, $OCH_2CH_2$), 23.8, $CH_2CH_2C{\equiv}C$), 18.4 (s, $CH_2C{\equiv}C$). IR (neat) $\nu$ 3399, 2236, 1718 $cm^{-1}$.

**Methyl 7-(*t*-Butyldimethylsiloxy)-2-heptynoate:**[42] Yield, 83%; $^1H$ NMR ($CDCl_3$, r. t., 500 MHz) $\delta$ 3.71 (s, 3H, $OCH_3$), 3.59 (t, H, $^3J_{HH} = 5.86$ Hz, $OCH_2$), 2.33 (t, 2H, $^3J_{HH} = 6.86$ Hz, $CH_2C{\equiv}C$), 1.55–1.65 (m, 4H, $OCH_2(CH_2)_2$), 0.84 (s, 9H, $SiC(CH_3)_3$), 0.00 (s, 6H, $Si(CH_3)_2$); $^{13}C\{^1H\}$ NMR ($CDCl_3$, r. t., 125.6 MHz) $\delta$ 154.2 (s, carbonyl C), 89.7 (s, $CH_2C{\equiv}C$), 73.0 (s, $CH_2C{\equiv}C$), 62.3 (s, $OCH_2$), 52.5 (s, $OCH_3$), 31.7 (s, $OCH_2CH_2$), 25.9 (s, $C(CH_3)_3$), 24.1 (s, $CH_2CH_2C{\equiv}C$), 18.5 (s, $CH_2C{\equiv}C$), 18.3 (s, $C(CH_3)_3$), −5.4 (s, $Si(CH_3)_2$). IR (neat) $\nu$ 2238, 1719 $cm^{-1}$.

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